The discoloration of polyethylene obtained from chemical separation of laminates

Investigating additives and other potential causes

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Investigating additives and other potential causes

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Abstract

PolyAl, the material composed of laminated polyethylene (PE) films and aluminum (Al) in carton, is a challenge in recycling due to the strong adhesion of the layers and the low value of the end products. In Europe, recent efforts to improve the circularity of carton packages include the chemical separation of PolyAl, in order to obtain higher values of the PE and Al separately. However, an undiagnosed green discoloration had been observed in the separated PE fraction after reprocessing into granules. The study aims to explore the potential causes of the green discoloration and discuss the impact of the phenomenon.

A review of literature combined with stakeholder interviews were conducted to identify potential causes of the discoloration throughout the base PE materials' value chain; residues from the metallocene catalyst, phenolic antioxidants (AOs) and acid scavengers in additives, oxidation during extrusion melting, ozone treatment, peroxide bath, impurities, and oxidation during delamination were identified as the potential contributors to the discoloration.

An analysis of the delaminated films through differential scanning calorimetry (DSC) and colorimetry (L*a*b*, ΔE, RGB) suggested that the green discoloration was a combination of yellow and grey, and the thermo-oxidation of AOs producing yellow species may be the root cause for a yellow discoloration. The second hypothesis was tested in subsequent experimental analysis; after oven-aging various metallocene PE grades with known additives, their color changes were measured and compared (L*a*b*, ΔE). At 250ºC for 6 minutes, the samples without additives showed yellow discoloration which the AOs were able to protect against, although further treatment may result in aforementioned AO discoloration; calcium (Ca) stearate was linked to more advanced yellow discoloration when used with AOs. The thesis concluded that the cause of the final green discoloration was complex, with the choices of additives being a potential root cause. Future studies concerning other possible causes and the impact of different PolyAl recycling methods are recommended.

Keywords: Delamination, multilayered packaging, polymer discoloration, plastic film, recycling

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Lund, May 2021

Can Feng

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List of Acronyms and Abbreviations

ACE	Alliance for Beverage Cartons and the Environment
Al	Aluminum
AO	Antioxidant
Ca	Calcium
DSC	Differential scanning calorimetry
EL	External laboratory
HDPE	High-density polyethylene
HPLC	High-performance liquid chromatography
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MAO	Methylalumoxane
MDPE	Medium-density polyethylene
mLLDPE	Metallocene linear low-density polyethylene
Na	Sodium
OIT	Oxidation induction temperature/time
PE	Polyethylene
PP	Polypropylene
QM	Quinone methide
TLC	Thin-layer chromatography
UBC	Used Beverage Carton

1 Introduction

1.1 Background

In 2019, 190 billion Tetra Pak packages were sold globally, 50 billions of which were recycled (Tetra Pak, 2020). Tetra Pak's laminated cartons use different grades of polyethylene (PE) as the main polymer component, in the form of extrusion laminated films. Figure 1.1 demonstrates the applications and dominate polymers in Europe.

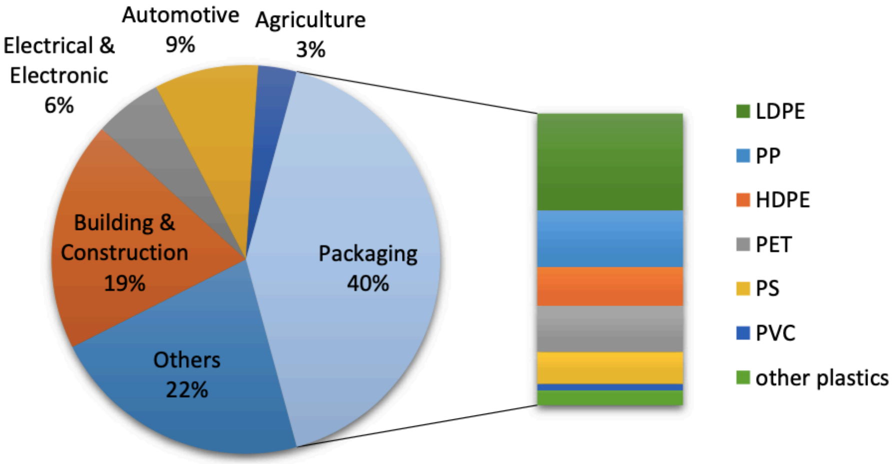


Figure 1. 1 Plastic materials in Europe (Kaiser, Schmid and Schlummer, 2017)

In the recycling of laminated cartons, paper fiber is commonly recovered, leaving behind the remainder mixed material of polymers and aluminum (Al), PolyAl. In Europe, PolyAl from used beverage cartons (UBCs) is mostly incinerated for energy recovery, commercial recycling is done in seven countries in the EU, mostly as composite materials. The composite materials already improve the overall recyclability of carton packages, expanding their post-consumer value chain beyond fiber recovery.

The separation of PolyAl into its PE and Al fractions further extends the circularity of the material. However, in the PE fraction recovered from PolyAl, an undiagnosed green discoloration was observed (Figure 1.2), a phenomenon that remains little known or studied in academia. When encountered, the phenomenon is directly attributed to residual ink (Diop, Lavoie and Huneault, 2016). Nevertheless, with insufficient investigation, the exact cause of the discoloration remains unknown.

Figure 1. 2 Plastic from the PE fraction of PolyAl delaminated with formic acid (Diop, Lavoie and Huneault, 2016)

The green discoloration was found in the end-product of a separation process known as “chemical delamination”. The existing PolyAl separation technologies can be divided into two categories: chemical separation/recycling, where the polymer is broken down into its monomer building blocks to be used as a feedstock in manufacturing new polymers, and physical separation/recycling, where the polymer macromolecules remain intact.

Chemical delamination is one of the physical separation technologies. It has been employed in China since 2010 where the green discoloration was first observed, with established markets for the end products of PE pellets and oxidized Al powder (Hamskog and Nyström, 2017). Although Tetra Pak had developed an early chemical separation method as early as 1991 (Johansson and Ackermann, 1995), PolyAl separation was only commercialized in Europe in recent years, and the green discoloration is still observed.

In the coming years, the global displacement of virgin polymers feedstock with recycled plastics is expected to grow. It is projected that by 2030, mechanically recycled plastics will displace 1.7 million tons of virgin polymers, more than double the 668,000 tons of 2020 (Figure 1.3; Brooks, 2021).

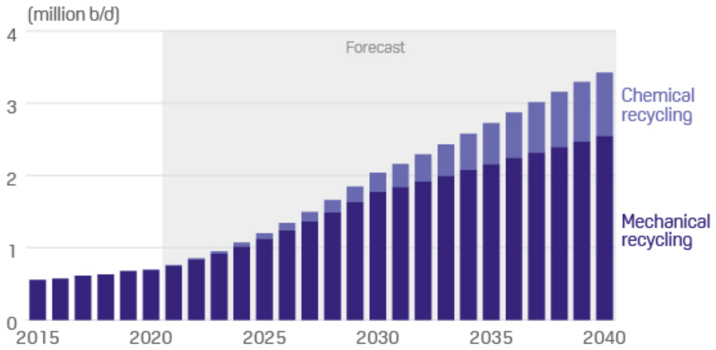


Figure 1. 3 Virgin polymer feedstocks displacement by recycled plastics (Brooks, 2021)

In order to vitalize its commercialization and improve the overall recycling rate of PolyAl, it is in the interest of Tetra Pak as well as recyclers to uplift end-product market values.

1.2 Objectives

The thesis originally aimed to identify the root cause of the reprocessed PE film's discoloration in the material's value chain and propose alternative solutions. During the explorative study, however, it was determined that the combined complexity of the material, the converting process, and recycling was vast. Upon interpreting the results of preliminary analysis of the separated films, the objective was re-focused on examining one of the potential causes, which was the formation of colored species during the oxidation of polymer additives. Therefore, the thesis aims to:

1. Provide a structured understanding of the green discoloration's background
2. Investigate the influence of additives on polymer discoloration within a selection of polymer grades used at Tetra Pak

Lastly, further recommendations will be proposed based on the review of literature, experiment results, and interviews with stakeholders.

1.3 Research question

Based on aforementioned objectives, a review of carton packaging's polymer materials was conducted contingent to discoloration, combined with experimental analysis and stakeholder interviews to answer two key research questions:

1) What are the potential causes for the green discoloration in the PE recycled via chemical delamination from PolyAl? Can polymer additives be a source of discoloration?
2) What are the impacts of the discoloration for the recyclers?

1.4 Scope and limitations

The green discoloration had persisted with the Chinese recycler since 2010, and again observed by the European recycler. Furthermore, the green discoloration involves multiple factors and actors at play, making it necessary to define the scope this thesis focuses on, as shown in Table 1.1. Note that topics deemed out-of-scope may still be discussed to form the overall context of the discoloration phenomenon.

Table 1. 1 Project scope definition

	Within scope	***Outside of scope***
Material	Current PolyAl from repulping Polymer layers by chemical delamination	Future materials Additional materials (caps and closures)
Sources	Tetra Pak cartons Polymer suppliers for Tetra Pak	Competitors & respective suppliers
Phenomenon	Polymer discoloration	General degradation of material properties
Geographical region	Europe	Data from China will be used as reference
Recycling method	Physical recycling Chemical delamination	Chemical recycling (monomer recycling) Other delamination methods PolyAl as a composite material

Within the potential root causes of the green discoloration, the experimental analysis focuses on the discoloration impact of polymer grades and additives, based on preliminary research. The specific phenomenon is little known and studied in academia, the lack of specific scientific literature presents another limitation, which will be supplemented with industry know-how and stakeholder interviews.

2 Literature Review

The literature review examines the base polymers throughout their value chain, covering their compositions and properties, additives, the manufacturing process, as well as post-consumer recycling. The review serves to screen through the relevant factors to identify potential causes and contributors of the green discoloration phenomenon.

2.1 Base polymers and additives

A basic knowledge of the base materials' roles in carton packaging is prerequisite to understanding the effects of processing and recycling conditions. Tetra Pak's aseptic packaging (such as Tetra Brik Aseptic®) has multiple laminated layers to protect the product and the packaging itself, as explained outside-in:

- Low-density polyethylene (LDPE), offers moisture protection, print protection, and flap sealing (when the corners of the carton folds onto itself)
- Paperboard, provides the package with bulk, strength, and shape stability
- LDPE, provides adhesion between the Al foil and paperboard
- Al foil, is a light, oxygen, and odor barrier
- LDPE, laminate layer between the Al foil and inner polymer
- Metallocene linear low-density polyethylene (mLLDPE), a food-contact protective barrier that enables secure sealing

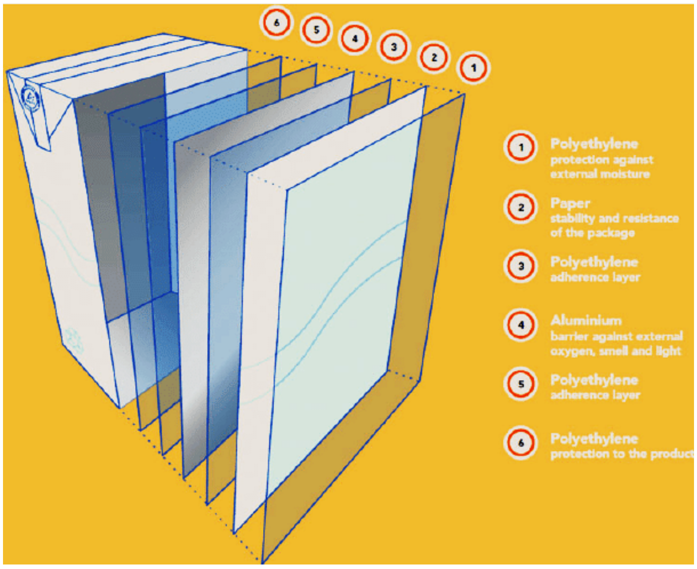


Figure 2. 1 The six-layer structure of an aseptic carton with functions (Ebadi et al., 2016)

Figure 2.1 shows the functionality of each layer in a typical laminated carton packaging; note that different cartons have varied designs, which may involve different PE film grades, as well as HDPE (high-density polyethylene) for caps and closures. Paperboard makes up 71% of the total materials used in Tetra Pak packages, polymers 24%, and Al at 5% (Tetra Pak, 2020). Some products such as Tetra Rex® do not have an Al layer, therefore recycled differently from TBA in some cases.

2.1.1 **Base polymers – LDPE and mLLDPE**

In developed countries, around 50% of domestic plastic waste is films (Horodytska, Valdés and Fullana, 2018). PE films are preferred for their soft, flexible, and clarity, while being tear and water-resistant. LDPE and mLLDPE are the two main polymers used in Tetra Pak's aseptic packaging, the appropriate grades of which are sourced from suppliers.

2.1.1.1 Low-density polyethylene (LDPE)

Polyethylene (PE) is synthesized from ethylene gas under high temperature and high pressure; after the removal of extra gas, the polymer enters a compounding extruder where additives are added before pelletizing. Figure 2.2 demonstrates the structures of HDPE, LLDPE, and LDPE.

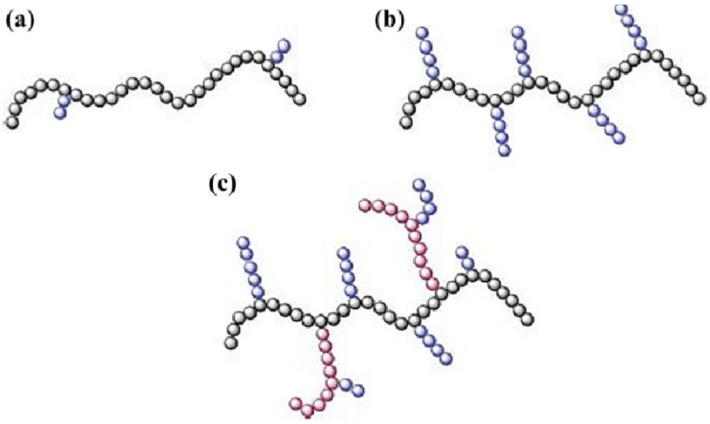


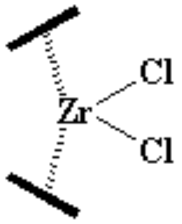
Figure 2. 2 Structures of HDPE (a), LLDPE (b), and LDPE (c) (Graziano, Jaffer and Sain, 2018)

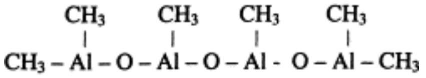
Low-density polyethylene (LDPE) offers good clarity, heat-sealing capability, moisture barrier, and chemical resistance, yet is a poor gas barrier. In use, LDPE films are typically chosen for superior clarity (gloss) and ease of processing (Polymer Properties Database, n.d.b). It is used for the décor layer and intermediate adhesive layers in Tetra Pak carton packages.

2.1.1.2 Metallocene linear low-density polyethylene (mLLDPE)

Linear low-density polyethylene (LLDPE) is similar to LDPE in its clarity, heat-sealing capability, chemical resistance and barrier properties, but it is typically used as inner linings due to their higher tensile and impact strengths (Polymer Properties Database, n.d.b). mLLDPE is LLDPE synthesized using the metal-based catalyst metallocene. Tailored to the cartons' needs, mLLDPE has been used as the inner-most layer at Tetra Pak since 2006, improving processing and reducing the thickness of the inner layer by 30% (Packmarknaden, 2006).

A metallocene is formed when a positively charged metal cation is sandwiched between two negatively charged cyclopentadienyl anions, usually in dichloride form (Figure 2.3). The effective catalysis using metallocene is achieved with cocatalyst methylalumoxane (MAO, Figure 2.4), which is assumed to first displace the chloride anions before attaching monomers to the metallocene. Figure 2.5 demonstrates the reaction mechanism of metallocene-catalyzed polymerization; First, the MAO converts the catalyst to an active species with a free coordination position; then the monomer is allocated to the free position; in step 3 the monomer is inserted with the zirconiumalkyl bond, forming new free coordination position; finally, step 3 is repeated to render a polymer chain. (Kaminsky and Laban, 2001)





$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{Al}}-O-\overset{CH_3}{\overset{|}{Al}}-O-\overset{CH_3}{\overset{|}{Al}}-O-\overset{CH_3}{\overset{|}{Al}}-CH_3}$$

Figure 2. 3. Zirconocene molecular structure in dichloride form, with black lines representing the cyclopentadienyl anions (Polymer Science Learning Center, n.d.)

Figure 2. 4. Methylalumoxane (Kaminsky and Laban, 2001)

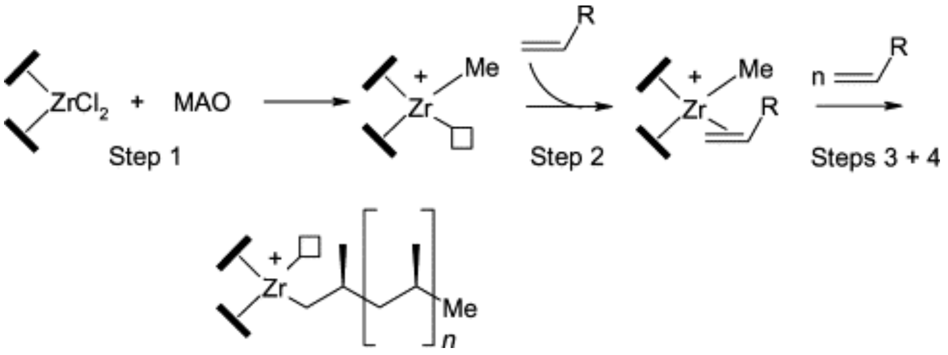


Figure 2. 5. Mechanism of olefin polymerization with zirconocenes and MAO (Kaminsky and Laban, 2001)

Excessive catalyst residue, as a result of incomplete removal, is known to be linked with discoloration (Epacher, Kröhnke and Pukánszky, 2000; Hoàng et al., 2006). While yellow is typical in PE discoloration, the literature reviewed for residues from the metallocene catalyst and discoloration did not describe the color change nor the mechanism, leaving metallocene catalyst a less understood potential factor for discoloration.

2.1.2 **Polymer additives and discoloration**

Additive packages required for polyolefin stabilization usually contain combinations of phenolic antioxidants (AOs), phosphorous AOs, and acid scavengers (Thürmer, 1998). While each additive has a specific role such as protection against aging and improving physical properties, they often interact with one another to synergistic or unwanted effects (Hoàng et al., 2004).

2.1.2.1 Phenolic antioxidants

Phenolic AOs are primary antioxidants or radical scavengers that protect the polymer from oxidative degradation. However, depending the type of phenolic AOs, they’re also capable of forming colored species after sacrificial reactions as they are depleted in the polymer system, the basic mechanism of which is shown in Figure 2.6.

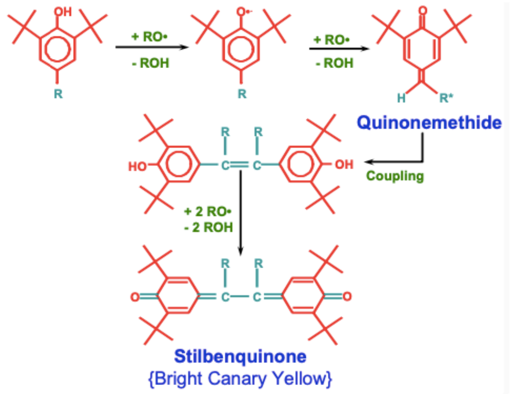
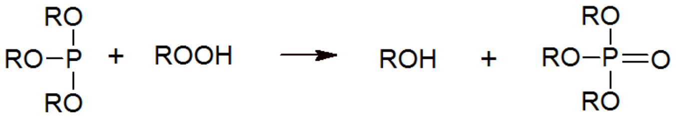


Figure 2. 6 Oxidation of phenolic AO forming colored species (Beusichem and Ruberto, n.d.)

In a 2002 study, Pospíšil et al. examined two commercial phenolic AOs in polypropylene (PP), where the samples were oven-aged and analyzed with thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC) after chloroform extraction. The results showed the formation of conjugated quinone methides (QM) which were yellow, and the colorless nonconjugated QM under different circumstances. (Pospíšil et al., 2002) The results explained the discoloration resistance of propionate-type phenolic AOs due to its formation of nonconjugated QM, leaving other phenolic AOs as potential culprits of the green discoloration.

2.1.2.2 Phosphorous antioxidants

Phosphites or phosphonites are often used as secondary AOs, which are peroxide scavengers that decompose hydroperoxides into nonreactive products, preventing them from forming alkoxy and hydroxy radicals. Phosphorous AOs are synergistic when used with primary AOs, its reaction mechanism is shown in Figure 2.7. (Polymer Properties Database, n.d.a).



$$\mathrm{RO{-}\overset{\displaystyle RO}{\underset{\displaystyle RO}{P}}} + \mathrm{ROOH} \longrightarrow \mathrm{ROH} + \mathrm{RO{-}\overset{\displaystyle RO}{\underset{\displaystyle RO}{P}}{=}O}$$

Figure 2. 7 Mechanism of phosphorous AO decomposing peroxide (Polymer Properties Database, n.d.a)

Földes et al. studied the ability of phosphorous AOs to protect polymers from degradation; phosphite was found to have weaker color protection than phosphonite, the authors assumed that the latter or its reaction products interacted with phenolic AOs or their derivatives, preventing the formation of colored species. Both offered similar protection against general degradation. (Földes et al., 2006) The literature examined offer little evidence that phosphorous AOs could be a potential cause of polymer discoloration.

2.1.2.3 Acid scavengers

Acid scavengers are salts of weak organic or inorganic acids, among those commonly used are salts of fatty acids, or inorganic salts such as synthetic hydrotalcites or zinc oxide. They are especially important in the context of mLLDPE, since the presence of catalyst residues often results in excessive acidity, which can lead to corrosion of equipment and chloride stress-cracking. In film production, the addition of stearate-type acid scavengers reduces shear forces during extrusion, while certain Na and Ca salts of higher fatty acids can also influence the crystallization of polyolefins, enhancing mechanical properties of the product. (Thürmer, 1998)

In a 2004 study, Hoàng et al investigated the effect of additive interactions on the thermal-oxidative stabilization of film-grade mLLDPE. While a synergistic effect of the primary and secondary AOs was confirmed, an antagonistic effect was discovered between the phenolic AO and calcium (Ca) stearate, an acid scavenger, in the form of yellow discoloration (Hoàng et al., 2004). This phenomenon is therefore the second possible cause of the green discoloration from the additive side if Ca stearate or similar acid scavengers are used in Tetra Pak's mLLDPE grades, along with phenolic AOs.

2.2 Converting and packaging

2.2.1 **Lamination process**

In extrusion lamination, the polymer is melted before exiting the die (Figure 2.8) as a hot film, continuously drawn onto the substrate (layer the polymer is adhering to) with the chill roll and pressure roll. The extruders operate at 190-220ºC, and the internal cooling between 10-12ºC. The converting process at Tetra Pak is divided into three stations:

- Lamination station – Extrusion lamination of the paperboard with aluminum foil, bound by LDPE adhesive layer (Figure 2.1)
- Inside station – Co-extrusion of inner polymers
- Décor station – Extrusion of décor polymer onto the paperboard/print side

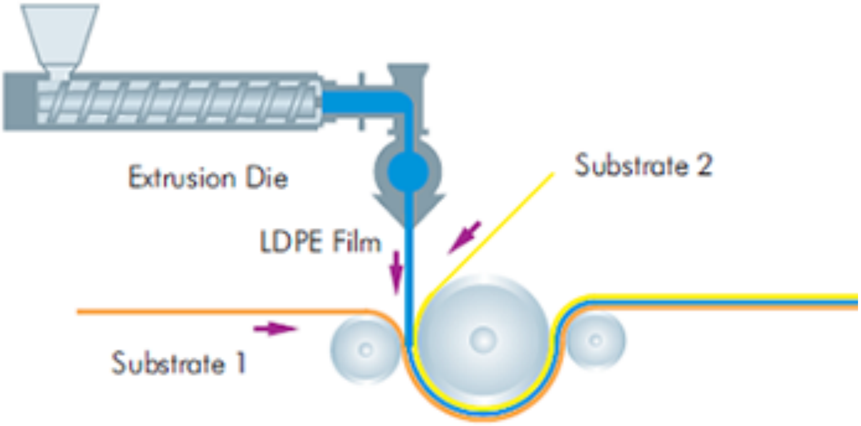


Figure 2. 8. Lamination station: Substrate 1 is paperboard, substrate 2 is Al foil; the laminate is cooled after LDPE had been casted (Safepack Industries, n.d.)

2.2.2 **Ozone treatment**

As the extruded film falls, ozone treatment is applied to oxidize the film's surface, improving its adhesion with the Al layer among other benefits. The treatment is highly controlled in order to achieve precise oxidation without excessive degradation, a picture of the ozone applicator in the lamination station is shown in Figure 2.9.

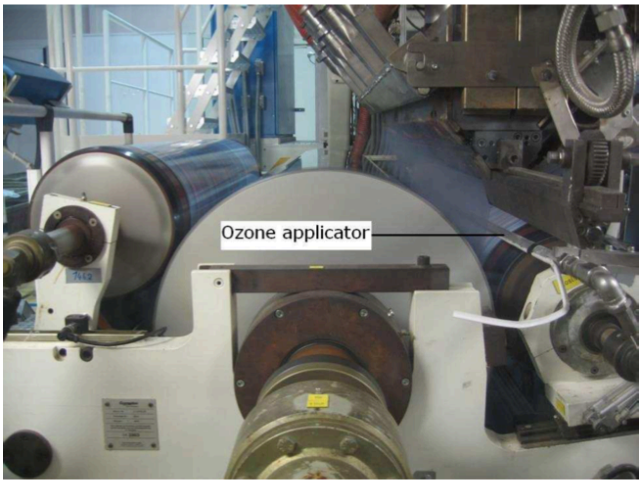


Figure 2. 9. Ozone applicator in the lamination station (Nordin, 2009)

2.2.3 **Peroxide bath**

In Tetra Pak's aseptic packaging method, unformed packaging material is sterilized in a heated hydrogen peroxide bath prior to forming and filling. H_2O_2 is a strong oxidizing agent. The peroxide bath consists of a 70ºC solution of hydrogen peroxide (H_2O_2) at 30% concentration, where the material is submerged for 6 seconds, the H_2O_2 is then removed using pressure rollers or hot air (Tetra Pak, 2019).

The high laminating temperature, ozone treatment, and the peroxide bath could therefore contribute to polymer oxidation, making mechanical recycling more challenging.

2.2.4 **Adhesion mechanism**

The adhesion forces between the polymer and the Al layers are mainly ionic bonds, hydrogen bonds, and Van der Waals forces, as a result of the interactions between the aluminum oxide and oxygen-containing groups on the surface of the polymer (Kaiser, Schmid and Schlummer, 2017; Bockhoff, McDonel and Rutzler, 1958). The combination of high processing temperatures and adhesion treatment, such as the use of ozone, may contribute to the degradation of the polymers, and reduce their resistance against thermo-oxidation during recycling.

2.3 Recycling and delamination

After collection and sorting, the laminated cartons first arrive at a paper mill where paper fiber is removed and recycled with water, leaving a mixture of laminated polymer films and PolyAl films, as well as hard plastic components used for caps and closures. The hard plastic components are then separated from the films.

Figure 2.10 shows an example of the recycling logistics of UBC and PolyAl (Tetra Pak, 2020), in which PolyAl can be manufactured into crates and pallets as a composite material. Globally, UBC PolyAl granules are manufactured in several countries, such as Russia, Brazil, South Africa, and Germany (Hamskog and Nyström, 2017).

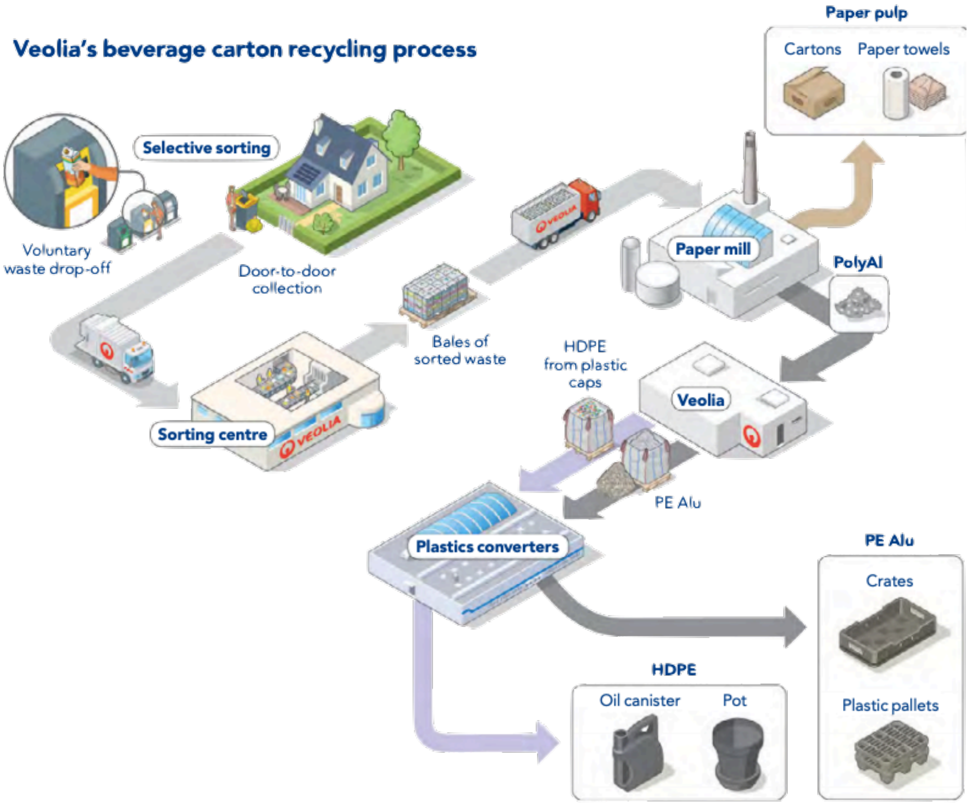


Figure 2. 10. Veolia's beverage carton recycling process, where PolyAl is recycled as a composite material; infographic by Art Presse (Tetra Pak, 2020)

It is important to note that the PolyAl processed at a recycling facility is usually from a mixture of carton packages by different converters. Globally, the Swiss packaging company SIG produced >38 billion (bn) beverage cartons in 2019 (SIG, 2019), the Norwegian Elopak produced 15 bn cartons with a development goal for all-wood packaging (Elopak, 2019), while Tetra Pak sold 184 bn in 2020 with advances in bio-based packages and elimination of Al foil (Tetra Laval, 2021). Depending on the geographic region, the companies' market shares differ. Without a common "design for recycling" strategy among the carton package converters, recovering the value of the PE films from carton packages will be challenging. In 2020, the Alliance for Beverage Cartons and the Environment (ACE) drafted a summary of best practices on beverage carton recycling, as an effort to align on design principles to address this challenge (ACE, 2020).

2.3.1 **PolyAl as a composite material**

PolyAl consists of PE films and Al foil strongly laminated together by the mechanism described in section 2.2.4. As a composite material, PolyAl was first recycled in the late 1990s to make roof tiles in Brazil (Hamskog and Nyström, 2017), nowadays it is also manufactured into pellets for injection molding. In the Netherlands, Recon Polymers had been in commercial production of composite PolyAl granules since 2020. Depending on the manufacturing method, products made from PolyAl have low water absorption rates and acceptable tensile strength, which makes it an adaptable material (Robertson, 2021).

Palurec in Germany takes a different approach, where the post-pulper mix is finely shredded to maximize the amount of LDPE recovered in the form of granules, while also yielding an Al fraction (Palurec GmbH, 2017). Since the separation of materials is purely mechanical, the LDPE fraction likely contains Al residue.

In theory, products made from composite PolyAl can be recycled, although its future use cycles is still unknown. Whether composite PolyAl is of true recycling is increasingly called into question by definitions and global pursuits in circularity (New Plastics Economy, 2020). While Al acts as a filler in PolyAl composites, it is not recycled as a separate material. A separation process is still required.

2.3.2 **PolyAl separation methods**

This section introduces the main PolyAl separation technologies and relevant mechanism in the context of green discoloration.

2.3.2.1 Acid-based delamination

In 1991, Tetra Laval introduced a PolyAl delamination method that became the basis of other acid-based delamination technologies, in which an organic acid (preferably acetic acid) or a mixture of organic acids was used. The UBC waste entering the treatment would be mechanically reduced in size, agitated during the treatment that was preferably above 50ºC, while very good separation efficiency was achieved at 80ºC with 80% acetic acid (by weight). (Johansson and Ackermann, 1995). However, since the flash point of 80% acetic acid is >61ºC (Thermo Fisher Scientific, 2018), the safety of this method challenges its feasibility. Later research and patents involving methanoic acid (Zhang, Yan and Li, 2009) and formic acid (Li et al., 2012) were safer methods with lower rate of Al loss.

2.3.2.2 Emulsion-based delamination

In their 2015 patent, Lovis et al. of the German company Saperatec GmbH used a microemulsion mixture of swelling agents for the polymer, caboxylic acid, water, and surfactants (Lovis, Seibt and Kernbaum, 2015). The microemulsions were able to penetrate the interphase to reduce adhesion forces (Kaiser, Schmid and Schlummer, 2017).

2.3.2.3 Solvent dissolution/extraction

PolyAl can also be separated by selective dissolution at different temperatures or with different solvents (Nauman and Lynch, 1994; APK AG, 2019). This method differentiates from chemical recycling in that the polyolefins are extracted and precipitated as their original polymers, instead of being depolymerized (Yang et al., 2012). Compared to the other two methods based on delamination, solvent dissolution/extraction does not further degrade the polymer, several companies in Europe are at pilot stage with this technology.

Acid-based delamination, emulsion-based delamination, and solvent dissolution/extraction are the three physical PolyAl separation technologies currently more developed for the market. An example of the delaminated films is shown in Figure 2.11.

Figure 2. 11. Sample of clean delaminated PE films (Diop, Lavoie and Huneault, 2016)

Table 2.1 summarizes their pros and cons based on reviews of PolyAl recycling methods.

Table 2. 1 Pros and cons of three prominent PolyAl separation technologies

	Acid-based delamination	*Emulsion-based delamination*	*Solvent dissolution/extraction*
Pros	Already used in commercial recycling Simple reagents (one weak acid can suffice) (Robertson, 2021)	Separation liquid can be reused	High-quality PE fraction Solvent can be reused
Cons	Oxidized and contaminated Al Replenishing acid is often needed (Zawadiak et al., 2017)	High water and energy demand (Sustainable Packaging Coalition, 2019) No commercial plants available	Waste solvent treatment necessary Al fraction may be more contaminated (Zawadiak et al., 2017) No commercial plants available

2.3.3 **Acid-based delamination**

Since acid-based delamination is the method used at the commercially successful PolyAl separation plants as of the time of the thesis, the following section will focus on this technology as a background for the green discoloration.

In acid-based delamination, the oxidized surface of the Al layer reacts with an organic acid that diffuses through the LDPE layers (Zawadiak et al., 2017), reducing the adhesion forces. A in a 2012 patent, Li et al. used 3-5 mol/L formic acid as a delamination solution to separate the PolyAl. The patent explained the delamination mechanism being the reaction of the oxidized surface of the Al layer, Al_2O_3, with formic acid, which diffuses through the LDPE layers due to its small size in a heated system between 40-60ºC. The reaction scheme is provided as:

$$HCOOH \rightleftharpoons H^+ + COOH^-$$

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$

Once the elementary Al is exposed, the adhesion forces are weakened, the films then separate upon agitation. Meanwhile, a weaker reaction takes place between the Al and the acid, resulting in Al loss. After separation, the polymer foils float on top of the delamination liquid, while Al foils sink to the bottom, allowing mechanical separation before subsequent cleaning and reprocessing. Additionally, nitric acid is added to the separation solution to maintain the solution's pH upon reuse. (Li et al., 2019)

Figure 2.12 demonstrates an example of the acid-based delamination process with formic acid, derived from Recycler E's process flow; note that upon arriving at the processing facility, the mixed PolyAl material must first be removed of rough waste (rocks, metals) and dust waste (fibers, aluminum). Non-PE plastics, PE films, and PolyAl are also separated for different processing streams.

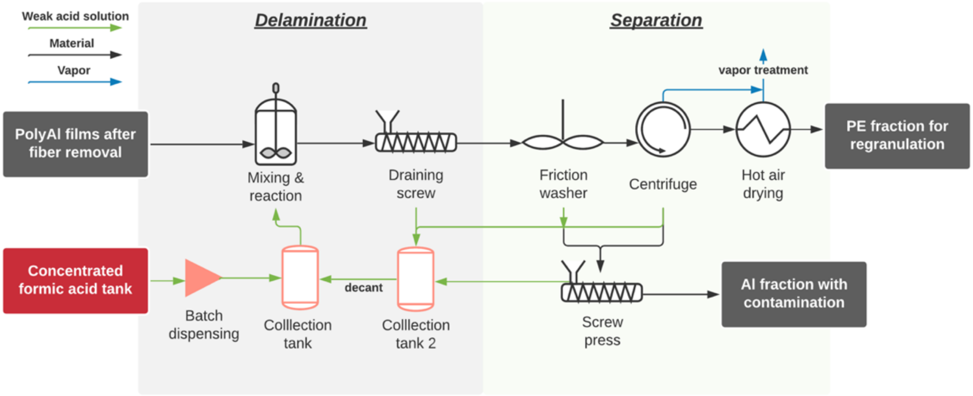


Figure 2. 12. Separation of PolyAl, simplified from the processing flow of Recycler E

2.4 Impurities

The cleanliness of PolyAl is important for both end product quality and avoiding damages to the equipment. While the exact effects of the impurities are not fully understood through literature, Table 2.2 compiles a list of impurities and their known impacts in PolyAl recycling.

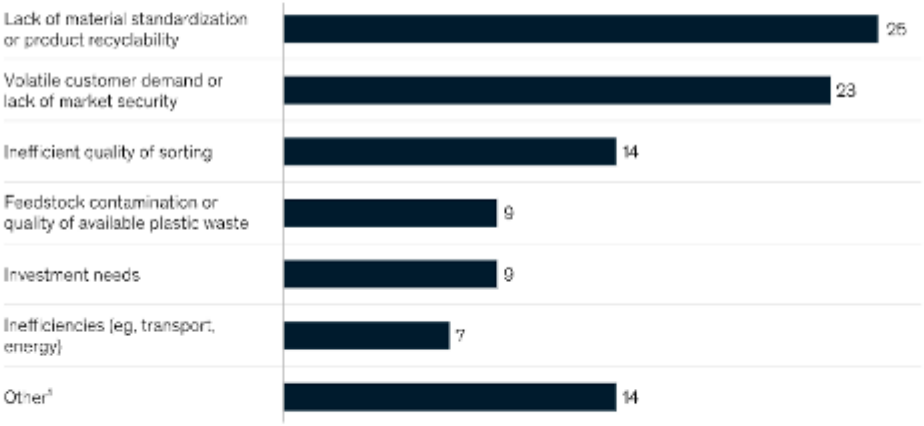
Table 2. 2 Impurities found in PolyAl after pulping and their known effects

Impurities	***Known effects***
Stones, non-Al metal	Damage or clog equipment, unnecessary transportation weight
Water from pulper	Form bubbles in recycled products via evaporation, unnecessary transportation & wastewater weight
Leftover fiber (cellulose)	Carries moisture, clog filters, contaminates end products
Non-PE plastics	Contaminates end products (e.g., adhesives, PP caps)
Inks and additives	Undesired colors and odors

A post-pulper treatment is therefore important to remove any harmful and unhelpful impurities. In a review of flexible plastic waste management, Horodytska et al. explored deinking technologies, having identified ink residue as a contributor to the low value of recycled flexible plastic. Similar to the delamination technologies, deinking method development had not reached technical maturity: solvent-based deinking raised environmental concerns, water-based methods rely on ink properties, the deinking company must also consider cost and end-product quality. (Horodytska, Valdés and Fullana, 2018)

2.5 PolyAl valorization

A 2020 survey by McKinsey & Company interviewed 57 recycling companies in 12 European countries. The lack of material standardization or product recyclability was identified as the most common hurdle, while the lack of market security came to a close second in the absence of centralized trading platforms (Figure 2.13). Of the companies surveyed, PE is the most processed plastic resin, where 66% of the companies processing PE are small-medium sized players. (Mikhail Kirilyuk et al., 2020)



[1] Includes competition with players in low-cost regions, bidding process, etc.

Figure 2. 13. Current hurdles to the recycling business, % answers provided (Mikhail Kirilyuk et al., 2020)

As a part of the survey's conclusion, the recycling industry should be made more economically attractive and investable, and a common marketplace for feedstock and products can improve the material flow on the market (Mikhail Kirilyuk et al., 2020).

2.5.1 **Business case in China**

Since commercial PolyAl separation is relatively new in Europe, the existing business cases in China provide a reference for PolyAl separation valorization.

In 2010, the Chinese recycler Fulun had processed more than 30 thousand tons of cartons, returning 6000 tons of recycled PE and 1500 tons of Al powder to the market through PolyAl separation (Hangzhou Fulun Ecological Technology Co., n.d.). Given its own challenges and legislative differences, the past decade of commercial PolyAl separation in China may be partially attributed to its flourishing online trading platforms. From the all-trading 1688.com by Alibaba group to specialized sites for plastic recycling feedstock and products (e.g. zaisubao.cn and zssl.net/buy), the accessibility and visibility of small and medium-sized players can be seen improved, answering the challenge identified above by European recyclers.

3 Method and Approach

3.1 Research approach

As the choice of methodology depends on the goal and nature of the project, it is inevitable that sometimes a project involves more than one approach.

The identification and investigation of a potential cause of the green discoloration is largely exploratory, although the report should also serve to systematically explain the background of the phenomenon. With that in mind, the review of literature and interviews proceeded simultaneously, the literature review enhancing the depth of the interviews, while the interviews offered important insights for new areas to research. Even though an analysis had been commissioned to an external laboratory for the project, an experimental component was added internally when the availability of materials emerged, serving as a source of primary quantitative data to explore the hypothesis.

3.2 Research design

The multiple channels of data with the addition of shifting development of the project brought added complexity to the research process. Figure 3.1 offers an overview of the design.

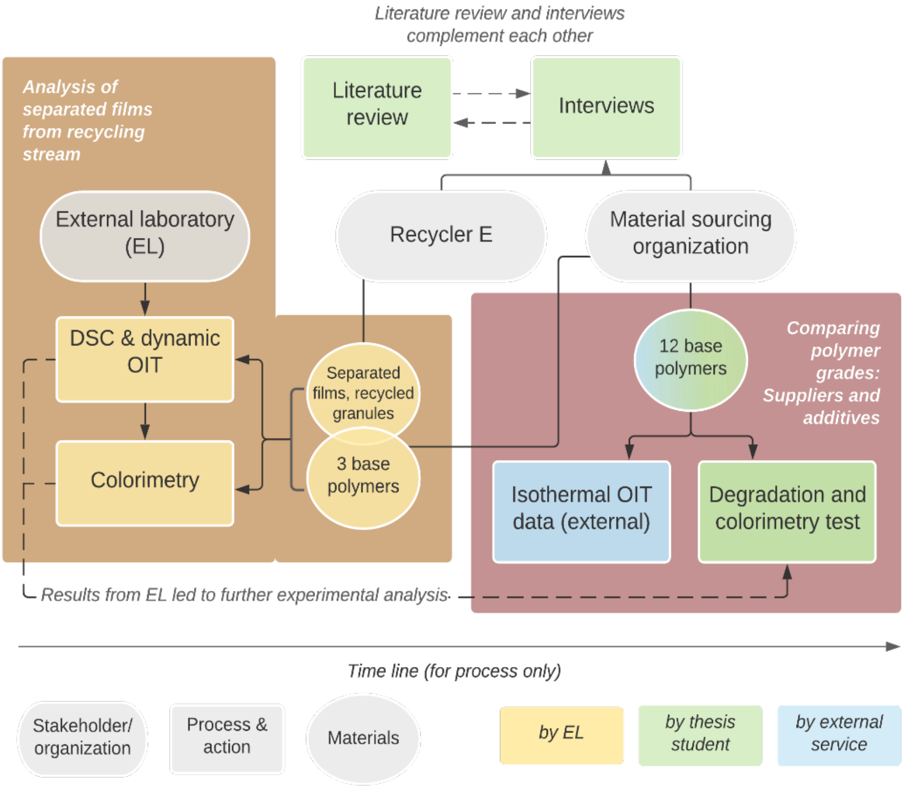


Figure 3. 1 Overview of research design; the shaded areas represent two parts of experimental analysis

The results from EL's analysis became available early in the process, hence it allowed the scope of the review to be more focused and in depth, consequently shifting the central question of the project towards additive oxidation. However, by narrowing the field of vision at an early stage, other important factors in the polymer materials' lifetimes were neglected, leading to supplemental literature review later on to capture the fuller picture of the discoloration phenomenon.

3.3 Stakeholder interviews

Throughout the thesis project, different stakeholders participated in interviews for different purposes summarized in Table 3.1. The results from the interviews form qualitative results to discuss. The interviews were transcribed real-time and organized based on topics afterwards.

Table 3. 1 Stakeholder interviews – outline

Stakeholder	*Setup*	*Purpose*
Vice Chair of Recycler E	Prepared questions, video conference, email correspondence	Understanding the separation technology, technical limitations Learn about the value chain for PolyAl separation, product market, and future plans Understanding the business case of green discoloration
Tetra Pak material specialist	Prepared questions, video conference, email correspondence, follow-up meetings	Seek more information about the inner polymer grades within the perimeter of confidentiality Obtain the perspectives and insights from the organization responsible for material sourcing

The questions for each of the stakeholders were based on an understanding of their areas of expertise, roles, and responsibilities, developed to fill the gap between the existing knowledge and the phenomenon of the green discoloration. The questions for Recycler E include:

- Since when did the green discoloration become a problem? What had been done in order to minimize the discoloration (process change, etc.), to what effect?
- What is Recycler B doing/planning to do to maximize the values of the end polymer products?

All questions and the full interview with Recycler E can be found in Appendix A. Since the detailed interview and follow-up meetings with the material specialist contained confidential information, only a disclosable summary is shown as a part of the results.

3.4 Experimental analysis

The experimental analysis aims to explore two areas of interest: the thermal stability of the polymer grades in terms of color change, and the degree of discoloration in relation to additives and suppliers. The latter was proposed after the preliminary analysis by an external laboratory (hereby referred to as EL).

The experimental analysis can be divided into two stages, each stage involving a different set of materials to be tested. Stage one is the preliminary experiments by EL, which mostly involved recycled materials, studying their thermal behavior and color spectra. Stage two was done internally at Tetra Pak by the thesis student, comparing the degrees of discoloration of the inner polymer mixes from different suppliers, as well as formulations with different additives from the same supplier.

DSC (differential scanning calorimetry) and OIT (oxidation induction temperature/time) are two methods used by EL, for the preliminary investigation of the thermal behaviors of the recycled and virgin materials. Additional DSC & OIT results on a collection of virgin polymer grades from different suppliers were also provided through external service.

The degree of discoloration is assessed through colorimetry. EL analyzed the L*a*b* and RGB values of recycled films and three virgin grades in comparison, additional color analysis was done to compare the degrees of discoloration between polymer grades sourced from different suppliers.

3.4.1 **Analysis of separated films from recycling stream**

3.4.1.1 Materials

EL received 1kg of recycled films from the recycler, chemically separated PolyAl, originating from UBC recycled in Germany. Tetra Pak provided virgin polymers (décor layer, adhesive, and two PE grades that formed the inner polymer mix denoted as PE1 and PE2). The recycled films were manually sorted based on their colors into 15 fractions by EL.

3.4.1.2 DSC & dynamic OIT

DSC was performed on all fractions of the separated film, as well as the PE grades from Tetra Pak. DSC, or differential scanning calorimetry, is a common method used for the thermal analysis of polymers and polymer blends, making observations and measurements of the physical transitions, chemical reactions, oxidative stability, and heat capacity associated with the materials (Swedish Standards Institute, 2016).

As outlined in ISO 11357-1:2016, a DSC instrument measures the difference in the heat flow rate between a specimen and a reference crucible (usually empty), while both undergo the same temperature-control program and atmosphere. The heat flow rate, $\mathrm{d}Q/\mathrm{d}t$ in unite of W or mW, is expressed in a function of temperature or time, where positive values indicate an endothermic process unless stated otherwise. (Swedish Standards Institute, 2016). In EL's DSC analysis, all samples were heated from 25ºC to 240ºC, at a rate of 10K/minute, under a constant flow of N_2. The inert gas prevented the samples from further oxidation by the presence of oxygen. Along with the DSC plot, the physical appearances of the samples before and after DSC are also observed.

EL also analyzed the OIT of PE1 and PE2. OIT as an acronym denotes two different meanings – oxidation induction time and oxidation induction temperature, while dynamic OIT is the latter; Figure 3.2 offers a structured explanation of DSC nomenclature. The OIT (both types) of a polymeric material is determined through DSC as an indicator for the degree of its oxidation stabilization, and even the effective level of antioxidant present in the sample. In dynamic OIT, a sample undergoes thermal treatment at a given rate of heating and atmospheric pressure with oxygen or atmospheric air flow; the onset temperature of exothermic oxidation reaction is registered as the OIT in degree Celsius (ºC). (Swedish Standards Institute, 2018). In EL’s experiment, the same temperature program as the previous DSC was applied, only with the addition of air flow. Like the DSC analysis, the physical appearances of the samples were observed before and after the OIT analysis.

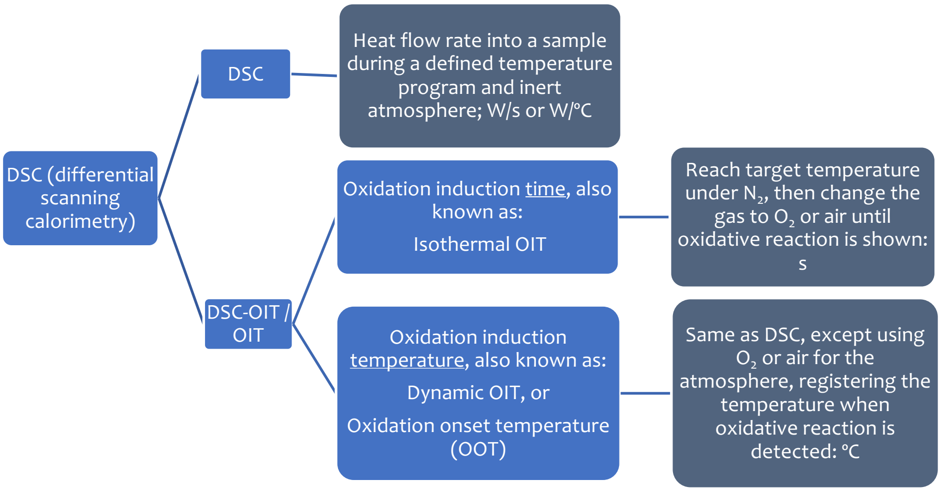


Figure 3. 2 DSC nomenclature and definitions

3.4.1.3 Colorimetry

In order to analyze each fraction’s impact on the overall color of the final granules, the fractions were reconstituted with a virgin inner polymer blend (PE1 and PE2 at production ratio) by weight proportions. For example, fraction 1 made up 74.1% of the separated films by weight, therefore the colorimetry blend consisted of 74.1% fraction 1 and 25.9% inner polymer blend.

Each mixture was compounded in a lab-scale kneader for 15 minutes, before being injection-molded into test plates, this is a common preparation method used to distinguish between good and bad formulations. An alternative method is used for the sample prepared from fraction 1, where the proportion of film made the mixture too bulky to be injection-molded; the fraction and inner polymer mix were treated in an oven at 180ºC for 10 minutes instead of kneader, preserving similar thermal histories between all the samples.

The optical analysis of the samples involved the CIELAB colorimetric reference system as the modeling basis. The operation of CIELAB is based on the "principle of color opposition correlation", pitting opposite colors on two ends of a spectrum to construct the final colors perceived by the brain. The three-dimensional model includes lightness vs. darkness (L*), red vs. green (a*), and yellow vs. blue (b*), visualized in Figure 3.3. (Sappi Fine Paper North America, 2013)

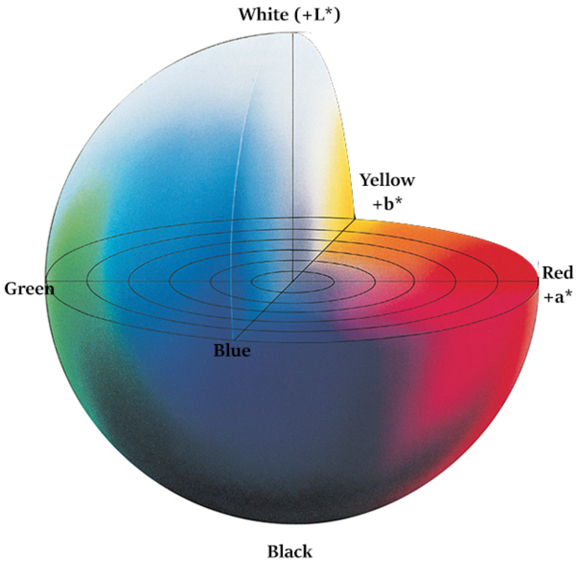


Figure 3. 3 3D representation of the L*a*b* color space, each factor measures up to 100 (Konica Minolta, 2018)

The color differences between samples were quantified based on a reference sample, the recycled granules, and expressed as

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

so that ΔE indicates the distance between a sample and a reference in the color space. However, it does not distinguish in what way the two colors are different (Sappi Fine Paper North America, 2013). Therefore, the quantified color differences are more applicable in this study when sample treatment and original colors are consistent.

3.4.2 Comparing polymer grades: suppliers and additives

Further experimentation is done based on EL's findings, in order to investigate one of the prominent factors that could result in the green discoloration – the polymer grades themselves. The tests are done at Tetra Pak, the methods designed and adapted to best suit the equipment available.

3.4.2.1 Materials

The Base Material organization at Tetra Pak provided 12 samples of interest. The samples come from 5 different suppliers, coded A through E, distinguished by different additives and dosages (Table 3.2). Antioxidant is denoted as AO, where AO1-3 are three different antioxidants.

Table 3. 2 List of samples used to compare discoloration between different polymer grades

Supplier	Sample	Additives
A	A1	Additive free
	A2	AO1 low amounts
	A3	AO1 + Ca stearate
	A4	AO1 medium level
	A14	AO1 high level
	A15	AO2
B	B	AO1 + Ca stearate
	B1	AO1 + Ca stearate
C	C	Additive free
	C1	Additive free
D	D	Additive free
E	E	AO3

3.4.2.2 Thermal oxidation and colorimetry

The goal of this experiment is to have a preliminary comparison of discoloration properties between the inner polymer grades, where the suppliers and additives used are the only differentiating factors. The experimentation followed three steps: sample discs forming, oven degradation, and L*a*b* analysis.

The samples were available in the form of extruded sheets (Figure 3.4). The sheets were cut into small pieces (roughly 2cm^2), to be thermally formed into discs using Collin high performance press S, sandwiched between two 16-plate Teflon forms at 150ºC for 150 seconds followed by a cooling cycle of another 30 seconds, a standard program for LDPE plates. The Teflon forms and Teflon sheets (Figure 3.5) were cleaned of any residue with a scrub between each sample. The sample plates are 2cm in diameter and on average 1.364mm thick with visible unevenness.

Figure 3. 4 Samples in the form of film

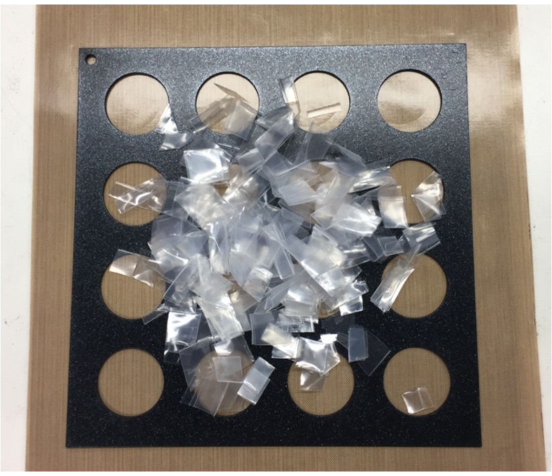


Figure 3. 5 Cut sample on Teflon form and Teflon sheet ready to be covered and formed into discs

The discs were heated in Binder drying and heating oven operating at 250ºC for 6 minutes with convection, in triplicates. The thermal degradation was done in three batches, each batch contained one disc from each sample, with three discs placed on each metal plate lined with non-stick liners (Figures 3.6 & 3.7). The metal plates were placed at a different location for each trial in order to randomize any potential effects of hotspots in the oven.

Figure 3. 6 All 12 samples placed in the oven; placement on the top rack avoids strong convection that may disturb the samples

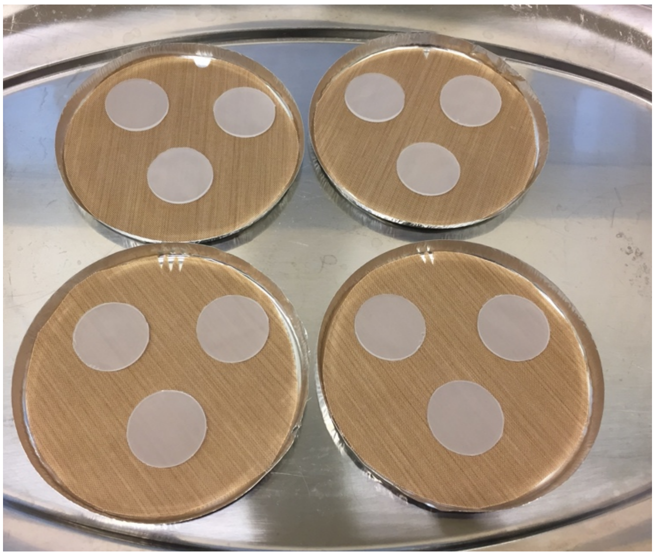


Figure 3. 7 Sample distribution on the plates, each plate was marked by the Teflon sheet to avoid potential impacts from ink

The colorimetric or L*a*b* analysis was performed on L&W Elrepho colorimeter (Figure 3.8), an equipment designed for the paper industry, as no instrument designed for polymer colorimetry was available. Therefore, the following method shows the best proximation to legible data that can be used to compare the degree of discoloration between samples. With a diameter between 20 to 22mm, the samples were analyzed at 36mm aperture, allowing the surface of each disc to be assessed completely. One measurement is taken for each disc, the same is done for untreated sample discs. In calculation of the color differences, the L*a*b* values of each degraded sample were referenced against said sample's untreated counterparts, thus producing the degree of degradation.

Figure 3. 8 L&W Elrepho colorimeter

3.4.2.3 Isothermal OIT

Additional isothermal OIT data of the samples (all samples but A1 in Table 3.2) was provided by an external R&D service provider other than EL, obtained through the material specialist. Compared to the dynamic OIT described in 2.2.1, isothermal OIT measures a stabilized material's resistance against oxidative decomposition, where a sample is held at a constant temperature and air/O2 flow. The time it takes to reach the onset of oxidative decomposition becomes the OIT, in minutes. (Swedish Standards Institute, 2018). Isothermal OIT is more time-consuming, as it is usually conducted at a lower temperature than the end temperature of dynamic OIT. The results serve as supplemental material to the colorimetry analysis.

4 Results

4.1 Interviews

4.1.1 **Recycler E**

The green discoloration was observed in transparent recycled films that had been melted; however, in an experiment when the films were washed with a solvent, the phenomenon was no longer observed. Recycler E reported that while there was no lack of buyers, transparent recycled material enjoyed higher prices on the market than their green counterparts, therefore the removal of green discoloration should have positive impact. However, other contaminants are also present, such as remaining solids from the washing step, other plastics from imperfect post-consumer sorting, and polymer-polymer laminates like PE-PET. Recycler E originally targeted the Al fraction, which was later proven to be too oxidized and impure for more valuable applications.

Recycler E uses acid-based separation technology. Making changes to the current process and equipment will be quite challenging, as it affects not only the economy of operation, but also waste water/gas logistics.

4.1.2 **Internal material specialist**

In the converting process, the PE layers needed to be intentionally degraded to enhance adhesion – a statement that aligns with earlier literature review. A balanced approach to using antioxidant was therefore needed, as polymers without an additive could be affected by extrusion while antioxidants may also lead to unpleasant odor.

The material specialist also provided several relevant observations from the industry:

- The peroxide bath in the packaging line oxidizes the inner polymer
- Suppliers are looking into chemical recycling for the future, as the products from chemical recycling can be compared with virgin material

4.2 Experimental analysis

4.2.1 **EL: Separation of colored fractions**

The weight distribution of the separated fractions is demonstrated with color-coding in Figure 4.1. Of the 1kg mixed recycled film, 71.4% was sorted as "colorless", while the other fractions contained heavily colored films or mixed colors on one film. The "colorless" films (Fraction 1) are of the most interest in this study, for its proximity to the colorless inner polymer layers, and the lack of interference from ink. It is also observed that much of the ink was not removed in Recycler E's separation process.

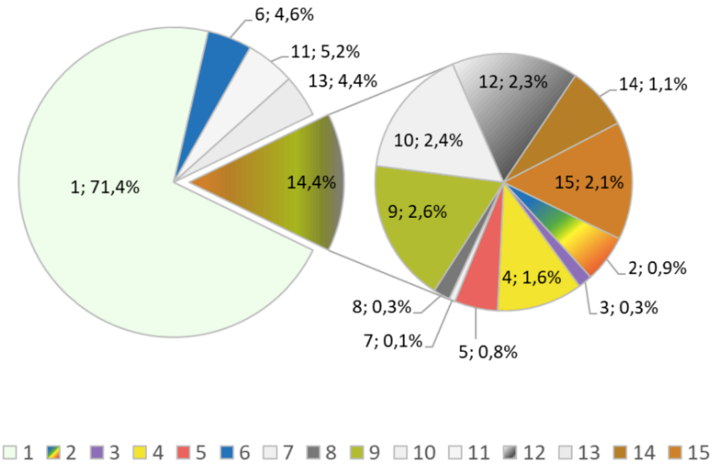


Figure 4. 1 Fifteen colored fractions manually sorted from polymer films from delamination

4.2.2 **EL: DSC & DSC-OIT**

After the DSC analysis, a yellowish-green discoloration was observed in the colorless fraction, while the green fraction had turned visibly darker (Figure 4.2).

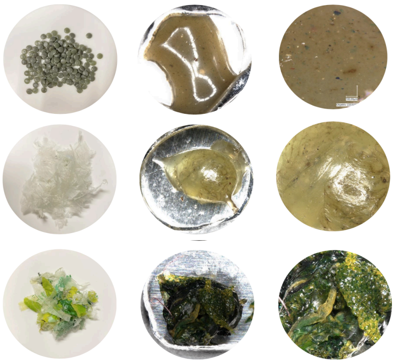
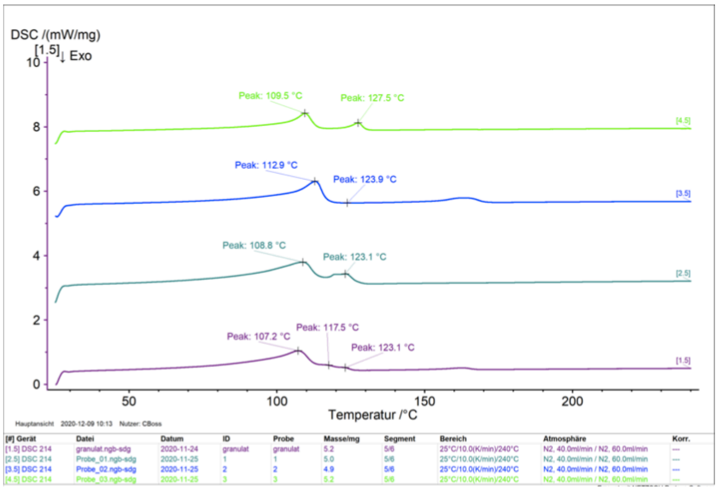


Figure 4. 2 An example of separated films used in DSC analysis. Top to bottom: recycled granules, Fraction 1 (colorless), Fraction 9 (green); left to right: before DSC, after DSC, close-up after DSC

The DSC of separated film fractions showed the differentiating melting points of different polymers in each fraction. In Figure 4.3 for example, the earlier peak is identified as the presence of LDPE, with a melting point around 108ºC, and the following peaks suggest the presence of LLDPE (T_m = 121ºC), MDPE (medium-density polyethylene, T_m = 124ºC), and HDPE (T_m = 125ºC; Li, et al., 2019); the last peak that is more prominent in the second and the last curves at around 160ºC most likely indicates polypropylene, the melting point of which was determined at 162ºC by Kaiser, Schmid and Schlummer (Kaiser, Schmid and Schlummer, 2017).



[#] Gerät	Datei	Datum	ID	Probe	Masse/mg	Segment	Bereich	Atmosphäre	Korr.
[1.5] DSC 214	granulat.ngb-sdg	2020-11-24	granulat	granulat	5.2	5/6	25°C/10.0(K/min)/240°C	N2, 40.0ml/min / N2, 60.0ml/min	---
[2.5] DSC 214	Probe_01.ngb-sdg	2020-11-25	1	1	5.0	5/6	25°C/10.0(K/min)/240°C	N2, 40.0ml/min / N2, 60.0ml/min	---
[3.5] DSC 214	Probe_02.ngb-sdg	2020-11-25	2	2	4.9	5/6	25°C/10.0(K/min)/240°C	N2, 40.0ml/min / N2, 60.0ml/min	---
[4.5] DSC 214	Probe_03.ngb-sdg	2020-11-25	3	3	5.2	5/6	25°C/10.0(K/min)/240°C	N2, 40.0ml/min / N2, 60.0ml/min	---

Figure 4. 3 An example of DSC analysis of the separated films, showing presence of LDPE, PP, and LLDPE/MDPE based on their respective melting points

The results indicate the prominence of various PE in the green granules, as well as mainly LDPE in the colorless fraction, with secondary presence of PP and a small amount of LLDPE/MDPE (first and second curves in Figure 4.3). The mixing of different polymers should come from the initial post-consumer mix, which contained not only cartons from Tetra Pak and competitors in the German market. The risk of mixing material from non-carton packages is very low but can't be excluded, depending on post-consumer sorting efficiency.

Unknown degradation hotspots were observed after the dynamic OIT analysis of the virgin samples (Figure 4.4). According to the EL, the thermal stability of the virgin granules was amongst the lowest they had observed in the industry, as a result they predicted a lack of protection for further processing during recycling and regranulation.

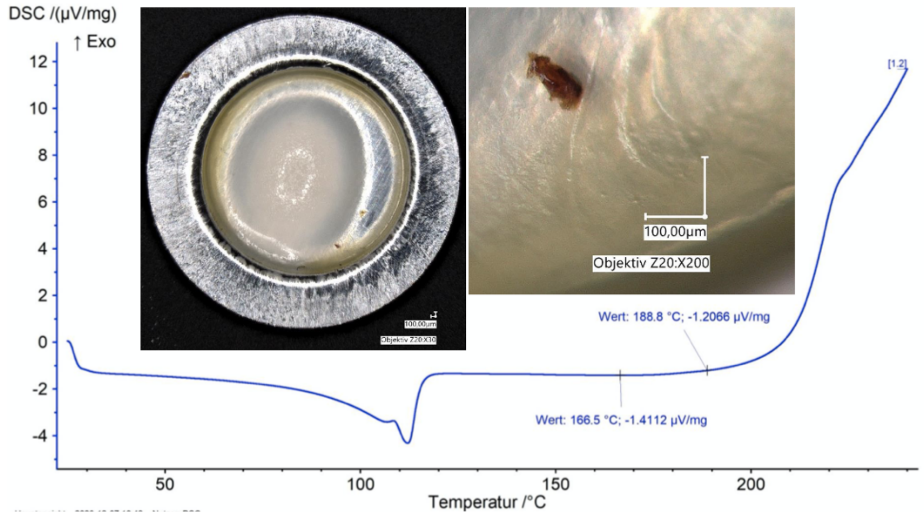


Figure 4. 4 Highly discolored degradation hotspot in PE2 and its dynamic OIT exotherm graph, with oxidative degradation initiating at 188.8ºC.

4.2.3 **EL: Colorimetry**

Fraction 1 (“colorless” fraction, Sample 1 in Figure 4.5) exhibited visually significant green discoloration after oven treatment and injection molding; it was treated in an oven instead of a kneader like the other samples due to its bulk. With the lack of ink, the phenomenon can be attributed to its different thermal-oxidative treatment, high weight percentage in the compounded plate (71.4%, compared to the next highest fraction, 5.2%), and differences in polymer grades. It is noted that the polymer layers with ink should be identified as the décor layer (LDPE).

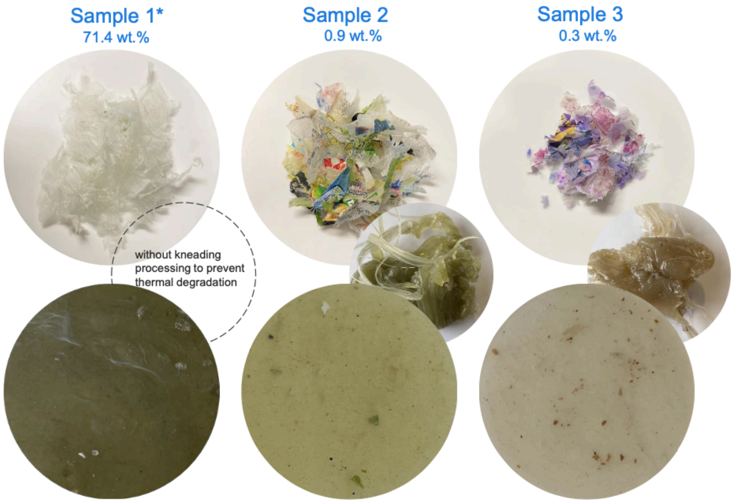
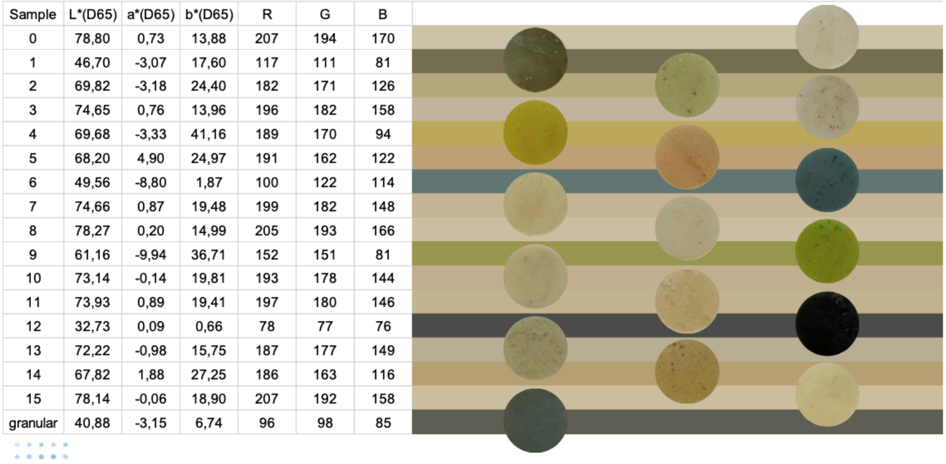


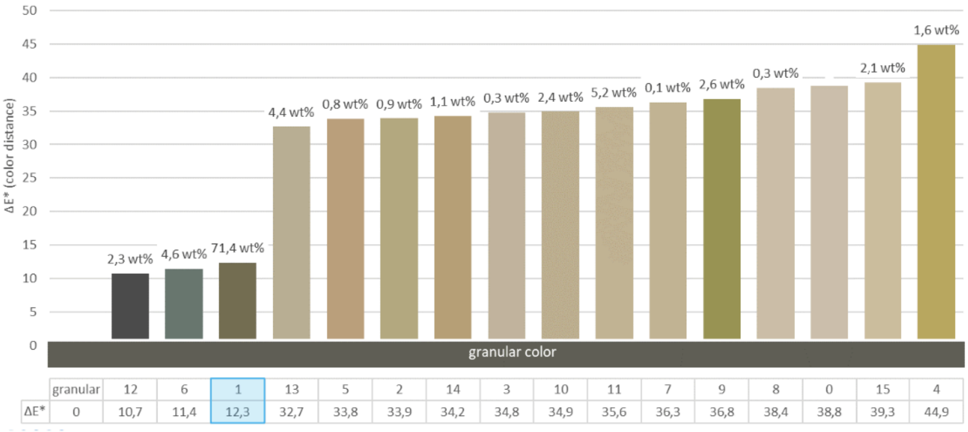
Figure 4. 5 Fractions 1-3 compounded. Top to bottom: before kneading, after kneading, after plate-forming

The L*a*b* and RGB measurements of the fractions are shown in Figure 4.6, and the ΔE values are shown in Figure 4.7. Using the recycled granules as a standard, the colorless Fraction 1 ranks third in its proximity when evaluated in L*a*b*, after the heavily pigmented Fractions 12 (black/grey) and 6 (blue). Due to the presence of ink and low proportions in the sample plates, Fractions 2-15 are best compared amongst themselves.



Sample	L*(D65)	a*(D65)	b*(D65)	R	G	B
0	78,80	0,73	13,88	207	194	170
1	46,70	-3,07	17,60	117	111	81
2	69,82	-3,18	24,40	182	171	126
3	74,65	0,76	13,96	196	182	158
4	69,68	-3,33	41,16	189	170	94
5	68,20	4,90	24,97	191	162	122
6	49,56	-8,80	1,87	100	122	114
7	74,66	0,87	19,48	199	182	148
8	78,27	0,20	14,99	205	193	166
9	61,16	-9,94	36,71	152	151	81
10	73,14	-0,14	19,81	193	178	144
11	73,93	0,89	19,41	197	180	146
12	32,73	0,09	0,66	78	77	76
13	72,22	-0,98	15,75	187	177	149
14	67,82	1,88	27,25	186	163	116
15	78,14	-0,06	18,90	207	192	158
granular	40,88	-3,15	6,74	96	98	85

Figure 4. 6 L*a*b* and RGB values of the reconstituted fractions and recycled granules, with visual representations



granular	12	6	1	13	5	2	14	3	10	11	7	9	8	0	15	4
ΔE* 0	10,7	11,4	12,3	32,7	33,8	33,9	34,2	34,8	34,9	35,6	36,3	36,8	38,4	38,8	39,3	44,9

Figure 4. 7 ΔE of the reconstituted fractions calculated using the L*a*b* values of the recycled granules as standard.

EL also analyzed the color composition of the recycled granules and the colorless Fraction 1; Figure 4.8 points out the key differences between human color feeling (dark green) and color composition (yellow & grey) based on color coordinates.

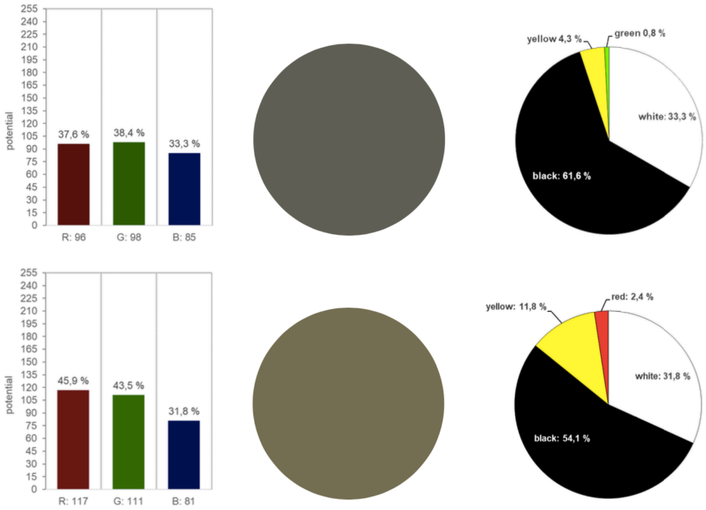


Figure 4. 8 Left to right: RGB (color stimuli in the eye), human color feeling, and color composition; top to bottom: recycled granules, Fraction 1

4.2.4 **Isothermal OIT on selected grades**

Isothermal OIT is typically used to estimate the thermal-oxidative stability of a polymeric material (Schmid, Ritter and Affolter, 2006). Figure 4.9 shows an example of the measurements, where the isothermal OIT is determined at the intersection of pre-degradation and degradation trendlines; time 0 (mins) marks the beginning of the purge of oxygen that replaces nitrogen.

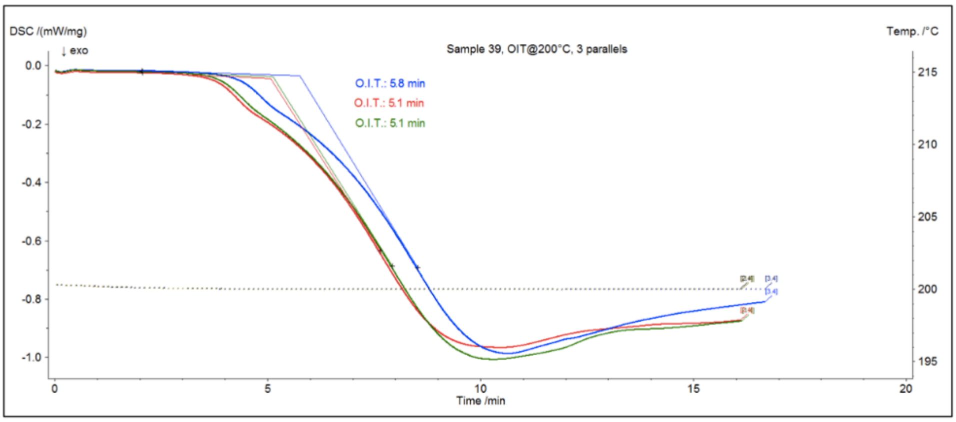


Figure 4. 9 Isothermal OIT showing the exothermal breakdown of sample A2

Figure 4.10 compares the isothermal OIT of the samples. As Schmid et al. reported, unstable polymers can produce uncertainly low results with notable standard deviation, in line with the comment from the internal material specialist. The selected samples exhibit a wide range of isothermal OIT, most of which are below 10 (A2, A3, B, B1, C, C1, D, E), considered as low values by Schmid et al. However, the highest standard deviation is observed in sample A15, where isothermal OIT = 26.2±0.42.

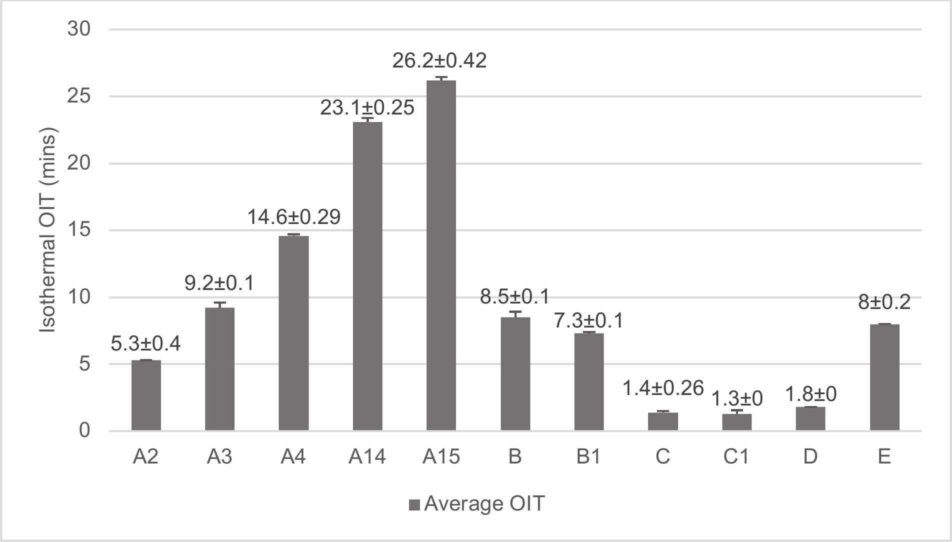


Figure 4. 10 Average isothermal OIT of selected polymer grades

4.2.5 **Tetra Pak laboratory results: Colorimetry**

Even when shrouded in uncertainty and a lack of standard procedure, the oven-treated samples yielded visibly consistent results (Figure 4.11).

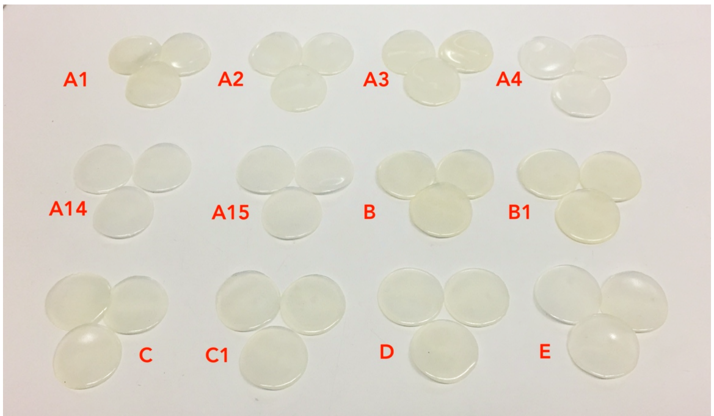


Figure 4. 11 All samples after oven treatment

Through L*a*b* colorimetry, the color difference (*Δ*E) was calculated based on each sample's L*a*b* measurements prior to thermal-oxidative treatment. However, in order to understand the contribution of yellow discoloration in the overall color difference, the coordinate-specific differences (ΔE_{L^*}, ΔE_{a^*}, ΔE_{b^*}) were also calculated, similar to the calculation of ΔE; for each sample, the ΔE_{b^*} is calculated based on its b* values pre- and post-treatment:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

$$\Delta E_{b^*} = \sqrt{\Delta b^{*2}}$$

Figure 4.12. compares the overall discoloration (ΔE) to all the coordinate-specific discolorations after the samples had been treated. It can be observed that the yellow discoloration is the most consistent with the discoloration overall, and a main contributing factor, even though the values for L* are significantly higher (Table 4.1). All samples became darker (decreased L*), greener (decreased a*), and yellower (increased b*) after thermal-oxidative treatment.

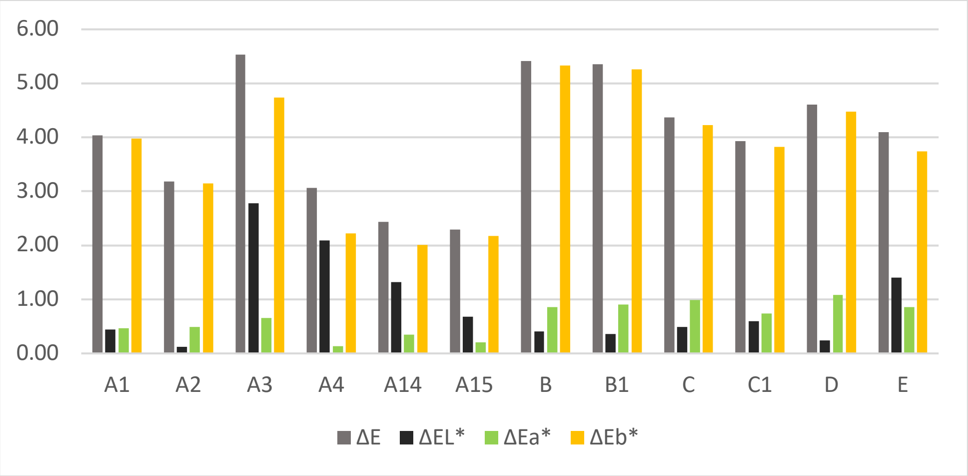


Figure 4. 12 Overall discoloration and coordinate-specific discoloration of the selected samples

Table 4. 1 Example of L*a*b* data gathering, sample A1 (treated)

Sample	Trial	L*	a*	b*
A1	1	81.08	-1.44	5.57
	2	79.49	-1.31	4.91
	3	81.15	-1.35	5.21
	Mean	80.57	-1.37	5.23
	St. Dev	0.94	0.07	0.33

The trend in colorimetry aligns with that of the isothermal OIT, where samples that withstood thermal oxidation longer had experienced less discoloration (A14 and A15), and vice versa. Samples A3, B, and B1 with just below-average isothermal OIT were among the most discolored samples, highly influenced by b*; this result is in line with the internal material specialist’s comment on the yellowing of polymer grades containing Ca stearate.

Since the convection oven loses a significant amount of heat each time the oven door opens, the oven temperature can only maintain at 250ºC for less than one minute at the end of each trial, taking most of the run time returning to that temperature. However, this thermal experience was relatively consistent between trials.

5 Discussion and Recommendations

5.1 Impact of the discoloration on end-product value

The green, or yellow and grey discoloration, combined with other impurities, puts the PE end-product of chemical delamination in disadvantage in terms of market price (Recycler E, 2021). From a business incentive perspective, the value of recycled PE film from PolyAl should be improved to make the recycling industry more attractive for companies and investors (Mikhail Kirilyuk et al., 2020), which will support the continual development of the industry and technologies.

As changing the existing delamination process or equipment will be difficult (Recycler E, 2021), the removal of the discoloration should take into account the cost and limitations of implementation, to not off-set the higher margin of colorless/light-colored PE.

5.2 Exploring the potential root causes

The review of literature examined the life cycle of polymers used in Tetra Pak's carton packages, from raw materials and additives, to converting and recycling. During the review, a list of potential root causes for the green/yellow discoloration was identified, which were further confirmed and refined by interviews.

The potential root causes, stage of life cycle, and relevant stakeholders are summarized in Table 5.1, where the potential requirements for modification at each stage is also discussed.

Table 5. 1 Potential root causes of green discoloration in PE recovered from acid-based separation of PolyAl

Potential root cause	***Stage of life cycle***	***Stakeholders***	***Requirements for modification***
Residue from the metallocene catalyst	Raw material sourcing	Material sourcing at Tetra Pak	

Potential root cause	***Stage of life cycle***	***Stakeholders***	***Requirements for modification***
Phenolic AOs ***Phenolic AOs + acid scavenger***			Requires specification and collaboration with suppliers
Oxidation during processing (high extrusion temperature, ozone treatment and peroxide bath)	Converting	Process engineering at Tetra Pak	Challenging to introduce equipment change, renew processing calibration, possibly requiring long-term commitment
Impurities during recycling (inks and additives)	PolyAl recycling	Paper mill/PolyAl recycler	Technically feasible, requires ink-chemistry optimization and cost-balancing
Delamination method ***(acid-based)***		PolyAl recycler	Influenced by technology and market trends: Small-medium sized players are often based on their flagship technology, since equipment investment is high

The experiment results from EL offered valuable insights. Although ink-tinted recycled films predictably contributed to the overall darkening of the final PE granules, the majority (71.4%) of the films were colorless yet experienced discoloration similar to that of the mixed films, therefore the contribution by ink was likely small. Through analyzing the RGB composition, it was proposed that the green appearance of the discoloration had been a combination of generic graying and a yellow discoloration, further directing the scope towards the oxidation products of phenolic antioxidants and other additives.

With the understanding that a degree of oxidation is necessary for the adhesion of PE films to Al (Internal Material Specialist, 2021), the practicality of changing the converting process in order to reduce discoloration is very low. The above frame of understanding left base materials and their additives as the primary focus for the thesis. However, other factors should not be excluded, as the formation of the green discoloration is complex and likely linked to multiple factors in polymers' value chain.

5.3 Additives linked with yellow discoloration

Overall, supplier A provided the most discoloration-resistant samples. The results from in-house experiments showed the effectiveness of AO1 against overall discoloration and yellowing, shown across supplier A's polymer grades, except when used with Ca stearate. Ca stearate, as used with a phenolic AO, is a key proponent in discoloration of the mLLDPE, as agreed by previous studies by Hoàng et al. (Hoàng et al., 2004). However, Ca stearate is more often used in metallocene polymers; considering that the proportion of mLLDPE in the base polymers is rather small (Figure 2.1), Ca stearate may not be a strong contributor to the discoloration overall.

The level of discoloration generally decreased with increasing amounts of AOs within the thermo-oxidative treatment, showing the protective properties of phenolic AOs on mLLDPE. However, this does not disprove the formation of yellow species by oxidation of AOs; as the yellowing of AOs is linked with their depletion (Pospíšil et al., 2002), the oven aging at 250ºC for 6 minutes may have simply not depleted the AOs in the samples.

The phenolic AOs are necessary for protection against the thermo-oxidative degradation of the base polymers (Internal Material Specialist, 2021). Additive-free samples were shown to turn yellow (no more than samples with Ca stearate), indicating that mLLDPE alone could turn yellow, which is possibly led by the residues from the metallocene catalyst (Epacher, Kröhnke and Pukánszky, 2000; Hoàng et al., 2006).

5.4 Answering the research questions

The research questions were defined as:

1. What are the potential causes for the green discoloration in the PE recycled via chemical delamination from PolyAl? Can polymer additives be a source of discoloration?
2. What are the impacts of the discoloration for the recyclers?

Question 1 was first answered through the review of literature and interviews, where potential causes were examined and summarized in Table 5.1. Polymer additives can be a source of discoloration, as discussed previously, although the scale of their effects is unclear, therefore polymer additives cannot be concluded as a "main" source of discoloration based on this study.

Question 2 was answered through the interview with Recycler E and literature research on challenges faced by the plastic recycling industry, the main impact of discoloration is the end-product's disadvantaged market price. However, with a more extensive outreach of interviewees including other recyclers who had also observed similar discoloration and buyers of recycled PE, the impacts could be better defined.

5.5 Recommendations

In outlining the challenges, a few opportunities were identified:

- When choosing a polymer grade, the discoloration potential of the additives should be taken into account (package of phenolic AO, phosphorous AO, and acid scavengers).
- The use of Ca stearate (or similar acid scavengers such as Zn stearate) may best be avoided with the presence of phenolic AO.
- Additional AO can be used by recyclers; instead of selecting base polymer grades with low discoloration potential, adding protective additives at the recycling stage could improve the condition when a wider range of materials from different companies are present.
- Introduce a de-inking step and/or enhance the pre-treatment of the PolyAl should help remove as much impurities as possible.

5.5.1 **Future studies**

While the yellowing tendencies of Ca stearate and mLLDPE were confirmed in this study, and that the AOs could still be a source of yellow discoloration, their exact effect on discoloration in post-consumer recycling remains unknown. Future studies with more extensive experimental analysis, including expanding the thermo-oxidative treatment range and with more controlled amounts of additives in the polymer grades, could help quantify the effect of each contributor on the overall discoloration.

EL's DSC analysis indicated the presence of foreign polymers, such as HDPE and PP, while an observation of the compounded sample plates and post-DSC sample masses showed solid impurities. Future studies may examine the effect of such impurities on the color of recycled PE film.

As propionate-type phenolic AOs are found to be discoloration-resistant, this property can be further explored with laboratory trials. Collaboration between suppliers, packaging manufacturers such as Tetra Pak, and recycling companies may accelerate the development of additive packages against discoloration.

While acid-based delamination is much more mature as a commercialized process with lower chemical waste, alternative PolyAl separation methods may also be monitored, namely solvent extraction and chemical recycling which produce higher purity in the recovered PE. The continued development of alternatives may out-grow their current shortcomings and become suitable UBC recycling methods for Tetra Pak.

Furthermore, much about the environmental footprint of UBC recycling remains uncertain, analyzing the overall emissions and water usage in this sector of recycling is still niche and new. The development and integration of Life Cycle Analysis (LCA) is therefore recommended to track the real impact of UBCs, giving the different recycling options a fuller understanding.

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Appendix A Stakeholder interviews

A.1 Interview with Recycler E

What are some positive business impacts of reducing the discoloration?

- In short, there is no firm answer
- On the market, transparent recycled materials have higher prices, so the impact should be positive

Since there are other contaminants - what else affect the price of the recycled PE?

- Even if the color is gone, there are other unknown contaminants
- There can be solids from under-optimum washing process, unremoved Al (can be seen on monitor but not sure what they are)
- Other plastics - sorting at post-consumer level is not perfect
- Polymer-polymer laminates (like PE-PET) cannot be separated
- PE and PP are okay when mixed in

What are some of the technical limitations, or things that cannot be changed?

- It is very hard to change the process or any existing equipment
- It's also hard to add anything else to the wet process (20% formic acid in water), since it would affect the whole process and the water treatment. If anything is added it should be after the flakes are dried
- We could add an equipment after that but economically it's very difficult
- Generated gases need to be treated (air incoming with the material after caps removed; hot wash 12 mins at 55ºC, mechanical drying with centrifuge, still 12% moisture)

What are the potential uses and markets for the end products?

- LDPE granulates/pellets
    - Additives may be tried (when the recycled material is in use), and possibly used for polymer blenders

- Recycled Al from foil was the target market but that is not sure anymore, since the material is not pure
- Al powder is very difficult to render from the foil, which are 6-7um thin, burn fast, partially reacted off by formic acid, and the end product is only 60% Al
- Impossible to recycle the films through standard Al recycling process, when the film is already heavily oxidized
- Potentially used in steel furnaces as an additive, for Al-oxide as a carrier of catalysts, or a flocculation agent
- Recycler E is looking for special applications, the main seekers are traders

Since when did the green discoloration become a problem? What had been done in order to minimize the discoloration (process change, etc.), to what effect?

- Transparent films were sent to a research institute, and they turned green when melted
- When solvent was used to wash the flakes (PE after separation before reprocessing), they didn't turn green when melted (190ºC, the regranulation temperature)

Does Recycler E have any future plans in the development of the chemical separation technology?

- Recycler E had been trying to start the separation line with challenges during COVID-19

What is Recycler E doing/planning to do to maximize the values of the end polymer products?

- Recycler E has a database of stakeholders interested in plastic, mainly speaking with PE seekers
- The recycled LDPE definitely sells (has a market), the issue is price