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Infrared Spectroscopy for Masterbatch Characterisation

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Thesis to obtain the Master of Science Degree in

Materials Engineering

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Declaration

I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa.

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Abstract

Synthetic polymers are broadly used today, with applications in diverse industries such as food, automotive, and packaging. The quality of plastic products relies upon at the quality of the polymers or polymer blends used for their manufacturing, so identification and characterisation of these substances is essential to make sure that the end product is up to standards when used.

Fourier Transform Infrared (FTIR) spectroscopy is ideal to perform qualitative analysis of polymeric raw materials as well as finished products and its components. It is a reliable, fast and cost-effective technique that requires little to no sample preparation.

The following work aims to explore the multiple utilities of a IR Spectroscopy (FTIR and NIR) at Poliversal - Plásticos e Tecnologia S.A., both for Research and Development (R&D) and for Quality Control, by developing an analysis methodology for polymer identification and quantification of additives present in masterbatches.

FTIR in transmission mode was proven to be helpful for the quantification of additives in thin films, filling a gap in the State of Art.

In Europe, the sorting of plastic products in recycling facilities is typically made using NIR separation techniques, that classify the polymers based on their spectral signatures and is characterised by efficiencies of about 57% to 89%, considered low due to the presence of black-coloured plastics [1].

Carbon Black is one of the most important coloured additives [2], but regulatory and sorting issues in waste management facilities that use near-infrared (NIR) sensors for polymer sorting represent new challenges for the use of this additive. Samples with different concentrations of carbon black and alternative pigment to carbon black (Black CI 11 and Brown CI 29) were analysed in order to determine the limit of detection of NIR, which for carbon black was found to be between 0,04 and 0,1% and for alternative pigments (Black CI 11) between 0,17 to 0,95%. Researching the detection limit of carbon black by NIR spectroscopy served a primary goal of better advising clients on the formulation of the MB.

Keywords: FTIR, Masterbatch, Polymers, Identification, Quantification, Carbon Black, NIR

Resumo

Os polímeros sintéticos são amplamente utilizados, com aplicações em diversos setores, como alimentar, automóvel e embalagens. A qualidade dos produtos de plástico depende da qualidade dos polímeros e misturas de polímeros usados no seu fabrico. Portanto, a identificação e caracterização dessas substâncias é essencial para garantir que o produto final esteja de acordo com os requisitos.

A espectroscopia de Infravermelhos é ideal para realizar análises qualitativas de matérias-primas poliméricas, bem como de produtos acabados e os seus componentes. É uma técnica fiável, rápida e económica que requer mínima preparação de amostras.

O seguinte trabalho visa explorar as múltiplas utilidades da espectroscopia IR (FTIR e NIR) na Poliversal - Plásticos e Tecnologia S.A., tanto para Pesquisa e Desenvolvimento como para o Controlo da Qualidade, desenvolvendo uma metodologia de análise para identificação e quantificação de polímeros e aditivos presentes em masterbatches.

O FTIR no modo de transmissão mostrou-se útil para a quantificação de aditivos em filmes finos, preenchendo uma lacuna no Estado da Arte.

Na Europa, a triagem de produtos plásticos em instalações de reciclagem é normalmente feita por meio de técnicas de separação NIR, que classificam os polímeros com base na sua assinatura espectral. Este método de triagem é caracterizado por eficiências de cerca de 57% a 89%, consideradas baixas devido à presença de plásticos de cor preta [1].

O Carbon Black, ou negro de fumo, é um dos aditivos coloridos mais importantes [2], mas questões regulatórias e de separação em instalações de gestão de resíduos que usam sensores de infravermelho próximo (NIR) para identificação de polímeros representam novos desafios para o uso desse aditivo. Amostras com diferentes concentrações de negro de fumo e pigmentos alternativos ao negro de fumo foram analisadas para determinar o limite de detecção em NIR, o qual para o negro de fumo foi determinado entre 0,04 e 0,1% e para pigmentos alternativos (Black CI 11 e Brown CI 29) entre 0,17 e 0,95%. A pesquisa do limite de detecção de negro de fumo por espectroscopia NIR atendeu ao objetivo principal de melhor aconselhar os clientes na formulação dos MB.

Keywords: FTIR, Masterbatch, Polímeros, Identificação, Quantificação, Carbon Black, Negro de fumo, NIR

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Acronyms

ATR Attenuated Total Reflection.

DRIFTS Diffuse Reflectance.

EU European Union.

EVA ethylene and vinyl acetate copolymer.

FT Fourier Transform.

FTIR Fourier Transform Infrared.

GMS Glycerol Monostearate.

HALS Hindered Amine Light Stabiliser.

HDPE high-density polyethylene.

IR Infrared.

LDPE low density polyethylene.

LLDPE linear low-density polyethylene.

MB Masterbatch.

MIR Mid-infrared.

NIR Near-infrared.

PE polyethylene.

PLS Partial least squares.

PLSR partial least squares regression.

PP polypropylene.

PS polystyrene.

QC Quality Control.

SNR Signal-to-noise ratio.

T Transmittance.

UV-Vis Ultraviolet–visible.

Chapter 1

Introduction

Poliversal - Plásticos e Tecnologia S.A. was founded in 1980, in Portugal. Initially it was positioned in the market as a thermoplastic raw materials distributor. Masterbatch production started in 1991. For more information about Poliversal and its products, please consult <http://www.poliversal.pt>.

The present work was developed in the R&D laboratory as well as in the Quality Control laboratory of Poliversal. For FT-NIR analysis, the experimental analysis were made at Instituto Superior de Agronomia from Universidade de Lisboa.

1.1 Context and Problem Definition

Masterbatch (MB) is a plastic concentrated compound that contains additives [3]. It consists of a base carrier polymer mixed with additives, such as pigments, which are usually in the 2 to 30 wt% concentration range.

The MB market is estimated to be "USD 11.1 billion in 2020 and projected to reach USD 14.3 billion by 2025" [4]. The drive for the growth of the MB market is the replacement of metal with plastic in the automotive industry and the increasing demand for packaging applications. In the Asia-Pacific, which is now the largest consumer of MB, the market growth can be attributed to the rising demand for consumer goods and also the construction industry.

With growing demands, the need to differentiate from competitors offering a high-quality reliable MB is becoming the priority. In order to assure the quality of a product, Quality Control (QC) procedures are implemented using various characterisation methods to assure the compliance of the MB. Also, the acquisition of new data and information about the most used additives in the market allows Poliversal to better advise their clients on the best suited product for their application, offering a personalised consultation service.

In an industrial setting like Poliversal's, where compounding is the main manufacturing activity, polymer identification and quantification of additives present in the the masterbatch is an important task for both quality control and research and development activities. For those, Poliversal's R&D department acquired a Bruker Alpha II FTIR Spectrometer. FTIR spectroscopy is a tool that allows identification and quantification of substances in a quick, inexpensive way requiring little to no sample preparation. This tool is even more important because it gives Poliversal an opportunity to establish a QC method for colourless MB that are bought from another manufacturer.

Carbon black "is by far the most important black pigment and is the second most important in terms of volume of all pigments used by the plastics industry" [2], but regulatory issuers are limiting their use and are bringing change to the plastic compounding industry. Also, carbon black faces issues with

sorting techniques used in the recycling sector [5]. High volume recycling of plastic starts with collection and sorting of mixed plastic waste, the sorting process is done using Near-infrared (NIR) sensors that identify the polymeric base of what the plastic waste is made from [5, 2]. Identifying the polymeric base of a product becomes a challenge when carbon black pigments are used, because they do not reflect sufficient energy. These products will likely end up in a landfill or an incinerator [5]. The market trend became the use of alternative pigments that are transparent to NIR radiation, although they are an alternative, the same opacity and black colour is not obtained.

Determining the detection limit of carbon black by NIR spectroscopy served a primary goal of better advising clients on the formulation of the MB, so that the resulting plastic components can still be recyclable.

1.2 Research Questions and Strategies

This work was developed with the following research questions in mind:

1. Is it possible to identify different grades of polyethylene (PE) using ATR-FTIR?
2. Is it possible to identify additives in the MB using ATR-FTIR and Transmission mode?
3. Is it possible to quantify the additives present in a masterbatch using FTIR in Transmission mode?
4. What is the maximum amount of carbon black allowed to be used in a plastic part, in order to enable identification of the polymer matrix by NIR sorting systems?

In an effort to provide answers for the questions that catalysed this thesis, the following strategy was followed:

- Questions 1, 2 and 3: use FTIR in ATR and Transmission mode in order to build a spectra library of the polymers and additives of interest. Produce and prepare the samples to be analysed. Collect the spectras from samples and analyse them. Develop a quantification method in order to quantify uncoloured additives present in film samples.
- Question 4: prepare samples with varying quantities of carbon black and use FT-NIR to obtain their spectra and determine the detection limit by this technique.

1.3 Thesis Outline

The present thesis is composed of six chapters.

Chapter 1 - Introduction to the problematic related to the polymer identification and additive quantification in an industrial environment.

Chapter 2 - Extensive literature review on masterbatches and its components (polymers and additives) and manufacturing processes. Additionally, working principles and description of the components of FTIR and NIR are described in Chapter 2.

Chapter 3 - State of art on using FTIR spectroscopy for identification of polymers as well as quantification of additives in polymeric products. Also, characterisation of the FTIR spectra of different additives (Erucamide, Glycerol Monostearate, HALS Tinuvin 622 and HALS Chimassorb 944). State of art on using NIR spectroscopy for identification of polymers, the problematic around carbon black and possible solutions.

Chapter 4 - Description of the materials used in the experimental work and experimental methods adopted.

Chapter 5 - Presentation and discussion of the obtained results.

Chapter 6 - Conclusions of this work, with emphasis for the most significant achievements, and recommendations for future works.

Chapter 2

Literature Review

2.1 Masterbatch

A Masterbatch (MB) is a plastic concentrate compound that contains additives, such as pigments which are essential for the appearance and performance of the final plastic product [3]. During the manufacturing process, the additives are incorporated into a molten carrier resin, by proper mixing techniques to promote good dispersion of the additives, followed by cooling and cutting into granules.

A MB is mainly composed of a carrier (base resin), filled with additive(s) such as colourants (dyes or pigments), and a dispersing agent. They are blended with the resin being coloured (application polymer) in a predetermined proportion by weight, known as the let-down ratio, to produce the desired colour and opacity in the end-product. The down let-ratio - dosage level at which a masterbatch is incorporated into the application polymer - is around 1 to 25%. To ensure compatibility between the concentrate and the application polymer, the MB is generally made from the same generic polymer as the application polymer but with a higher melt index to promote ready and even mixing.

Masterbatches offer the plastic processor a convenient means of handling additives and no need for dispersive mixing equipment and know-how, since the MB only needs to be diluted with the application polymer in a processing machine. They offer a big advantage in inventory size and raw material storage space as well as limit the exposure of workers to potentially hazardous components. Using a MB allows for optimum dispersion of pigments and additives, eliminate dust, and eliminate the "trial and error" formula development as this will now be done by the masterbatch manufacturer.

When the chosen carrier is different from the application polymer, the carrier polymer can modify the end resulting plastic's properties. A universal carrier like ethylene and vinyl acetate copolymer (EVA) can be used in order to carry high quantities of additives necessary for the end use and assure the essential compatibility required across a broad range of polymers. Universal masterbatches are generally available and affordable when used correctly. However, as for compatibility they act as a compromise and processing difficulties can arise with some materials. It is always better to use the best compatible or identical carrier to the application polymer.

2.2 Additives

Plastic additives are products, generally used in small portions, which enhance the properties of plastic materials by means of improving their processability, performance, and appearance during manufacture and in use [6].

There are many polymer additives that can be mixed into a polymer to improve its properties. Some

additives have multiple effects, for instance, talc is added to PP to improve stiffness and heat stability, pigments can help with UV protection, plasticizers also act as lubricants and anti-static agents [6].

The main additives used in the plastic industry and their functions are presented in table 2.1.

Table 2.1: Additives and their functions, adapted from [6]

| Additives | Functions |
|------------------------------|---|
| Filler | Add volume and fill the compound, improve stiffness and aid in cost reduction |
| blowing Agent | Foam and expanded plastics production |
| Anti-static Agents | Increase electrical conductivity to prevent electrostatic discharge |
| UV Stabilisers | Delay or prevent polymers degradation under sunlight exposure |
| Colourants | Add colour to the compound |
| Flame retardants | Prevent ignition of the polymer |
| Plasticizers | Increase flexibility and improve processability |
| Processing aids | Improve mixing and control viscosity |
| Lubricants, Slip, Anti-block | Reduce friction, improve processability, reduce coefficient of friction and blocking in films |

2.2.1 Fillers

Fillers are used to take up space and reduce the amount of resin needed to produce a plastic product, and thus reducing the price of the final plastic product.

Fillers can be divided into two categories, [2, 7]:

- Reinforcing fillers: can be added in large amounts and are used to enhance properties of the polymer. Some examples are talc, wollastonite and reinforcing fibers such as glass and carbon fibers.
- Non-reinforcing fillers: used only as filler in order to reduce the amount of resin needed in the plastic product. Calcium carbonate is a non-reinforcing filler and also one of the most vastly used fillers in the industry.

Silicates

Wollastonite, a pure white, non-hydrous needle-shaped crystal, is fit for use where resistance to water and ultraviolet light is important [6, 8].

Talc

Talc is a naturally occurring hydrated magnesium silicate that is added to thermoplastic polymers for reinforcement reasons and for better dimensional stability of the final part. It is a very soft mineral so it does not cause wearing during processing [6, 2].

Calcium Carbonate

Calcium carbonate is the most important filler for plastics. It is cheap and nonabrasive and can also be used in part replacement of white pigment to achieve a high gloss finish [2].

2.2.2 Anti-static Agents

Polymers can build-up electric charges due to their low electric conductivity. A good anti-static agent should be an ionizable additive that allows charge migration to the surface, while creating bridges toward the atmosphere by the humidity in the surroundings [9].

Barnes [10] mentions common uses for antistats:

- In foam production to prevent sparks when hydrocarbon blowing agents are used;
- In injection moulding to improve stackability of parts;
- In packaging so it remains dust free.

Additives can be added before or during plastic processing and they can migrate continuously to the surface, where a deposit of material may occur [8].

The molecules of these additives have a hydrophilic head and hydrophilic body, forcing them to migrate to the surface and attract moisture from the environment and increasing surface conductivity, and do not alter the surface appearance. These additives are easy to use and often provide other benefits such as facilitating processability and mould release [11, 12]. Figure 2.1 illustrates the migration of anti-static agents in a thin film.

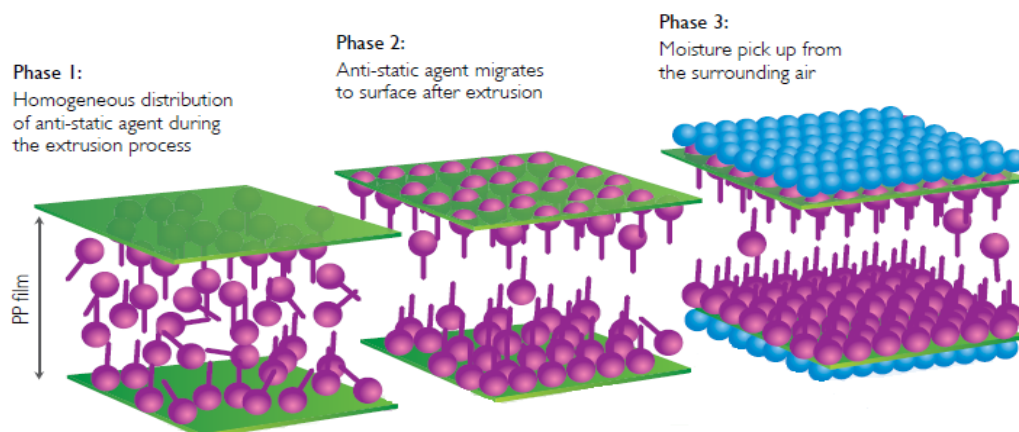


Figure 2.1: Migration of anti-static agents. Reproduced from ref. [11].

Anti-static agents can be classified by application method (as internal or external) and by chemistry (as ionic and non ionic) [8, 11, 12]:

- **Ionic anti-static agents:** Molecules with long chains that allow for a good compatibility with the polymer. Cationic compounds, that include quaternary ammonium, phosphonium, or sulfonium salts, and anionic compounds, such as sulfones, phosphates and carboxylic acids.
- **Non ionic anti-static agents:** The most important group, where glycerol Glycerol Monostearate (GMS) and ethyloxyate amines make up more than 50% of the anti-static market and are mainly used in polyolefins and styrenics.
- **Internal agents:** Are incorporated directly into plastic materials during compounding and give a long-lasting benefit. They have a slight compatibility with the polymer, allowing them to migrate to the surface when incorporated in a polymer.
- **External agents:** Are dissolved in an appropriate solvent and are applied by spraying, dipping or wiping the surface of the processed product.

GMS is the main anti-static agent used in Poliversal. GMS is present in many different polymeric systems and can function as a dispersant, slip agent, ageing modifier, lubricant, antifog, mould release and antistat [10].

2.2.3 Ultraviolet (UV) Stabilisers (Anti-UV)

UV stabilisers are used to block UV radiation and prevent oxidation of plastics by UV light [8]. These additives act by absorbing energy and deactivating and decomposing the by-products of oxidation, preventing cracking, chalking, changes in colour and loss of physical properties of the polymer.

Murphy [8] and Maier [12] divide anti-UV agents into four types:

- **Absorbers:** absorb the UV radiation to protect the polymer from degradation, acting as optical filters. The UV energy is converted into heat and dissipated throughout the polymer matrix. These Anti-UV additives are limited by the absorption process. Benzophenones are a general-purpose UV absorbers and can be used for clear or coloured polyolefins with concentrations between 0,23 and 1%.
- **Quenchers/Energy Transfer Agents:** return excited state molecules to their stable state resulting in the formation of free radicals, by accepting energy from these molecules. The energy is dissipated as heat, fluorescence or phosphorescence and there is no degradation of the polymer.
- **Scavengers:** Hindered Amine Light Stabiliser (HALS) are efficient scavengers. Commercially they are the single most important light stabilisers and can be used with most polymer resins. They function by inhibiting degradation of the polymer that has already formed free radicals. The stabilisation mechanism is represented in figure 2.2, the hindered amine oxidises forming a nitroxyl radical that reacts with a polypropylene or other free radical to form alkoxy amine that then, reacts with a peroxy radical to regenerate the original hindered amine and the cycle begins again.

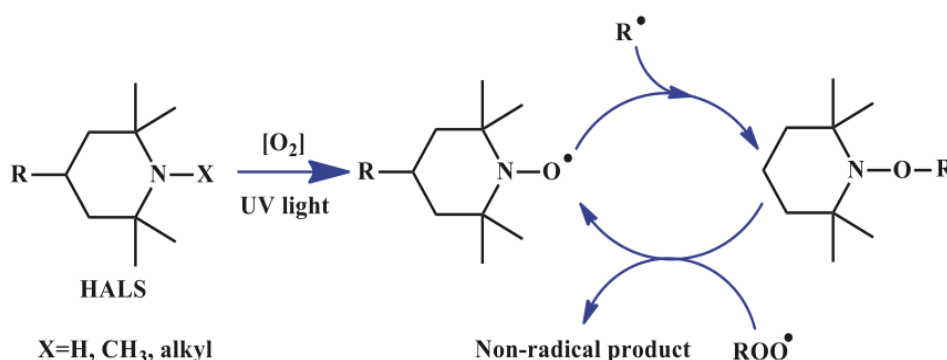


Figure 2.2: Stabilisation mechanism of HALS. Reproduced from ref. [13]

The main advantage of these stabilisers is that they bind additives to the polymer at the molecular level, however the degree of protection may be reduced by migration of the stabiliser and interaction with acid rain and agricultural chemicals.

- **Screening Pigments:** compounds that shield from the UV radiation by providing opacity such as carbon black, titanium and zinc oxide. These act as UV screeners by absorbing or reflecting UV radiation.

2.2.4 Lubricants and Processing Aids

Lubricants have performance and processing enhancement functions. During processing, internal lubricants can be used to improve throughput and external lubricants may be used for mould release [8].

Typical lubricants for specific performance improvements are: graphite, molybdenum disulfide, PTFE, and polyethylene.

Lubricants are used in order to lower melt viscosity to prevent the polymer from sticking to metal surfaces [12].

Metalic Stearate

These additives are inexpensive and allow to modify melt viscosity without delaying fusion of the polymer, they are the most widely used internal lubricants [8, 12].

Polyolefin Waxes

Polar polyolefin waxes have an anti-sticking effect and are suitable for transparent items. They are highly effective as an external lubricant for PVC allowing for a higher quality of the surface finish [8].

2.2.5 Pigments and Dyes

Robert M. Christie, in the chapter about Pigments and Dyes [2], defines a pigment as "a finely-divide solid which is (...) insoluble in its polymeric application medium (...) where it is incorporated by a dispersion process while the polymer is in a liquid phase and, after solidification the dispersed pigment particles are retained physically within the solid polymer matrix". The main function of pigments when incorporated in plastics is to introduce colour, however they can improve mechanical properties as well as protection against degradation. Pigments can be either organic or inorganic: organic pigments show an increase in colour intensity as the particle size is reduced, while with many inorganic pigments there is an optimum particle size at which the colour strength reaches a maximum [2].

In the other hand, "a dye dissolves in the polymeric application medium and is usually retained as a result of an affinity between individual dye molecules and molecules of the polymer" [2].

When choosing a pigment for an application, it must not only produce the desired optimal effect in the plastic product but also must be capable of withstanding the effects of the working environment.

Titanium Dioxide

R. E. Day reported on the role of titanium dioxide in the degradation of polymers [14], according to him, the plastic industry consumes about one fifth of the worlds titanium dioxide, and it is the most widely used colourant for plastics.

Titanium dioxide has high light scattering efficiency due to its high refractive index, resulting in bright and clean coloured plastic products. It also has the ability to scatter efficiently all the wavelengths of visible radiation, it shows strong absorption of UV resulting in protection of the polymer matrix from photo-chemical degradation [15, 2]. However, the absorbed UV radiation releases electrons and positive holes in the titanium dioxide structure resulting in the production of free radicals that can attack the polymer leading to photo-oxidation and polymer degradation, this is why the quantity of titanium dioxide present is important to determine the rate of degradation [14, 2].

Titanium dioxide is widely used in the PE masterbatch production. The PE base resin used in the production of masterbatches has higher melt flow index than the let-down polymer because when we incorporate titanium dioxide into the masterbatch, it results in decrease in melt flow index [14].

Carbon Black

Carbon black "is by far the most important black pigment and is the second most important in terms of volume of all pigments used by the plastics industry, ranking behind only titanium dioxide" [2]. Although its main role is to provide a black colour to the plastic part, carbon blacks is described as an ideal universal additive by John Murphy [8], since "it can provide pigmentation, reinforcement, ultraviolet shielding, and anti-static properties". These pigments are produced by combustion of petrochemical feed-stock and absorb strongly in the ultraviolet, visible and near infrared regions [16].

As described in the November issue of the "Compounding World" magazine [5], regulatory issues are the root of change in the use of carbon black and titanium dioxide: carbon black is facing issues around its compliance with sorting techniques used in the recycling sector.

2.2.6 Slip and Anti-block Additives

Slip is the ability of a film to slip over itself or another film, describing how easily films can be separated.

Slip additives have limited compatibility with the polymer and exude to the surface, creating a coating that reduces the coefficient of friction [12, 17] and therefore also reduces the tendency for the polymer to stick to itself which facilitates high-speed production of plastic parts.

Anti-blocking additives reduce the tendency of film layers to stick together. These additives can be incorporated internally or externally and when incorporated internally they must be partially incompatible with the polymer so that they can exude to the surface [12, 17]. However, using anti-block additives can affect the performance of anti-static additives. So, it is important to evaluate the suitability of the combination of additives [8].

Erucamide is a primary amide, namely an unsaturated long chain carboxylic acid amide. [17, 7]. It contains long unsaturated C22 chains and a polar amine group, responsible for its high surface polarity, high melting point and good thermal stability. It is the slip agent used by Poliversal, and it acts by modifying the surface of polyolefins so that the coefficient of friction and blocking tendency are reduced.

2.3 Masterbatch Manufacturing Process

Compounding consists in incorporating one or more additives in a polymeric matrix with the goal of adjusting and adapting the properties of the material to the final use of the product [18]. These additives can be dyes, stabilisers, lubricants, and other above discussed.

The general steps in the manufacturing process of a masterbatch are:

- **Weighing:** weighing the raw materials that will be used in the compounding process. The higher the accuracy the better.
- **Mixing:** the weighed materials are mixed together in a high-speed mixer.
- **Extrusion:** The mixture is melted and extruded.
- **Water bath and drying:** As the molten product comes out of the die, it passes through a water bath in order to solidify and is cooled.

- **Cutting:** The solid strands are cut into pellets and then packaged.

The main goal when manufacturing a masterbatch is to optimise dispersion and distribution of the additives within the polymeric matrix.

In figure 2.3, the masterbatch manufacturing process and applications are presented.

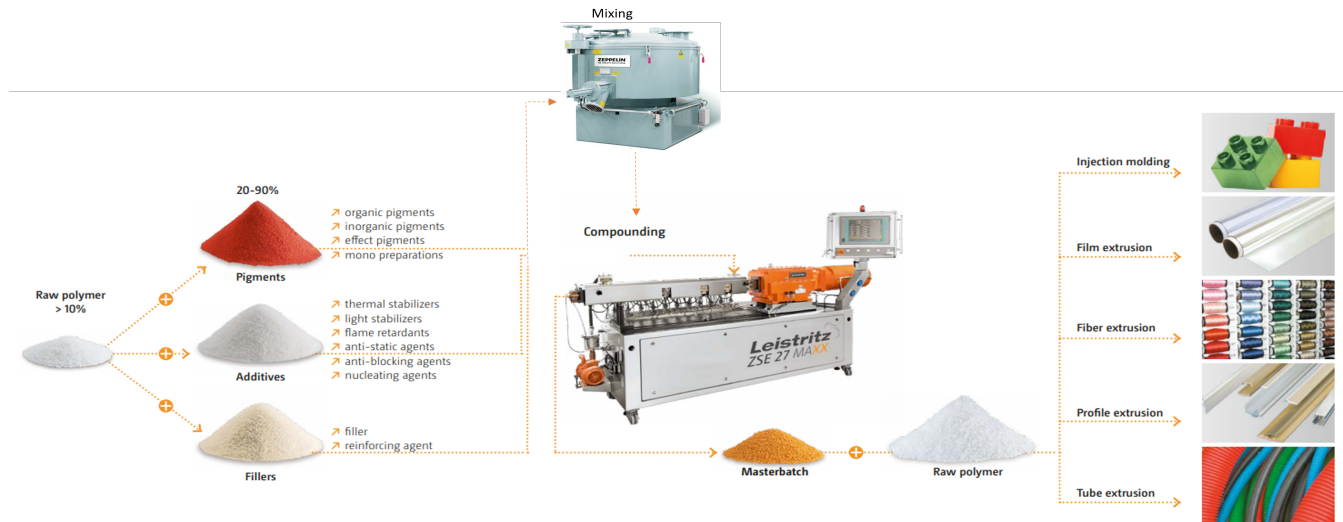


Figure 2.3: Masterbatch manufacturing process and applications. Reproduced from [19]

From the compounding process two different products can be obtained: a masterbatch and a compound, such as a pre-coloured compound. The main difference between these two products is that the compound is meant to be used as is (100% with no dilution) by the manufacturer of plastic parts and the masterbatch (a concentrate), meaning it is meant to be diluted with a virgin polymer by the manufacturer in order to make the final plastic part.

2.3.1 Mixers

In any mixing device there are two processes that may occur simultaneously or step-wise, depending on the balance between the cohesive forces holding agglomerates or droplets together and the disruptive hydrodynamic forces[9]:

- **Distributive mixing:** Process of spreading the minor component throughout the matrix in order to obtain a good spacial distribution;
- **Dispersive mixing:** Process of breaking a secondary (minor component) immiscible fluid or agglomerate of solid particles and dispersing them throughout the matrix.

In figure 2.4 a schematic representation of dispersive and distributive mixing is presented.

The most suitable mixer for homogenisation during MB processing is an intensive mixer, due to its efficiency in carrying out the mixing process and is also easy to clean after use. This is the type of mixers used at Poliversal.

The intensive mixer consists of a container of variable size, with several blades driven by a motor. When rapid cooling of the mixture is required, the mixer uses a cooling jacket, where water circulates in order to cool the equipment.

During the mixing process, the components inside are heated up due to friction. Generally, a small amount of wax, with a low melting point, is added to the mixture so that it melts during the process,

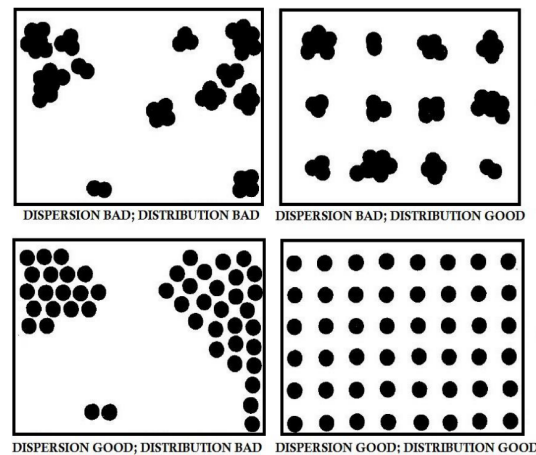


Figure 2.4: Schematic representation of dispersion and distribution. Reproduced from [20]

leading to any powder additives to be aggregated into the polymer granules, resulting in a considerably more homogeneous mixture.

2.3.2 Extrusion

Extrusion is a continuous processing (mixing) technique for converting thermoplastic materials into a homogeneous polymer melt, which is pumped through a shaping die, forming items of uniform cross-sectional area [9].

An extruder consists essentially of the barrel, which runs from the hopper to the die at the front end of the extruder. The screw, which is moving inside the barrel, is designed to pick up, mix, compress, and move the polymer as it changes from solid granules to a viscous melt [21, 22].

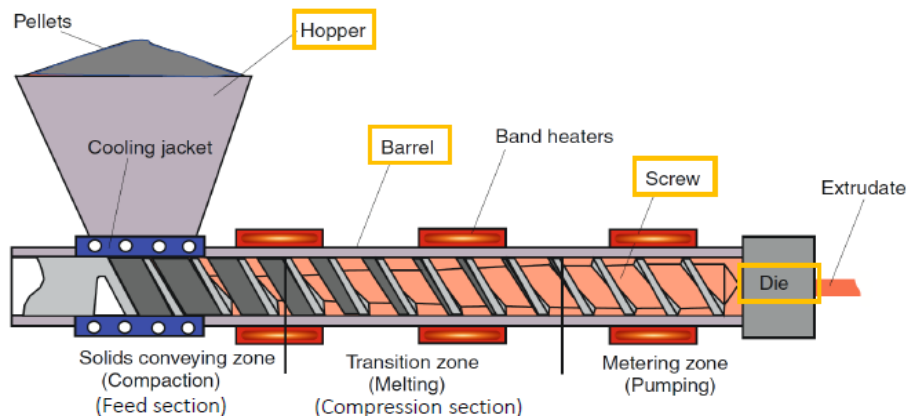


Figure 2.5: Schematic representation of single screw extruder. Reproduced from ref. [9]

After pre-mixing, the mixture is fed into the extrusion line. This line consists of an extruder and various auxiliary equipment, as illustrated in figure 2.5.

The extruder can be divided into three main sections [9, 21]:

- **Feeding section:** The material to be processed is placed in the feeding section. Generally, a large volume of polymer and additives are placed in the main feed (often these have already been subjected to a pre-mixing step). Preheating of the polymer for the subsequent sections can take place by pulling the polymer pellets from the hopper. The screw depth is constant.

- **Compression section:** Compression of the material leads to density change during melting. There is a gradual increase in the diameter of the root along the length of the sections, the compression of the resin forces air and volatile out of the resin melt, avoiding pores voids.
- **Metering section:** in this section there is a constant screw depth. In this section an homogenisation of the melt and supply to the die region occurs at constant temperature and pressure.

Extruder Screw

The extruder screw has three main functions:

- Transport solid feedstock.
- Compress and melt the solid.
- Homogenise, meter, and generate sufficient pressure to pump the melt against the resistance of the die.

Figure 2.6 is a schematic representation of part of a extruder screw.

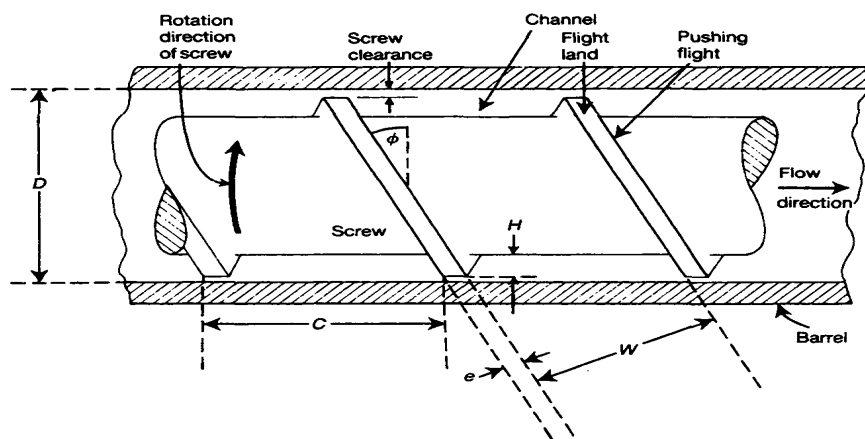


Figure 2.6: Schematic representation of a extruder screw components. Reproduced from ref. [9]

The screw, working on the Archimedean principle, rotates at about 1 to 2 revolutions per second.

The polymer is contained within the channels between the flights. It is pushed along the barrel by the forward edge of the flight (pushing flight). The clearance between the barrel and the nearest surface of the flight (flight land) is very small (of order 10^{-2} mm) and is constant along the screw [21].

The flight land and inner surface of the barrel are made of hardened steel in order to resist wear. The alloy steel barrel normally has the thin wear-resistant layer centrifugally cast on the inside. The barrel must tolerate high internal pressured and though elastic deformation above the 0.15% strain at which the wear resistant layer with crack [9, 22].

The area of the screw channel must decrease as the polymer is transformed from solid granules to liquid. For constant-pitch screw this means the channel depth decreases along the length of the screw (in the compression zone) [9].

Single Screw and Twin Screw Extruder

Single or twin screw refers to the number of screws existing in the extruder, one or two respectively.

In a twin screw extruder, the screws can be co-rotating when rotating in the same direction or counter-rotating when rotating in the opposite direction. The screws can be intermeshing or non-intermeshing. Figure 2.7 is a schematic representation of different twin screw extruders.

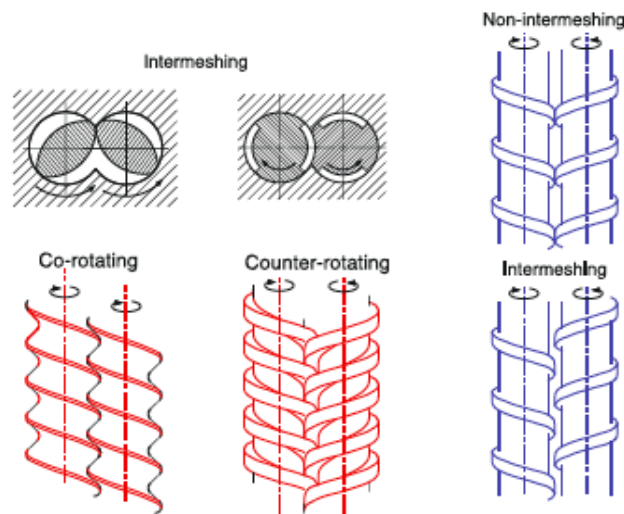


Figure 2.7: Schematic representation of screw configurations. Reproduced from ref. [9]

Single Screw Extruders: Consists of a feeding section, compression section, and metering section that often fails to homogenise the melt. Homogenisation is specially important for compounding techniques. There is some shear and friction between the material and the barrel. The material that is closest to the screw is only transported to the die, and not being cut as much as the rest of the material, since there is only one screw, and therefore the material next to the screw is not forced to change its position frequently [9, 21].

Co-rotating Twin-screw Extruders: There is frequent change in the position of the material in relation to the screw since the material changes screw every three quarters of a turn. It is important that the extruder does not retain material from previous compounding activity for the next extrusion, to avoid contamination. This is specially important when we switch from a MB with a strong colour (eg. red) to a white MB. To prevent this, virgin polymer is feed during a period of time in order for the extruder to self-clean [9, 21].

Counter-rotating Twin-screw Extruders: Some material goes through between the screw, undergoing high shear, but a considerable part does not go between the screws and is transported to the die without being subjected to significant shear forces [20].

In twin-screw extruders, the morphology of the screws is much more complex than for single screw extruders because the main goal is to obtain good dispersion and distribution in the mixture that is done in the extruder. Figure 2.8 shows one possible configuration of a screw in a twin extruder.

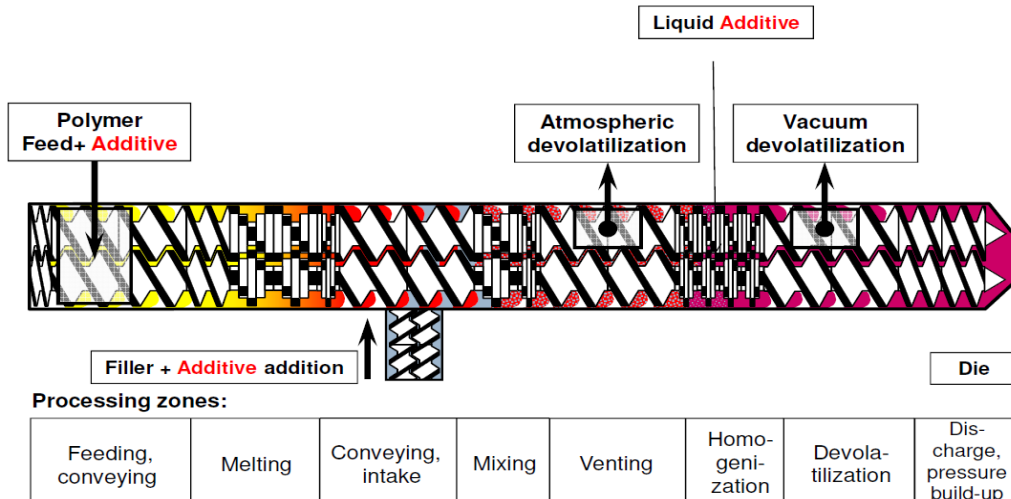


Figure 2.8: Schematic representation of a twin screw configuration in an extruder (from Coperion).

Accessory Equipment for Masterbatch Production

- **Cooling Water Bath:** After leaving the extruder, the polymer strands are dipped in a tub of water for cooling and solidification. In this way, the strands are cooled so that they harden enough to be cut.
- **Dryer:** Structure through which the polymer strands pass after being cooled, which by suction removes the residual water coming from the cooling bath.
- **Palletizer:** After drying, the strands pass through the cutter and the polymer strands are cut into granules. They are then stored in plastic bags, which are then sealed and labelled.

Blown film (Tubular Film) Extrusion

A tubular film extruder (figure 2.9), consists of extruding a thin tube of the molten material through a ring-shaped tube die, and then continuously inflating it to several times its initial diameter [21]. Air is introduced via a hole in the centre of the die to blown up the tube like a balloon. The tube of film is pulled upwards, continually cooling until it passes through nip rolls where the tube is flattened to create a lay-flat tube of film.

2.4 Recycling of Plastic Products

With the increase manufacturing rates of plastic products, managing plastic waste has become a priority not only due to environmental agendas but also due to the limited space in landfills. The European Union (EU), has set targets for recycling: 65% of municipal waste and 75% of packaging waste by 2030 according to the EU Directive of Waste [23].

Post consumer plastic waste is very diverse, since plastic products are made from different polymers that have different chemical and mechanical characteristics. This makes plastic waste one of the most complex materials from a recycling perspective [23, 1].

As of today, the main recycling method of post consumer plastic waste is mechanical recycling: the plastic parts are separated based on shape, density, size, colour and chemical composition; washed to remove organic contaminants; ground in to flakes, and remelted [24]. The main barrier to recycle post

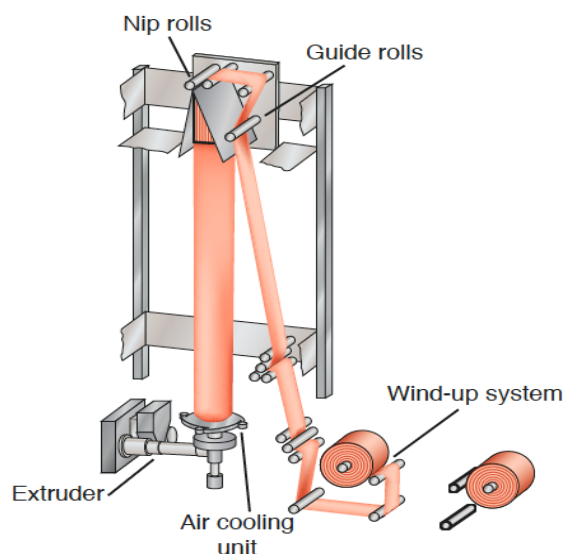


Figure 2.9: Schematic representation of a blown film extruder. Reproduced from ref. [21]

consumer plastic waste is the immiscibility of most polymers, and so the sorting of plastic materials by polymer is a very important step for a proper recycling of plastic products and to obtain a higher quality recycled product.

The Association of Plastic Recyclers [25] describe three of the most common used sorting technologies:

- **NIR:** uses the wavelength signature of the polymeric resins to distinguish between different polymers, but does not distinguish colour.
- **Visual Sensing:** the light source uses visible light and a high-speed camera in order to distinguish between different coloured plastic parts, but it does not distinguish between polymeric resin.
- **Manual Sorting:** most plastic recycling facilities rely on manual sorting operators to inspect the materials and remove contaminants.

According to the Association of Plastic Recyclers [25] "the large volume of incoming material necessitates processing equipment able to move and sort material at high speed". For this to be possible, automated sorting equipment was developed. This equipment sorts packaging by NIR signature, either in transmission or reflection.

In Europe, the sorting of plastic products in recycling facilities is typically made using NIR separation techniques, that classify the polymers based on their spectral signatures and are characterised by efficiencies of about 57% to 89%, considered low due to the presence of black-coloured plastics [1]. The main drawback of NIR spectroscopy, is that NIR "cannot be used for identification of plastic containing even low amounts (above 2% or 3%) of carbon black" [26]. Carbon black shows no spectral bands in the mid- or near-IR regions, however in the near-IR region it leads to very intense absorption, masking any other spectral features.

2.5 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy is an infrared spectroscopy in which the Fourier transform method is used to obtain an infrared spectrum in a whole range of wave numbers simultaneously[27].

2.5.1 Working Principles

Infrared radiation from a source enters the Michelson interferometer, represented in figure 2.10. The beam splitter reflects half of the infrared beam and transmits the other half. These beams reach a fixed mirror and a moving mirror separately, the mirrors reflect the beams and they combine again into one beam at the beam-splitter before irradiating the sample and being collected by a detector [17].

The molecular structure determines the light wavelengths that will be absorbed, and which will pass through unaffected.

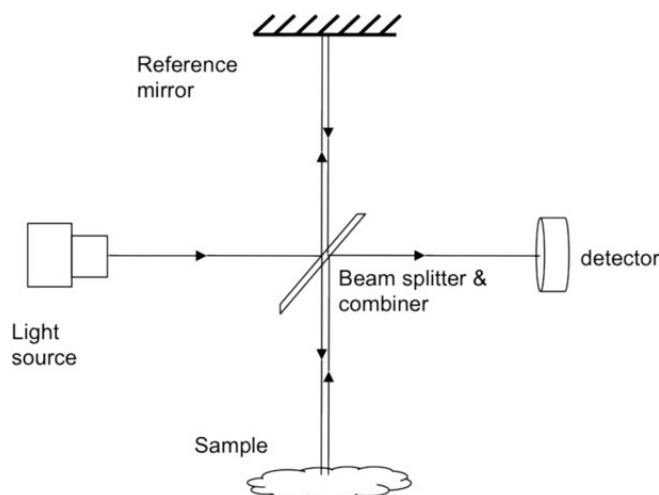


Figure 2.10: Diagram of Michelson Interferometer in FTIR. Reproduced from ref. [28]

The moving mirror changes the path lengths in order to generate light interference between the two split beams. The two split beams will show constructive (when $\delta = n\lambda$) and destructive interference (when $\delta = (0.5 + n)\lambda$) with continuous change of optical path difference (δ). The change in position of the moving mirror is responsible for the change of δ value [17].

Fourier transformation converts the interferogram (plot of light interference intensity as a function of optical path difference) into an infrared spectrum. It is based on the fact that any mathematical function can be expressed as a sum of sinusoidal waves, in this case it is used to transfer information between a function in the time domain and its corresponding one in the frequency domain. In FTIR spectroscopy, the Fourier transform converts intensity versus optical path difference to the intensity versus wavenumber [27, 29].

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \quad (2.1)$$

The result is a spectrum that characterises the vibration of the bonds within the molecules, each spectrum is considered a chemical fingerprint that characterises the molecular structure of a sample and its identification.

2.5.2 Components

An illustration of a FTIR spectrometer is presented in figure 2.11.

Infrared Light Source

FTIR spectrometers usually measure in the mid and near Infrared (IR) regions. The most common source is a silicon carbide element (Globar) heated to about 1200K. The range of IR wavelength and

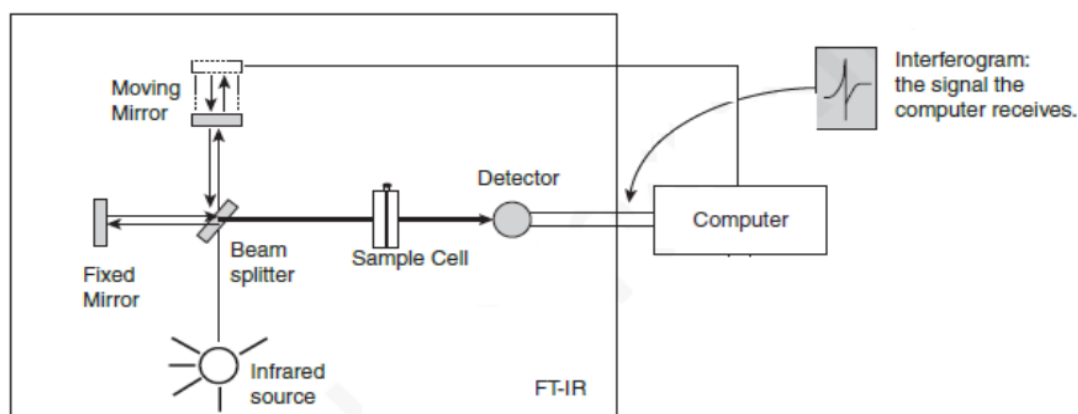


Figure 2.11: FTIR illustration. Reproduced from ref. [30]

energy distribution is highly temperature sensitive [27, 29].

Beam-Splitter

A beam-splitter should be made out of a material that is semi-transparent to IR radiation. Beam-splitters should transmit half of the incident radiation to a fixed mirror and the other half should be reflected to a moving mirror; multiple beam-splitters can be used interchangeably in order to cover a wide spectral range [27, 29]. The most common beam-splitter is a sandwich structure, with a thin layer of germanium (Ge) between two pieces of potassium bromide (KBr) working in the the 4000 - 400 cm^{-1} wavenumber range [17, 30]. Ge splits IR radiation and KBr is the substrate material transparent to infrared light with good mechanical strength. The drawback of using KBr as a substrate is that because it tends to absorb water vapour from the atmosphere, thus an environment with low humidity is required [17].

Infrared Detector

The IR detector is a device to measure the energy of IR light from the sample. There are two main IR detector types[27, 30, 29]:

- **Thermal detector/ Pyroelectric detector:** responds to changes in temperature as the intensity of IR radiation falling on them varies. the sensitive element is normally deuterated triglycine sulphate (DTGS) or lithium tantalate (LiTaO_3). These detectors operate at room temperature and provide sensitive and adequate readings. DTGS detectors operate in the range o 4000-400 cm^{-1} .
- **Semiconductor detector:** The most commonly used is made of mercury cadmium telluride (MCT). MCT detectors absorb IR photons which cause the electrons to migrate from the valence band to the conduction band of the semiconductor, generating electrical current signals. MCT detectors are up to 10 times, more sensitive than DTGS detectors, more expensive as well, and the band of detection is narrower, 4000-700 cm^{-1} . MCT detectors are cooled with liquid nitrogen before operation.

2.5.3 Signal-to-Noise Ratio

Signal-to-noise ratio (SNR) measures the instrument's ability to reproduce the spectrum from the same sample, same conditions, and same instrumental configurations over a certain amount of time [31].

2.5.4 Transmittance

Transmittance (T) as a ratio of intensities (I) [31]:

$$T = I/I_0 \quad (2.2)$$

Transmittance techniques generate a high signal-to-noise ratios, and are suitable for solid, liquid or gas phase samples [27]. The disadvantage of this technique is the thickness limitation of samples. Thick samples will absorb much of the IR radiation and detecting may become impossible [31]. To analyse polymeric samples, thin films are used.

2.5.5 Reflectance

Technique to obtain an infrared spectrum by reflecting IR radiation from a sample [27]. The main advantage is the possibility to analyse bulk samples without destructive preparation [31].

However, this technique has some disadvantages [29]:

- Limited sample penetration: 1 to 10 μm of a solid sample surface. This will become detrimental when analysing samples which chemical composition changes near its surface.
- Hard to capture infrared light than transmitted light.
- Reflectance spectrum show more noise than transmission spectrum.

There are three types of reflectance techniques [29, 31]:

- **Specular Reflectance:** for samples with smooth and polished surfaces;
- **ATR:** for samples with rough surfaces, strongly absorbing or thick;
- **Diffuse Reflectance (DRIFTS):** for IR-transparent thin films or IR opaque substrates.

Attenuated Total Reflection

An ATR accessory (illustrated in figure 2.12) measures the changes that occur in an internally reflected IR beam when in contact with a sample [31]. It uses an IR beam focused onto a crystal with a high refractive index at a set angle. ATR is performed at room temperature in a range between 4000-400 cm^{-1} [29].

The advantage of ATR is that sample preparation is not labour-intensive, spectra variation due to sample preparation is minimal [29, 27].

The following experimental factors can affect the final spectrum [32]:

- Refractive indexes of the ATR crystal and the sample;
- Angle of incidence of the IR beam;
- Depth of penetration;
- Wavelength of the IR beam;

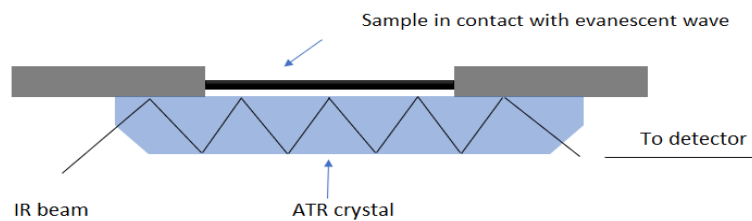


Figure 2.12: Diagram of ATR accessory. Reproduced from ref. [31]

- Effective pathlength (EPL);
- Number of reflections;
- Quality of the sample contact with ATR crystal;
- ATR crystal characteristics.

2.6 FT-NIR Spectroscopy

In the book *Handbook of Near-Infrared Analysis*, Burnes and Ciurczak [33] explain that the emergent use of NIR techniques over the first decade of the XXI century is linked with the increasing demand of product quality in different industries such as food, petrochemical, pharmaceutical, agricultural, polymer and cosmetic.

Near-infrared (NIR) radiation spans the wavelength range of 12500 - 4000cm⁻¹, in which absorption bands correspond to overtones and combinations of fundamental vibrations [34, 35]. When the radiation penetrates the samples, its spectral features change through wavelength dependent scattering and absorption processes, due to the sample's chemical microstructure [36].

2.6.1 FT-NIR Components

NIR spectroscopy incorporates a variety of devices, represented in figure 2.13, depending on the samples, analytical conditions and needs, being a very flexible technique [34].

The main components of a FT-NIR spectrometer are: light source, sample preparation accessories, monochromator, detector and optical components [36].

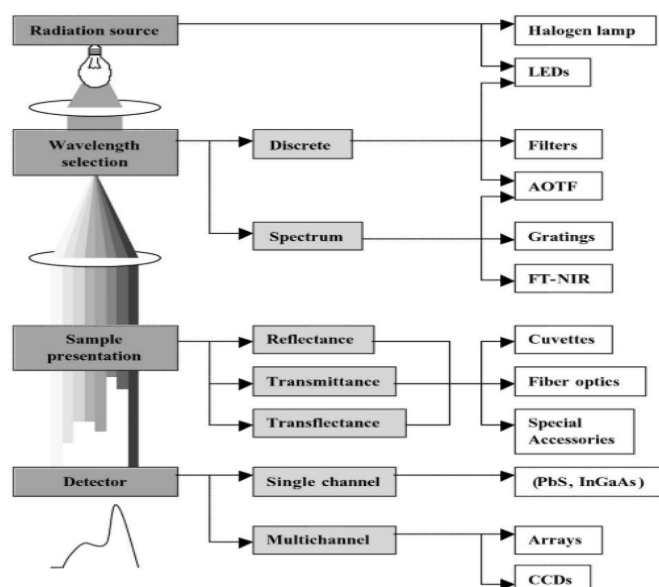


Figure 2.13: Principal features for NIR equipment. Reproduced from ref. [34]

As of the likes of FTIR spectroscopy, for FT-NIR spectroscopy there are three main types of optical measuring modes [35]:

- **Transmission:** The focused or parallel beam is directed in to the sample, some light is absorbed and the remainder is transmitted to the detector. This technique is mainly used for clear liquids.

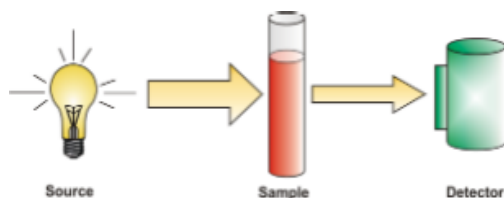


Figure 2.14: Transmission mode illustration for FT-NIR. Reproduced from ref. [35]

- **Transflection:** Similar to the transmission technique but a mirror is placed behind the samples, so the transmitted light is reflected to the detector. Transflection measured the combination of transmission and reflection. This technique is useful for emulsions, gels and turbid liquids.

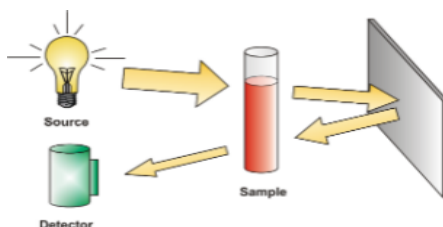


Figure 2.15: Transflection mode illustration for FT-NIR. Reproduced from ref. [35]

- **Diffuse Reflection:** Diffuse reflection is the light reflected from a solid surface. Part of the light that is diffused is caught by the detector sphere. This mode was used in the present work.

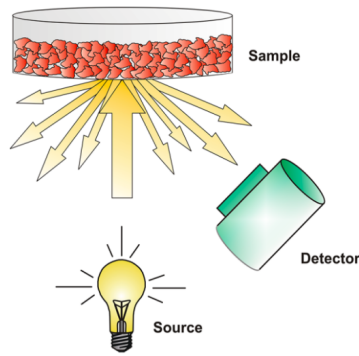


Figure 2.16: Diffuse Reflection mode illustration for FT-NIR. Reproduced from ref. [35]

2.6.2 FT-NIR Benefits

Using FT-NIR spectroscopy has useful advantages for Quality Control (QC) activities, since it often allows to analyse different parameters with one measurement and without sample preparation, proving to be an inexpensive analysis technique.

Other benefits of FT-NIR are as mentioned [35]:

- No sample preparation is required.
- Useful for heterogeneous materials, since NIR radiation penetrates the sample. It is also possible to continuously rotate the sample during the analysis, this allows to analyse a larger volume of the sample when compared to a single static measurement.
- It is a low time-consuming analysis method, and produces no waste or pollution.
- Since sample analysis is fast, it has a large samples throughput.

2.6.3 NIR Spectroscopy for Plastic Sorting

A common disposition of a sorting mechanism involves the scanning of packages across a conveyor belt illustrated in figure 2.17. Some sorting systems only sort by polymer while others sort by colour and polymer in one step combining NIR and UV-Vis spectroscopy [16].

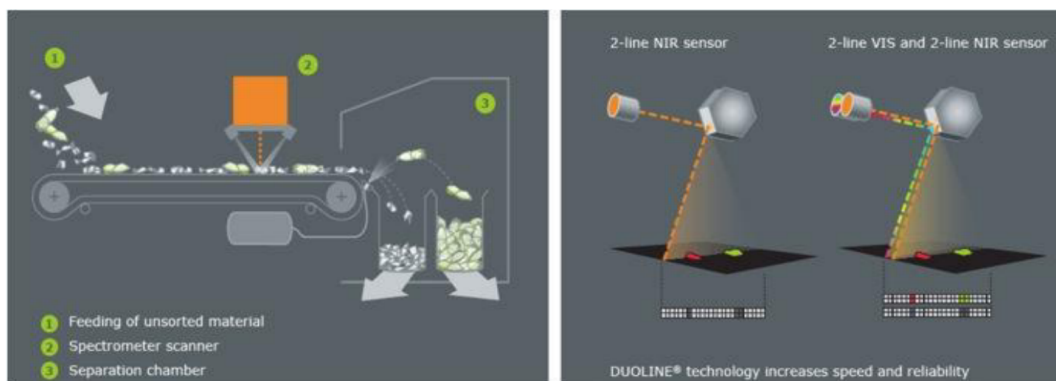


Figure 2.17: Configuration of scanning process in a waste management facility for plastic recycling. On the left the sorting is made only by polymer and on the right by polymer and colour of the polymeric part. Reproduced from [16]

The Association of Plastic Recyclers [25] enumerates a few issues associated with plastic sorting using NIR:

- **Sleeve labels:** Sleeve labels that cover the entire bottle are usually made from a different polymer than the bottle itself. NIR sorting equipment is not able to differentiate between the label and the bottle behind and so it will be directed to the wrong stream in the sorting facility.
- **Black and dark colored items:** NIR is not a reliable sorting method for dark and black colored plastic items. Since black absorbs the incident light waves, it provides no signature to be detected by the equipment. And so, dark colored items can be mis-sorted and combined with incompatible polymers.

Chapter 3

State of Art

3.1 Fourier Transform Infrared Spectroscopy for Different Grades of Polyethylene

Polyethylene is one of the most used polymers for masterbatch production.

For polyethylene (PE), the main stretching vibrations, shown in figure 3.1, appear at 2914 cm^{-1} corresponding to the asymmetric CH_2 stretch and 2848 cm^{-1} corresponding to the symmetric CH_2 stretching; they also noted that the main bending modes of CH_2 are located at 1470 and 1378 cm^{-1} corresponding to the CH_2 scissor vibration, and at 718 cm^{-1} corresponding to the CH_2 rocking [37].

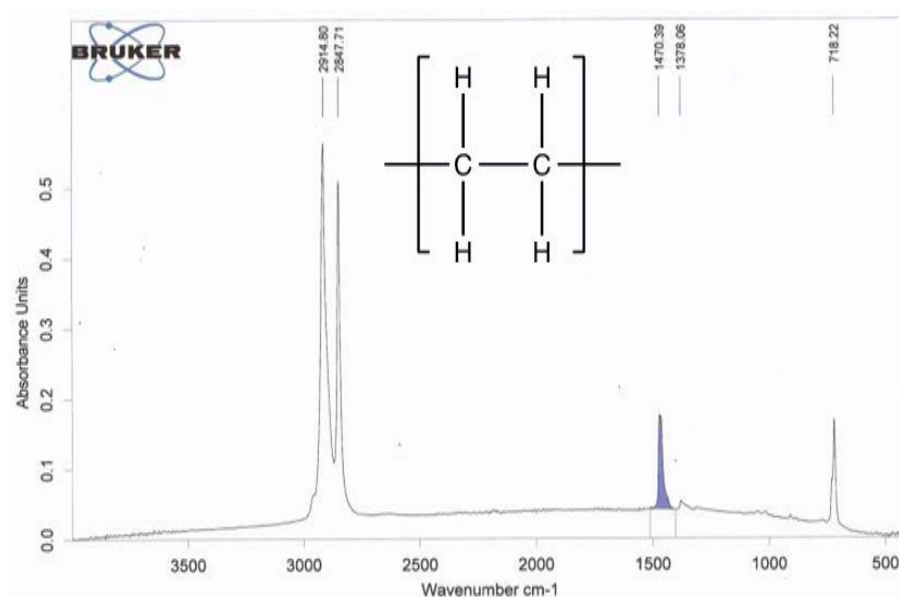


Figure 3.1: FTIR spectra of PE. Reproduced from ref. [38]

In order to successfully characterise different grades of polyethylene, such as low density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE), their manufacturing methods and crystalline structure are important to have in mind. LDPE is polymerised in radical reaction at elevated pressure and temperature having both short and long chain branching, making LDPE the most amorphous among the classes of polyethylene [37]. HDPE is polymerised via an ionic reaction mechanism, has a very small degree of branching and is a highly crystalline polymer [37]. LLDPE is polymerised via an ionic reaction involving small amounts of an α -olefin that when inserted

into the polymer chain the CH_3CH_2 becomes a short side chain of the PE molecule and so LLDPE has more short-chain branching than HDPE [37].

The difference between HDPE and LDPE can be revealed via the relative intensity of an absorption band at around 1377cm^{-1} that represents the methyl group which is more abundant in highly branched LDPE [39].

The difference between LLDPE and LDPE can be revealed by analysing the regions between 650cm^{-1} and 1000cm^{-1} where absorbance bands for vinylidene group (890cm^{-1}) and terminal vinyl group (910cm^{-1}) are located. These bands should be of similar intensities for LLDPE and the vinylidene group band should be predominant in LDPE [39].

3.2 FTIR for Additive Identification and Quantification

ATR-FTIR can be used to identify additives in a polymeric matrix, in the same way that it can identify polymers [40, 41].

One way to identify additives present in a plastic product is to first extract them using solvents [40]. This process is not ideal, not only because it is a complex process that involves handling hazardous solvents but also defeats the purpose of using FTIR spectroscopy as a non destructive technique. For these reasons, for the present work, the most appropriate way to identify additives would be to develop a complete spectra library with the fingerprint spectra of additives and comparing them to the unknown additive.

ATR-FTIR spectrometry can be used in qualitative studies to analyse the evolution of additives in a polymeric matrix [32, 42]. Formation and/or disappearance of functional groups can be monitored using ATR-FTIR, as done by Barbes et al. [32] that analysed PP samples with and without an anti-oxidant additive *Irganox 1010*, with different concentrations over a period of 7 days. Others have used ATR-FTIR to map the concentration profile of an additive in a polymeric matrix that migrated overtime [42, 41, 10].

Additive quantification with FTIR is widely used in the pharmaceutical industry [43, 44] and others [32, 40, 45]. For instance, Edi et al. [43] used ATR-FTIR coupled with partial least squares regression (PLSR) in order to obtain a quantification method for a drug with two components (vildagliptin and metformin). Solutions with different known concentration of the two components were prepared and PLSR was used in order create a model able to predict the concentration of these two components in a solution. Similarly, Kelani et al. [44] successfully studied ATR-FTIR coupled with partial least squares regression (PLSR) capacity for quantitative analysis of pharmaceutical active agents. FTIR quantitative analysis combined with PLSR chemometric calculations was successfully used for the quantification of active pharmaceutical components [43, 44], a similar approach was taken in the present work.

Spectral pre-treatments, such as using Savitzky-Golay first derivative, are sometimes useful [43]. However, for the present work, Savitzky-Golay first derivative was not performed because the obtained spectrum did not show much noise. For the present work, using normalisation as a spectra pre-treatment operation was chosen due to its simplicity. Normalisation consisted in adjusting the intensity of the peaks in relation to the peaks with the highest intensity, which is attributed the value 2.

In the construction industry, ATR-FTIR also proved useful when Weigel et al. [45] used this technique to quantify additives in bituminous binders, a crucial material for road construction. It was proven possible to determine the linear relationship between the additive concentration and the absorbance, since for ATR-FTIR the thickness of the sample can be considered a constant [45]. For the case of spectra of polymeric films obtained in transmission mode FTIR, the thickness is not usually content and that is why it needs to be taken into consideration when building the calibration curve that will be used to quantify

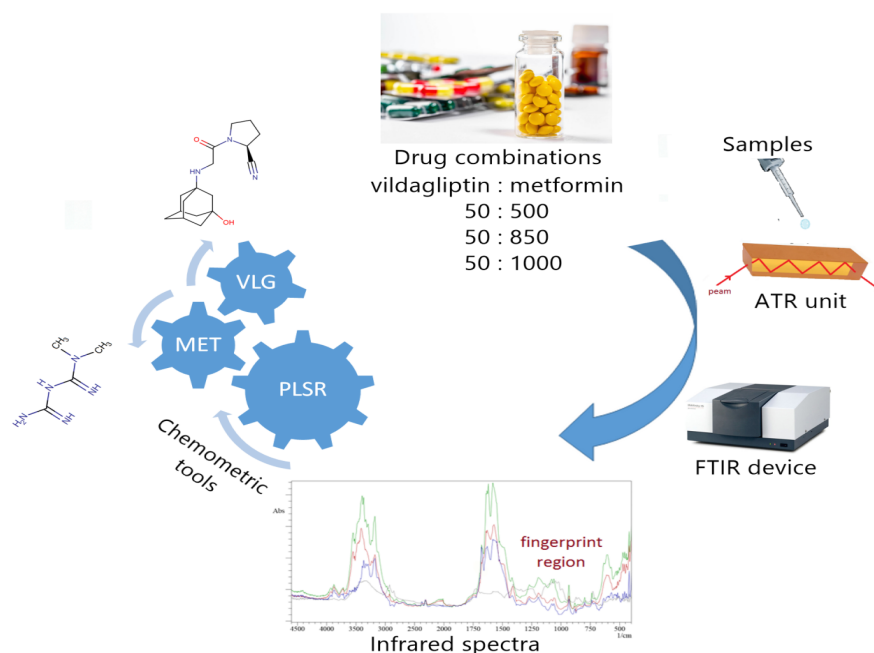


Figure 3.2: Workflow for obtaining a quantification method of components of a drug using ATR-FTIR. Reproduced from ref. [43]

the additive present in a film .

A combination of ATR-FTIR with PLSR allows for the development of a quantification method in order to make a prognostic quantitative evaluation of a concentration of an additive [43, 44, 45].

The studies on the use of transmission mode FTIR for the quantification of substances on solid samples are scarce.

Kaixian Qiu et al. [46] used and compared ATR and transmittance FTIR to quantify the presence of a prohibited substance, fipronil, in pesticide preparations. The calibration curves were obtained with liquid samples prepared with different amounts of the substance, that were deposited on the surface of the ATR crystal and the transmission plate. The correlation coefficients, R^2 , obtained were 0.9982 for the ATR measurements and 0.8830 and 0.9787, for two different peaks in the transmission mode measurements. Different data treatment was used to increase the quality of the fitting. For example, the application of the second derivative to the transmission spectra resulted in values for the R^2 of 0.9821 and 0.9843 for the same transmission mode peaks. The objective of this work was to compare different methods of obtaining the calibration curves, but these were not used to quantify the substance in pesticide samples. For the present work, second derivative spectra pretreatment was tested but not enforced since it did not lead to better results for the correlation coefficient.

Transmission mode FTIR presents several advantages for Poliversal's activity such as the possibility to analyse transparent films made out with masterbatches with colourless additives. Just like with ATR-FTIR, it is also possible to combine transmittance mode FTIR with PLSR and with Beer's Law to establish a method that determines the concentration of an additive [47]. Song et al. [47] noted that the combination of Beer's Law with PLS allowed to obtain a straightforward analytical method that did not require complex mathematical theories.

$$A = \epsilon * l * c \quad (3.1)$$

Where:

- A : absorbance
- ϵ : molar attenuation coefficient or absorptivity of the attenuating species
- l : optical path length
- c : concentration of the attenuating species

3.2.1 Slip additive - Erucamide

ATR-FTIR was used to map the concentration profile of erucamide in LLDPE films [42, 41].

Joshi et al. [41], used masterbatches of the polymer and additive that were compounded by a third party and the weight percents were determined using solvent extraction followed by gas chromatography in order to determine the concentration of erucamide in the master. The LLDPE films with 1.9 wt% erucamide were prepared using a Carver press by compression moulding pellets allowing for a constant thickness of 400 μm . For the present work, a Carver press was used to prepare films directly from the MB but, the obtained films were not thin enough for ATR in transmission mode, and so blown film moulding was used to prepare the samples as described in Chapter 4.

Joshi et al. [41] determined the profile of erucamide in the film by developing films with only one concentration of erucamide and analysing the erucamide migration over time in a designated area of the film.

Sankhe et al. [42], compounded using a Randcastle extrusion system obtaining 50 μm thick cast LLDPE films containing 1 wt% of erucamide that were frizzed after extrusion to prevent migration of erucamide. Then, samples were taken from the freezies and aged at room temperature to allow erucamide migration.

To identify the presence of erucamide by using -FTIR spectroscopy, the authors [42, 41] used the characteristic peak of amide I carbonyl stretch that occurs at around 1645cm^{-1} , evident in figure 3.3.

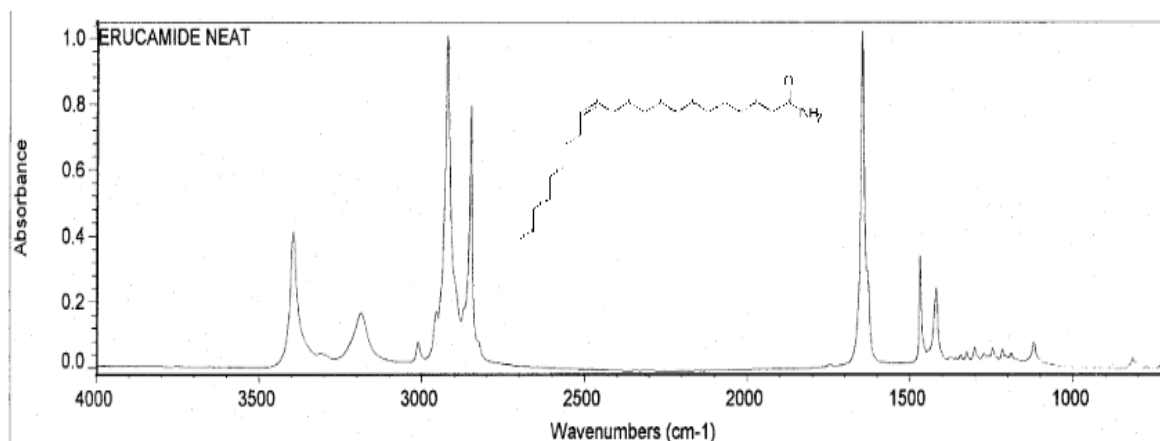


Figure 3.3: FT-IR spectra of erucamide. Reproduced from ref. [41]

3.2.2 Anti-static additive - GMS

Glycerol Monostearate (GMS) is the main anti-static agent used at Poliversal MB.

ATR-FTIR spectroscopy can be used to determine the amount of GMS at the surface of a plastic sample [10].

The peak used to identify the GMS presence was the carbonyl peak at 1736cm^{-1} , [10, 48]. In figure 3.4 the FTIR spectra for GMS is shown, where the 1736cm^{-1} peak is evident.

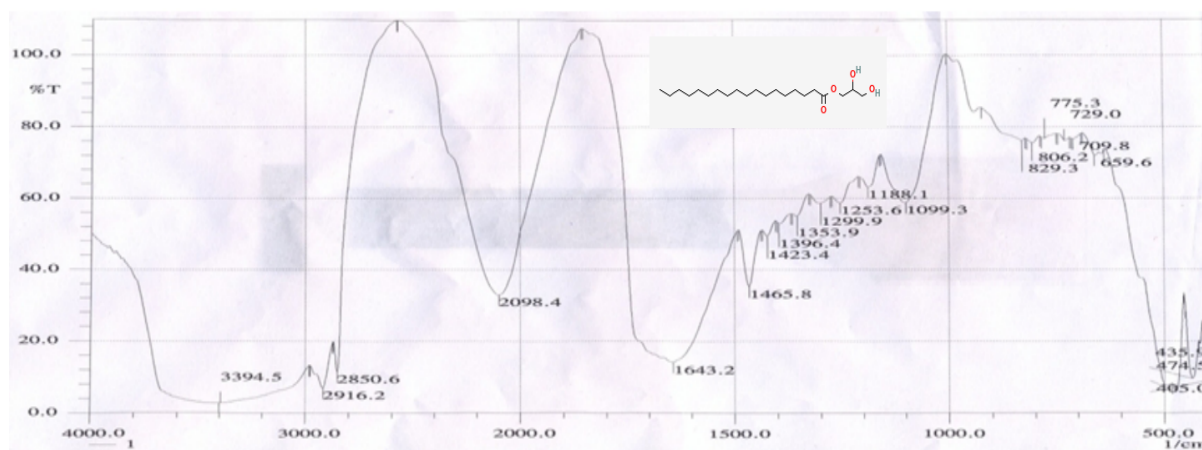


Figure 3.4: FTIR spectra of GMS. Reproduced from ref. [41]

3.2.3 Anti-UV additives - HALS Tinuvin 622 and HALS Chimassorb 944

HALS Tinuvin 622 is a macromolecular HALS with high molecular weight that exhibits excellent heat stability, starting its decomposition at around 400°C with the rearrangement of the intermolecular ester group, and ending at 900°C with the formation of nitrile and hydrogen cyanide [49]. Its chemical structure is presented in figure 3.5.

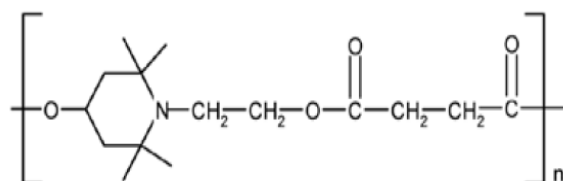


Figure 3.5: Chemical structure of HALS Tinuvin 622, Mw= 3100-4000g/mol.

Chimassorb 944 is a high molecular HALS. It shows excellent compatibility, good resistance to extraction and low volatility. Its chemical structure is presented in figure 3.6.

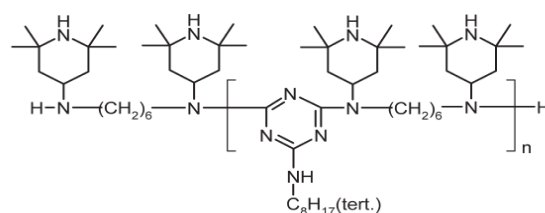


Figure 3.6: Chemical structure of HALS Chimassorb 944, Mw=2000-3100g/mol

Scorponi et al. [50] studied the photo-stabilisation mechanism of LDPE films for agricultural applications conducting measures on LDPE films formulated with equal parts of HALS Tinuvin 622 and HALS Chimassorb 944. They identify the absorption band at 1734 cm⁻¹ as the one that allows to determine HALS Tinuvin 622 concentration, attributed to ester groups in the oligomeric chains. For HALS Chimassorb 944, the ESR spectral band detected at 225 nm using a UV-Vis spectrometer. For the present work, other absorption bands were chosen to identify HALS Chimassorb 944 such as the absorption band between 1600 cm⁻¹ and 1500 cm⁻¹, which was found to change its intensity according to the concentration of Chimassorb 944.

3.3 Detection of Dark Coloured Items - New Alternatives

In order to overcome the difficulty of sorting plastic products that have carbon black in its composition, alternative pigments and dyes are used. The most common alternative to carbon black is Pigment Black 11 that is opaque to visible light and NIR absorbent, just like carbon black.

New NIR-transparent colourants have been developed by BASF, Fuji, Treffert GmbH and Ferro. These organic colourants do not absorb strongly in the IR region, but can be produced with high opacity and blackness [16].

Figure 3.7 shows the reflectance spectra for NIR-absorbing pigments, NIR-reflecting pigments and NIR-transparent pigments.

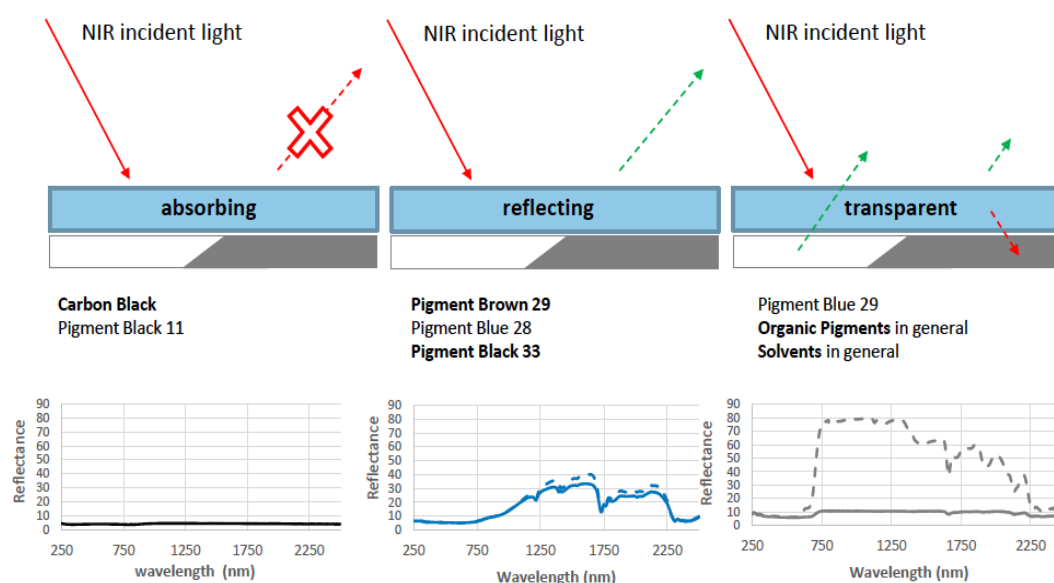


Figure 3.7: Reflectance spectra for NIR-absorbing pigments (left), NIR-reflecting pigments (centre) and NIR-transparent pigments (right). Reproduced from ref. [51]

NIR-reflective colourants were also developed (e.g. Pigment Brown 29), these colourants have high IR-reflectivity or low absorption. BASF, Shepherd Colour Company and Ferro have developed IR-reflective colourants that, at low concentration in a polymeric matrix, allow to obtain an NIR spectrum in reflectance mode [16].

Mid-infrared (MIR) spectroscopy is an efficient method for characterising black plastic parts with 0,5-3% in mass of carbon black, and successfully identify the base polymer resin [3, 26]. However, it is not fast enough to meet economic requirements in sorting plants, and that is why NIR spectroscopy is still widely used in sorting plants. Becker et al. [3], presents an alternative spectroscopy system based on photon up-conversion in the MIR spectrum that is fast and sensitive though so it can be applied to sort black polymer parts. This novel system is not yet used in sorting facilities.

Knowing the detection limit of FT-NIR for plastic products with carbon black or alternative pigments, is an advantage for Poliversal's activity and their costumers. It allows to better advise on the formulation of the products to develop and address concerns related to the recyclability potential of the final product.

Chapter 4

Experimental Work: Materials and Methods

The experimental work consisted in the preparation of samples for IR Spectroscopy analysis. Both transmission and reflection spectroscopy were used. In this chapter, the materials and methods used for sample preparation and spectra acquisition are described.

Figure 4.1 is a schematic representation of the experimental procedure.

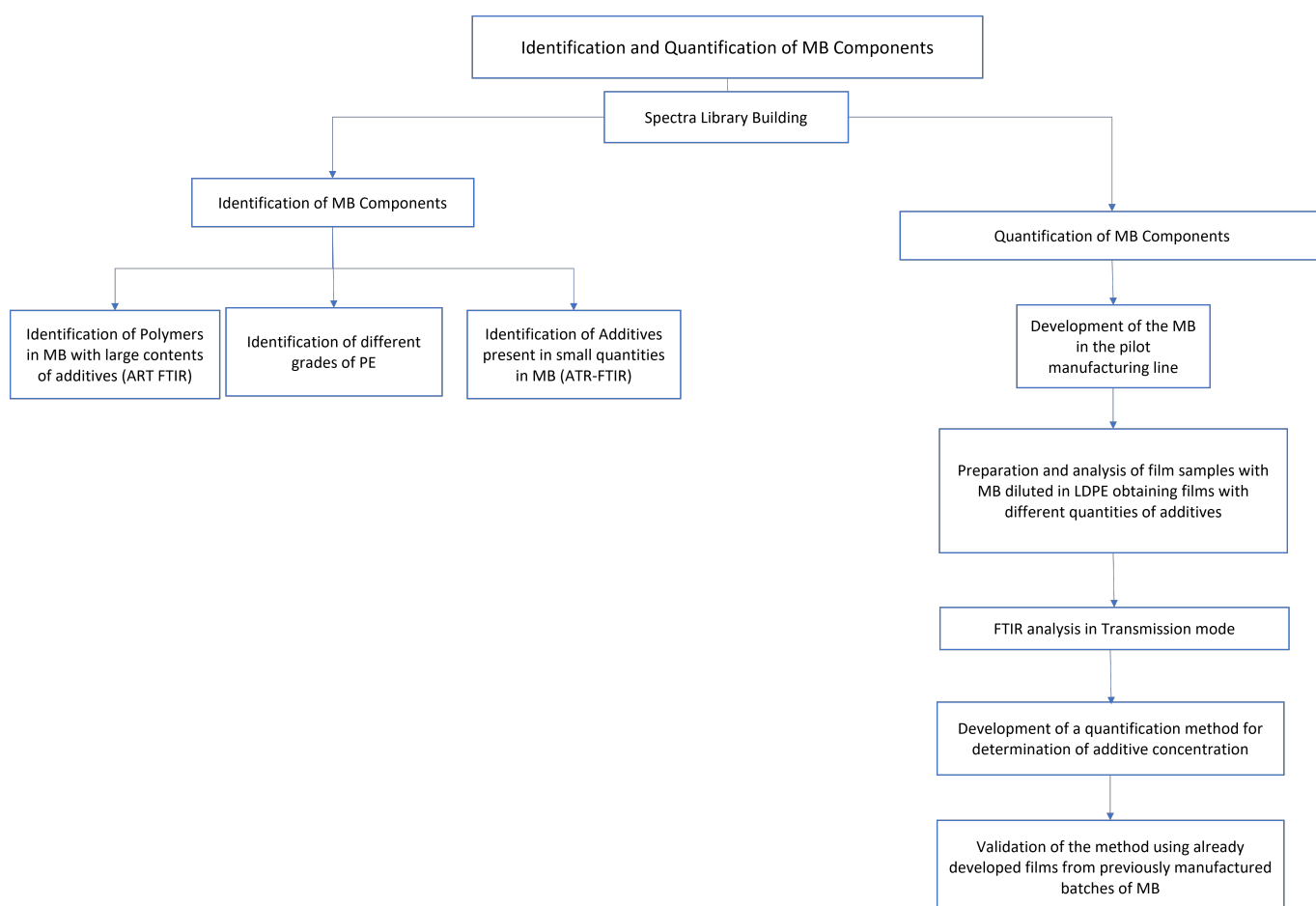


Figure 4.1: Schematic representation of the overall experimental methodology

Discrepancy between different libraries used will lead to incomparable results [46]. Since the libraries

that were provided by Bruker were considered incomplete for the present work, creating a libraries with the polymers and additives used at Poliversal was the best option.

4.1 Materials

A library in ATR mode was created using polymers, additives and some relevant masterbatches that are used at Poliversal. To create this library, measurements were taken in ATR mode from samples with different physical form - powder, granulates or injected samples - depending on the form of the raw material. This library will be used to identify samples of polymers, additives and masterbatches.

For the construction of the library of FTIR spectra, a series of different polymers, additives and masterbatches were analysed. These materials are listed in the table 4.1.

Table 4.1: Main polymers and additives added to the library and used in the present work. The specification information was collected from Technical Data Sheets of each product provided by the manufacturer.

| Material | Commercial Name | Manufacturer | Physical Form | Melting Point (°C) | Chemical formula |
|--------------------|------------------------|--------------|---------------------|--------------------|------------------------|
| HDPE | Eraclene MP 90 U | Versalis | Colourless granules | 135 | $(C_2H_4)_n$ |
| LDPE | Alcudia 2322M PE003 | Repsol | Colourless granules | 115 | $(C_2H_4)_n$ |
| | | Repsol | Colourless granules | 115 | $(C_2H_4)_n$ |
| LLDPE | Flexirene MT 40 A | Versalis | Colourless granules | 117 | $(C_2H_4)_n$ |
| PS | Edistir N 3910 | Versalis | Colourless granules | 105 | $(C_8H_8)_n$ |
| Erucamide | Crodamine ER | Croda | White granules | 78-81 | $C_{22}H_{43}NO$ |
| GMS | Atmer 1013 | Croda | White granules | 54-70 | $C_{21}H_{42}O_4$ |
| Anti-UV | HALS Tinuvin 622 | BASF | White granules | 100-135 | $C_{15}H_{27}NO_5$ |
| Anti-UV | HALS Chimassorb 944 | BASF | Yellowish granules | 50-70 | $C_{35}H_{69}Cl_3N_8$ |
| Talc | LUZENAC 8218 | IMERYS Talc | White powder | >1300 | $Mg_3Si_4O_{10}(OH)_2$ |
| Calcium carbonate | CARVAC 2M | VAC Minerais | White powder | 1340 | $CaCO_3$ |
| Carbon Black Black | Lamp Black 101 | Orion | Black powder | >3000 | C |
| Pigment Black 11 | Bayferrox 318M | Lanxess | Black powder | >1000 | Fe_3O_4 |
| Pigment Brown 29 | AL-81737 | AL-FARBEN | Black powder | >1000 | $(Cr, Fe)_2O_3$ |

The library was used for the identification of several polymeric samples, in the form of granules.

4.2 Samples and Sample Preparation Methods

4.2.1 Masterbatch manufacturing

For the quantitative analysis of additives using FTIR, firstly the MB with only LDPE and an additive were developed, in the pilot production line, using a twin screw co-rotating extruder Baker Perkins MPX24 Integra.

Masterbatches with the composition of MB Slip and MB Antistatic were already developed by Poliversal, but in an attempt to guarantee the exact composition, they were reproduced in the pilot production line at Poliversal.

The MB UV commercialised by Poliversal is not by them manufactured. The QC method used by the manufacturer does not seem accurate since it is based only on the comparison of the IR spectra and not a quantification method. In an attempt to develop a quantification technique to evaluate the quality of the purchased MB, its formulation was replicated and the MB was produced in the pilot production line at Poliversal.

The procedure for the MB manufacturing is described bellow and illustrated in figure 4.2. In table 4.2, the operational setting for the twin screw extruder are presented. The composition of these MB is presented in table 4.3.

To manufacture these masterbatches the following steps were taken :

- Weighing of the components using a Mettler Toledo RS232C scale with precision 0,1g (composition of the MB in table 4.2).
- Mixing of the components using a high intensity mixer.
- Extrusion, using a twin screw co-rotating extruder Baker Perkins MPX24 (parameters in table 4.5).
- Cooling of the extruded material using a water bath.
- Drying of the MB threads using a Maag SE 100-2 dryer.
- Cutting into pellets using Maag PRIMO 60E pelletiser, obtaining the masterbatch.



Figure 4.2: From left to right: (1) High intensity mixer, (2) Twin screw extruder,(3) Water bath, (4) Pelletiser

Table 4.2: Operational setting for the Baker Perkins Twin Screw Extruder.

| Parameters | Value |
|---------------------------------|-------|
| Temperature of Feeding Zone | 120°C |
| Temperature of Compression Zone | 130°C |
| Temperature of Metering Zone | 130°C |
| Die | 130 |

| | |
|------------------------------|---------|
| Rotation speed of the screws | 600 rpm |
| Pellet length | 15 mm |

Table 4.3: Composition of the MB used in the present work, some produced in the pilot production line at Poliversal

| Sample name | Components | Quantity (%) |
|--|----------------------|--------------|
| MB Slip | Erucamide | 5 |
| | LDPE (Alcudia 2322M) | 95 |
| MB Antistatic | GMS | 5 |
| | LDPE (Alcudia 2322M) | 95 |
| MB UV | HALS Tinuvin 622 | 10 |
| | HALS Chimassorb 944 | 10 |
| | LDPE (Alcudia 2322M) | 80 |
| MB Tinuvin | HALS Tinuvin 622 | 20 |
| | LDPE (Alcudia 2322M) | 80 |
| MB Chimassorb | HALS Chimassorb 944 | 20 |
| | LDPE (Alcudia 2322M) | 80 |
| MB Talc (not produced in the pilot line) | Talc | 60% |
| | PP | 30% |
| | other additives | 10% |
| MB CaCO ₃ (not produced in the pilot line) | Calcium Carbonate | 65% |
| | LDPE | 25% |
| | other additives | 10% |

All the manufactured MB have a similar look, they are pellets whitish colour, as seen in figure 4.3.

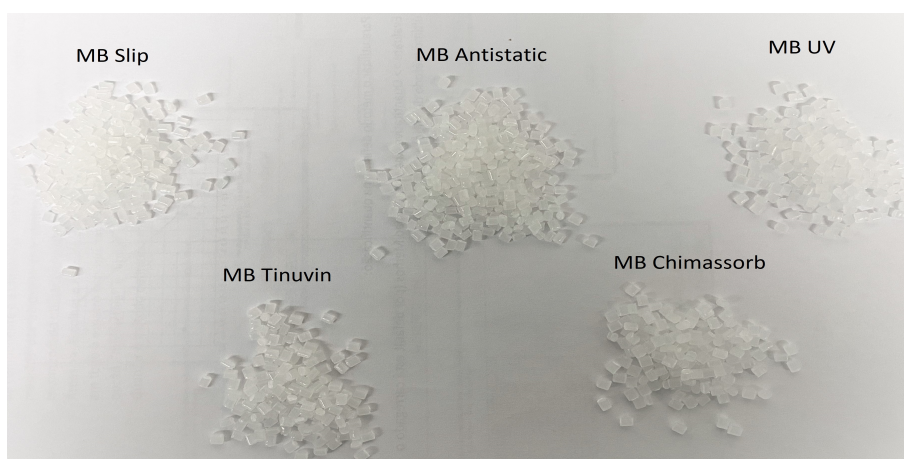


Figure 4.3: Picture of MB prepared in the pilot production line at Poliversal

4.2.2 Preparation of Film Samples

Samples of LDPE films containing different percentages of additives were prepared and extruded using a tubular film extruder *Shouman, D15cm*, by diluting the previously manufactured MB with a tubular

film extrusion grade LDPE (Alcudia PE003). These films will then be used in transmission mode FTIR spectroscopy.

The procedure to obtain these samples is described bellow. The parameters of the tubular film extruder are presented in table 4.4. Figure 4.4 shows the tubular film extruder used (Shouman D15) and table 4.5 presents the composition of the films later used for FTIR spectroscopy in transmission mode.

To produce film samples the following steps were taken :

- Weighing of the components using a Mettler Toledo RS232C scale with precision 0,1g.
- Manually mixing of the components .
- Tubular film extrusion using tubular film extruder Shouman D15cm.

The following table 4.4 has the parameters of the tubular film extruder Shouman D15cm used in the production of the film samples. Insufflation parameters were manually adjusted in order to obtain a stable bubble and a final film with the lowest thickness.

Table 4.4: Parameters of Tubular Film Extruder Shouman D15cm

| Parameters | Value |
|---------------------------------|---------|
| Temperature of Feeding zone | 145°C |
| Temperature of Compression zone | 145°C |
| Temperature of Metering zone | 145°C |
| Extruder speed | 710 rpm |
| Collection speed | 215 rpm |



Figure 4.4: Tubular Film Extruder Shouman D15cm

Table 4.5: Composition of the films used for FTIR Spectroscopy

| Sample Name | Theoretical wt% of additive | Additive |
|-----------------|-----------------------------|---------------------|
| Slip Film | 0,1% - 5% | Erucamide |
| Antistatic Film | 0,1% - 3% | GMS |
| UV Film | 0,1% - 10% | HALS Tinuvin 622 |
| | 0,1% - 10% | HALS Chimassorb 944 |

| | | |
|-----------------|------------|---------------------|
| Tinuvin Film | 0,1% - 10% | HALS Tinuvin 622 |
| Chimassorb Film | 0,1% - 10% | HALS Chimassorb 944 |

4.2.3 Injection moulding samples

Injection moulding plaques (figure 4.6) samples were obtained from already developed MB by Poliversal. These plaques will then be used in NIR spectroscopy in order to test its sensitivity to carbon black and alternative pigments to carbon black (Pigment Black 11 and Brown 29). By using injection moulding plaques we are simulating a plastic product in a waste management facility.

For every sample with carbon black, there is a sample identical in colour that does not have carbon black in its formulation. Instead, Pigment Black 11 or Brown 29 are used as an alternative, eventually combined with other non absorbing NIR pigments to obtain a similar colour.

To obtain injection moulding plaques the already developed MB is diluted with the application/dilution polymer, manually mixed and injected using injection moulding machine BOY 25E (figure 4.5).



Figure 4.5: Injection moulding machine BOY 25E

The parameters from the injection moulding extruder BOY 25E are presented in table 4.6 and depend on the dilution polymer. The composition of injection moulding plaques is presented in table 4.7. The samples are shown in figure 4.6.

Table 4.6: Parameter for Injection Moulding machine BOY25E

| Dilution Polymer | Parameters | Value |
|------------------|-------------------------------------|--------|
| PS and PP | Temperature of the Feeding Zone | 160°C |
| | Temperature of the Compression Zone | 220°C |
| | Temperature of the Metering Zone | 220°C |
| PS | Injection velocity | 2 mm/s |
| | Posterior pressure | 10MPa |
| | Action time of posterior pressure | 80 s |
| PP | Injection velocity | 5 mm/s |
| | Back pressure | 12 MPa |
| | Action time of posterior pressure | 80 s |

Table 4.7: Sample Composition for FT-NIR spectroscopy analysis.
Theoretical wt% of Carbon Black and Black 11/Brown 29 in the end product, after the MB is diluted with the application polymer

| Sample Name | MB Base Polymer | Dilution Polymer | Theoretical wt% of Carbon Black | Theoretical wt% of Black 11/Brown 29 |
|----------------|-----------------|------------------|---------------------------------|--------------------------------------|
| MB 81774 Black | PS | PS | 2 | - |
| T-17604/1/8 | PS | PS | - | 1 |
| MB 81373 Black | PE | PP | 1,2 | - |
| T-17302/1/8 | PE | PP | - | 1 |
| MB 7942 Brown | PE | PP | 0,125 | - |
| T-16270/2/7 | PE | PP | - | 0,95 |
| MB 7810 Brown | PE | PP | 0,041 | - |
| T-13301/5/7 | PE | PP | - | 0,17 |
| MB 62617 Blue | PE | PP | 0,025 | - |
| T-16266/4/6 | PE | PP | - | 0,075 |
| MB 82521 Grey | PE | PP | 0,021 | - |
| T-16268/7/8 | PE | PP | - | 0,005 |
| MB 7811 Brown | PE | PE | 0,0076 | - |
| T-13302/4/7 | PE | PE | - | 0,04 |
| MB 51939 Green | PE | PP | 0,00165 | - |
| T-16713/1/5 | PE | PP | - | 0,1 |



Figure 4.6: Injection moulding samples used for NIR spectroscopy

4.2.4 Obtaining the IR Spectrum

FTIR spectroscopy was done using the Bruker Compact FTIR Spectrometer ALPHA II, shown in figure 4.7. Its technical characteristics are described in table 4.8. The film samples prepared in Chapter 4 were used in FTIR spectroscopy.

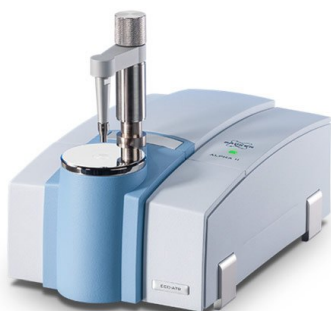


Figure 4.7: Bruker Compact FTIR Spectrometer ALPHA II. Reproduced from [52]

Table 4.8: Technical characteristics of Bruker's FTIR Alpha II, based on documents provided by Bruker.

| Component | Characteristic |
|---------------------|--|
| Interferometer | Permanent aligned RockSolid™ cube corner interferometer |
| Optical system | Sealed and desiccated |
| Beam splitter | KBr |
| Light source | SiC Globar |
| Detector | DLaRGS-detector |
| Wave number range | 4000-400cm ⁻¹ |
| Spectral resolution | Better than 2cm ⁻¹ , optical better than 0.75cm ⁻¹ |
| S/N ratio | > 55.000/1 |
| Software | OPUS 8.5.29 |

FTIR spectra were acquired with an ATR module, between 4000-400cm⁻¹ with 32 scans and spectral resolution of 4 cm⁻¹. ATR diamond crystal was cleaned with 70% isopropyl alcohol and background scans were performed between each sample.

FT-NIR spectroscopy was done using the Bruker Multi-purpose Analyser (MPA) FT-NIR, equipped with sample compartment and integrating sphere, shown in figure 4.8. Its technical characteristics are described in table 4.8. Injection moulding plaques obtained in chapter 4.2.3 were used.



Figure 4.8: Bruker Multi-purpose Analyser (MPA) FT-NIR. Reproduced from [35]

Table 4.9: Technical characteristics of Bruker's Multi-purpose Analyser (MPA) FT-NIR, based on documents provided by Bruker

| Component | Characteristic |
|---------------------|--|
| Interferometer | Permanent aligned RockSolid™ cube corner interferometer |
| Optical system | Sealed and desiccated |
| Beam splitter | Quartz |
| Light source | SiC Globar |
| Detector | DLaRGS-detector |
| Wave number range | 400-10 000cm ⁻¹ |
| Spectral resolution | Better than 2cm ⁻¹ , optical better than 0.75cm ⁻¹ |
| S/N ratio | > 55.000/1 |
| Software | OPUS 8.5.29 |

FT-NIR spectra were acquired in reflectance mode, between 400-10 000cm⁻¹ with 32 scans and spectral resolution of 4 cm⁻¹.

4.3 Identification of the Components in a Sample

The obtained spectras from the film samples were normalised using function *Min-Máx* described in Appendix A.2 between 0 and 2. The identification of a substance in the obtained spectra is done using *Spectrum Search* (Appendix A.1) tool and utilising the already built library.

4.4 Quantification of Components of a Sample

In order to quantify the desired additive, the following spectra treatments were performed:

- Normalisation of the obtained spectra using *Máx-Min* (Appendix A.2) function.
- Determination of the film thickness using *Layer Thickness*, function described in Appendix A.3.
- Determination the peak high using an integration method described in Appendix A.4 with integration method K.
- Determination of the peak area using integration method described in Appendix A.4 with integration method B.

The obtained data is presented in Appendix B, C, D, E and F.

For each film with different wt% of additive, 10 samples were analysed, and 3 out of those 10 with the closest values in thickness were used to obtain the linear relationship between peak area intensity and additive quantity. In order to get a predictive model, linear fitting was performed form the 3 samples of each films with different concentrations of additive. The obtained equations can be used to determine the approximate wt% of additive in the QC films.

When analysing samples used for QC at Poliversal, a protocol of taking 5 samples and choosing 3 with the closest values of thickness was adopted, allowing a quick analysis that is important when working in a QC laboratory of a factory with a high throughput.

To determine the concentration of additives in MB UV that contains two additives in equal quantity (HALS Tinuvin 622 and HALS Chimassorb 944), two approaches were taken:

- Manufacturing of MB UV containing both additives in equal quantity;
- Manufacturing of two MB (MB UV Tinuvin and MB UV Chimassorb) with only one of the additives.

These samples were analysed in the same way as described above. The goal in using both approaches is to determine which one would lead to the best fitting of data in the case of an MB with more than one additive.

Samples in film form were obtained using a tubular film extruder that does not allow for an even and regular thickness across the whole film. Thickness varies from sample to sample and so the resultant spectra is affected. In addition to transmission/absorption phenomena (compensated when the absorbance is divided by the thickness of the sample, using Lambert Beer's Law), in the interaction of the light with the sample there will be other phenomena such as refraction or dispersion/fusion, in the interaction light-samples, different for each sample, which will not be compensated. In order to mitigate this effect, a triage was made to only include the results for the samples with the most similar thicknesses, lowering the standard deviation for the thickness. That is why out of the 10 samples taken from each film, 3 with the closest thickness were chosen.

The best way to mitigate the phenomena above described would be to use a heated pellet press machine, this way samples would have a uniform distribution of the thickness.

Chapter 5

Results and Discussion

5.1 Polymer Identification with Attenuated Total Reflectance

For polymer identification, MB samples with different quantities of additives were analysed in order to evaluate the polymer identification capacity.

Fillers are the additives used in higher quantities for MB formulation. Since talc and calcium carbonate are the most used fillers in MB formulation, the samples analysed corresponded to MB with the highest wt% of these fillers. The samples evaluated are described in table 4.1.

In order to identify the base polymer of the MB and the primary additive, the *Spectrum Search* function (Appendix A.1) was used. The spectrum library used by this function was developed specially for this work as described in Chapter 4.

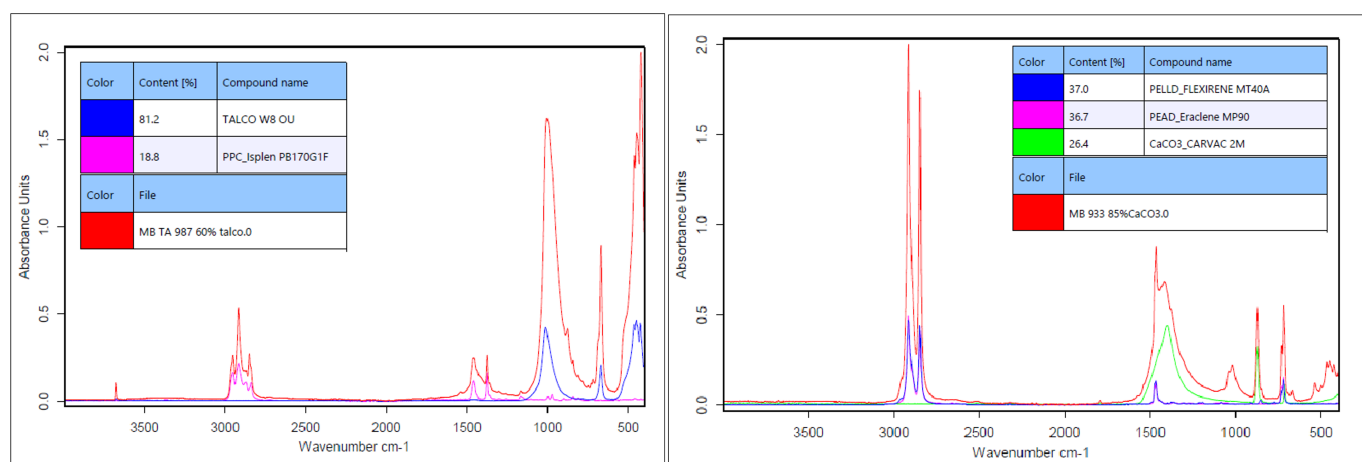


Figure 5.1: Left: Spectrum Search Report for samples MB Talc; Right: Spectrum Search Report for samples MB CaCO₃

Figure 5.1 (left) shows the report for identification of the base polymer in the sample where the main additive is talc. For the sample MB Talc with 60 wt% of talc, 30 wt% of PP and 10 wt% other additives, the *Spectrum Search* function identifies the polymer successfully as well as the talc which is the additive in the highest concentration. The *Spectrum Search* function broadly estimates a content of the components, based on the input parameter: mixture analysis spectrum search. None of the other additives present in 10% wt were identified.

Figure 5.1 (right) shows the report for identification of the base polymer in the sample where the main additive is calcium carbonate. For the sample MB CaCO₃ with 65 wt% of calcium carbonate, 25%

of LDPE and 10% other additives, the *Spectrum Search* function identifies the polymer successfully as well as the calcium carbonate which is the additive in the highest concentration. The *Spectrum Search* function broadly estimates a content of the components, based on the input parameter: mixture analysis spectrum search. None of the other additives present in 10% wt were identified.

5.1.1 Identification of Different Grades of Polyethylene

Using ATR allows to differentiate between different types of polyethylene, high density, low density, and linear low density [53]. To prove this, different grades of polyethylene (HDPE, LDPE and LLDPE) were tested to evaluate the ability of differentiate these grades via ATR. The polymers are identified in table 5.1.

It is possible to differentiate LDPE and HDPE by the relative intensity of the absorption band at 1378cm^{-1} , that represents the methyl group that is more abundant in highly branched LDPE [39].

After obtaining the spectra for HDPE and LDPE (figure 5.2), they were normalised and a closer look to spectral region between 1400 cm^{-1} and 1330 cm^{-1} was taken, evidenced in figure 5.2. The methyl group peak is deviated for both LDPE and HDPE samples, for LDPE it is located at 1371 cm^{-1} and for HDPE it is located at 1366 cm^{-1} .

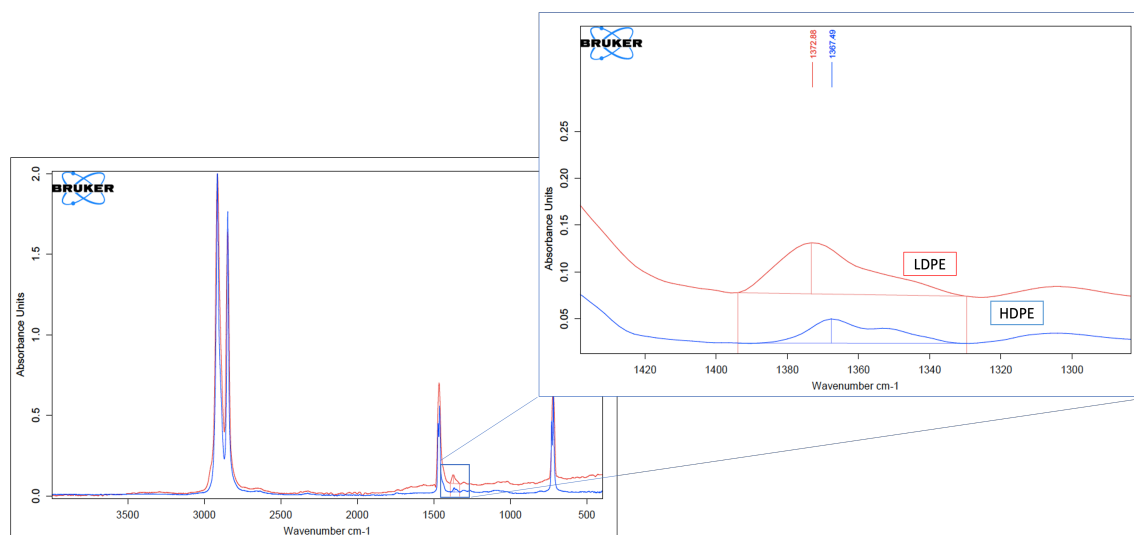


Figure 5.2: LDPE and HDPE spectra obtained in ATR mode, with evidence of the methyl group peak at about 1370 cm^{-1}

To determine the peak intensity for the methyl group band, an integration method was created. The set-up of an integration method is described in Appendix A.4, the integration mode used was integration mode K that determines peak intensity relative to the local baseline. The results are presented in table 5.1. From the results obtained, it is possible to confer that the intensity of the methyl group peak for LDPE is greater than for HDPE.

Table 5.1: Methyl group peak intensity for LDPE and HDPE.

| Integration mode | Samples | Range of Integration | Result in Absorbance units |
|------------------|---------|--------------------------------------|----------------------------|
| K | LDPE | $1394\text{ to }1330\text{ cm}^{-1}$ | 0,055 |
| K | HDPE | $1394\text{ to }1330\text{ cm}^{-1}$ | 0,027 |

To differentiate between LDPE and LLDPE a closer look to the 650cm^{-1} and 1000cm^{-1} area was taken (figure 5.3), after normalisation of both spectra. It is expected for the absorbance bands at 890cm^{-1} for

vinylidene group and at 910cm⁻¹ for vinyl group to have overall similar intensities in both LDPE and LLDPE [39]. It is expected for these bands to be less intense for LLDPE than for LDPE, also it is expected for the band for vinylidene group at 910cm⁻¹ to be more intense in LDPE [39].

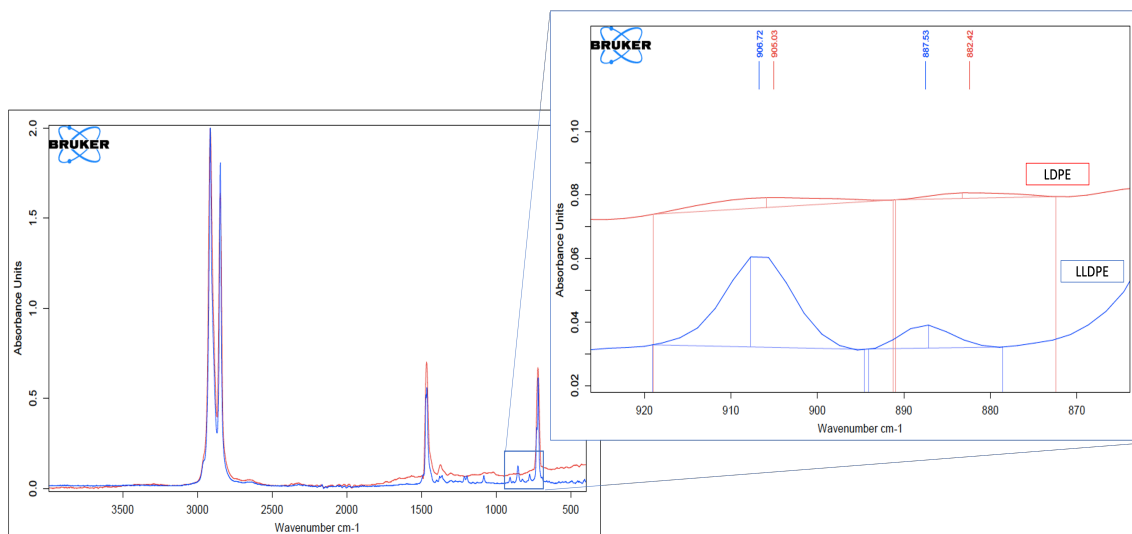


Figure 5.3: LDPE and LLDPE spectral obtained in ATR mode, with evidence of the terminal vinyl (between 862cm⁻¹ and 88cm⁻¹) group and vinylidene group (between 907cm⁻¹ and 905cm⁻¹)

Table 5.2: Terminal vinyl group and vinylidene group peak intensity for LDPE and LLDPE.

| Integration mode | Samples | Range of Integration | Result in Absorbance units |
|------------------|---------|-----------------------------|----------------------------|
| K | LLDPE | 919 to 894 cm ⁻¹ | 0,029 |
| K | LLDPE | 894 to 879 cm ⁻¹ | 0,070 |
| K | LDPE | 918 to 891 cm ⁻¹ | 0,002 |
| K | LDPE | 891 to 872 cm ⁻¹ | 0,003 |

Looking at the spectra for LDPE, the peaks for vinylidene and terminal vinyl group although similar, have very low intensities (results in table 5.2). For LLDPE, although the intensities of the absorption bands are not similar they are noticeable.

It was expected for the vinylidene group to be predominant at the LDPE spectra, but it is not the case. That is observed for the LLDPE spectra.

Differentiation between LDPE and LLDPE was not possible using ATR-FTIR, as observed by Nishikida and Coates [39].

5.2 Additive Identification and Quantification

5.2.1 Band Selection for Additive Identification

Slip additive - Erucamide

The FT-IR spectra for Erucamide and LDPE is shown in figure 5.4.

Normalised spectra for LDPE and Erucamide have different peaks that do not overlap mainly at 319cm⁻¹ and a double peak at 1645cm⁻¹ (C=C stretching), and 1631cm⁻¹ (C=O stretching). For the qualitative analysis the double peak was chosen to be used due to its higher absorbance.

Antistatic additive - GMS

The FT-IR spectra for GMS and LDPE is shown in figure 5.4, where the carbonyl group peak of GMS, at around 1736cm^{-1} is present at 1731cm^{-1} is well evidenced and is not masked by any peaks from LDPE. Therefore, it is possible to use this peak to study GMS additive in LDPE films.

Anti-UV additives - HALS Tinuvin 622 and HALS Chimassorb 944

The FT-IR spectra for HALS Tinuvin 622, HALS Chimassorb 944 and LDPE are shown in figure 5.4, where the absorption band at 1728cm^{-1} attributed to the ester groups in the oligomeric chains of HALS Tinuvin 622 and the bands at 1567cm^{-1} and at 1527cm^{-1} used to identify the presence of HALS Chimassorb 644 are not masked by the presence of each other or by any band from LDPE.

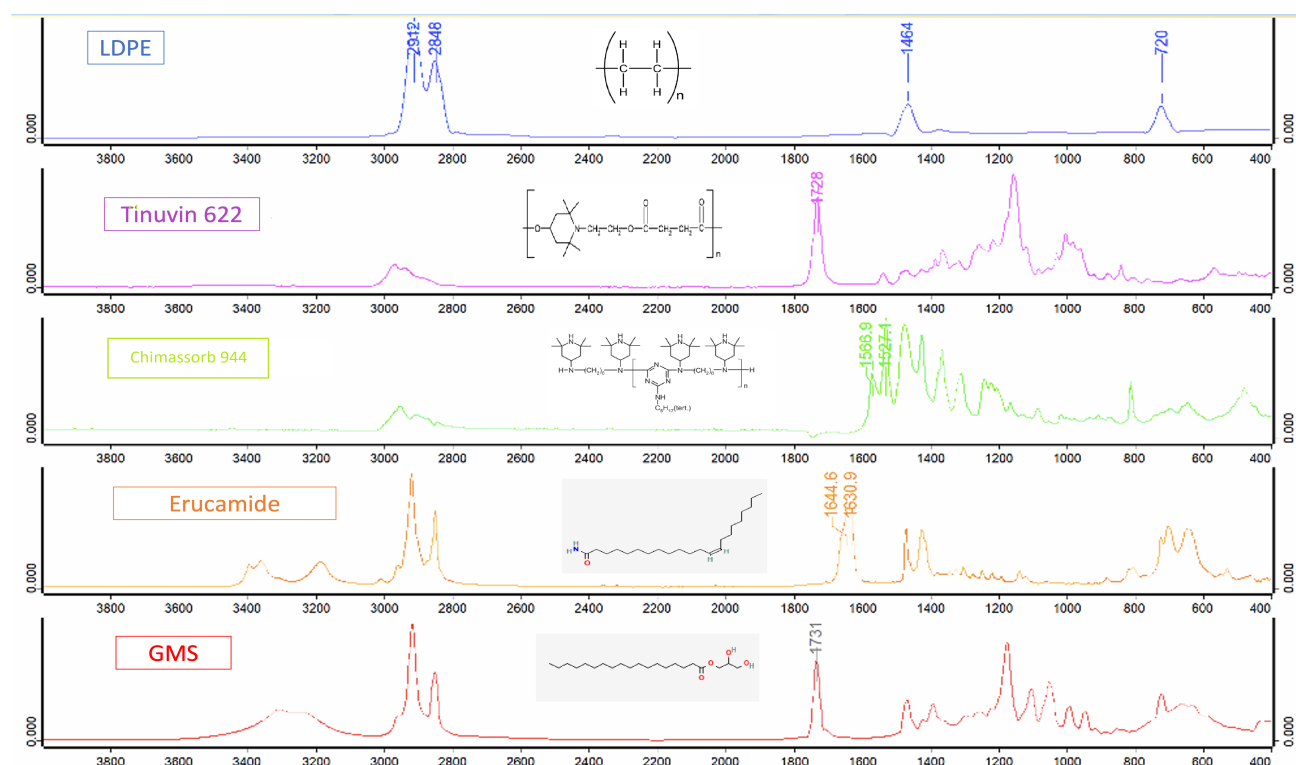


Figure 5.4: FT-IR spectra for LDPE, Erucamide, GMS, HALS Tinuvin 644 and HALS Chimassorb 944 in ATR mode

5.2.2 Additive Quantification

Slip additive - Erucamide

Figure 5.5 shows the normalised average spectra for the samples with different quantities of Erucamide additive, evidencing that the higher the concentration of Erucamide in the film, the higher the absorbance value for the peaks both at 1659cm^{-1} and 1630cm^{-1} .

The data obtained for the samples described in Chapter 4 are presented in Appendix B. As mentioned in Chapter 4, from each film with different concentration of additive 10 samples were analysed and the 3 with most similar thickness values were selected.

In order to get a predictive model, linear fitting was performed. The correlation obtained is shown in figure 5.6 (R^2 of 0,9772). Equation 5.1 can be used to determine the percentage of Erucamide from the spectra of LDPE films containing this additive.

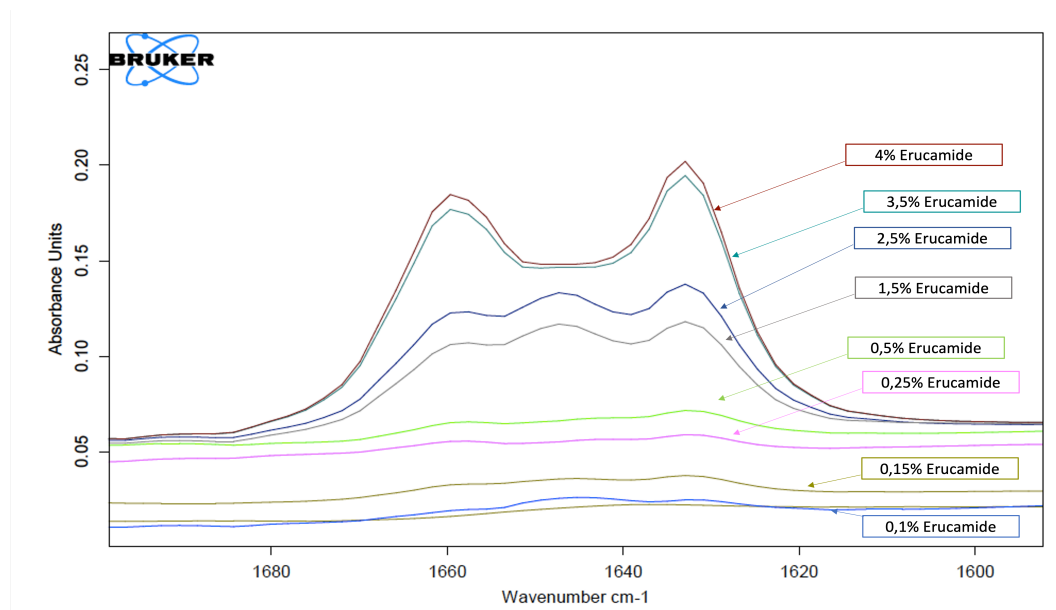


Figure 5.5: FTIR spectra for Erucamide in LDPE using transmission mode FTIR

$$y = 0,0228x + 0.0009; (R^2 = 0,9772) \quad (5.1)$$

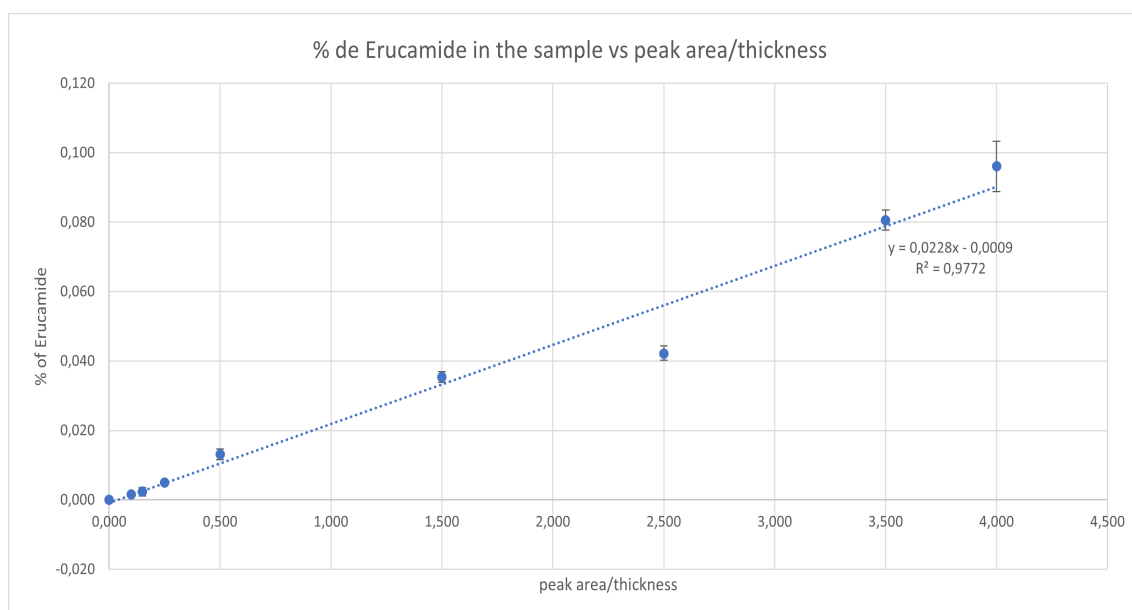


Figure 5.6: Calibration curve for Erucamide in LDPE

The data above was used to create a Quality Control (QC) method for MB Slip, a 5% erucamide concentrate on LDPE carrier manufactured by Poliversal.

Equation 5.1 was used for the determination of the Erucamide content in QC film samples (0,25% erucamide + LDPE) stored from different batches of MB Slip produced in 2021. QC samples are prepared from samples taken from production lines every 2 hours, by diluting 5% of MB Slip with tubular film extrusion grade LLDPE (PE003). A sample was analysed from batch 099581, a 1250 kg production batch, a sample from batch 101170, a 1250 kg production batch, and two samples from batch 103702, a 1965 kg production batch. The results are presented in table 5.3.

Equation 5.1 was used to determine the approximate quantity of erucamide present in the QC film (0,25% Erucamide + LDPE).

Table 5.3 contains the average values for the film thickness, peak area, peak area over thickness of the QC films and estimated concentration of Erucamide using equation 5.1.

Table 5.3: Results from quality control samples of MB Slip

| Sample Identification (batch nr, production date, hour of QC) | Film Thickness (μm) | Peak Area | Peak Area/Thickness | wt% of Erucamide |
|--|-------------------------------|-----------|---------------------|---------------------|
| Batch 099581 (10/03/2021, 11h) | 73,24 | 0,549 | 0,008 | 0,37 |
| Batch 101170 (15/06/2021, 11h41) | 74,11 | 0,421 | 0,006 | 0,29 |
| Batch 103702 (22/10/2021, 08h50) | 69,69 | 0,592 | 0,008 | 0,26 |
| Batch 103702 (25/10/2021, 10h40) | 70,78 | 0,422 | 0,006 | 0,30 |

The results in table 5.3 show values close to the expected erucamide content in the films, 0,25%.

Antistatic Additive - GMS

Figure 5.7 shows the normalised average spectra for the samples with different quantities of GMS additive, evidencing that the higher the concentration of GMS in the film, the higher the absorbance value for the absorption band at 1737cm^{-1} .

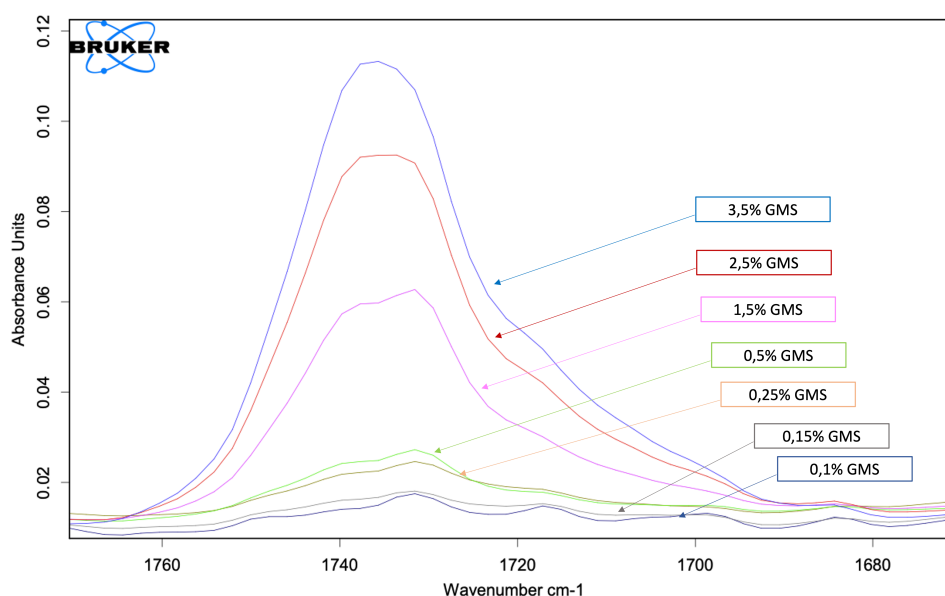


Figure 5.7: FTIR spectra for GMS in LDPE using transmission mode FTIR

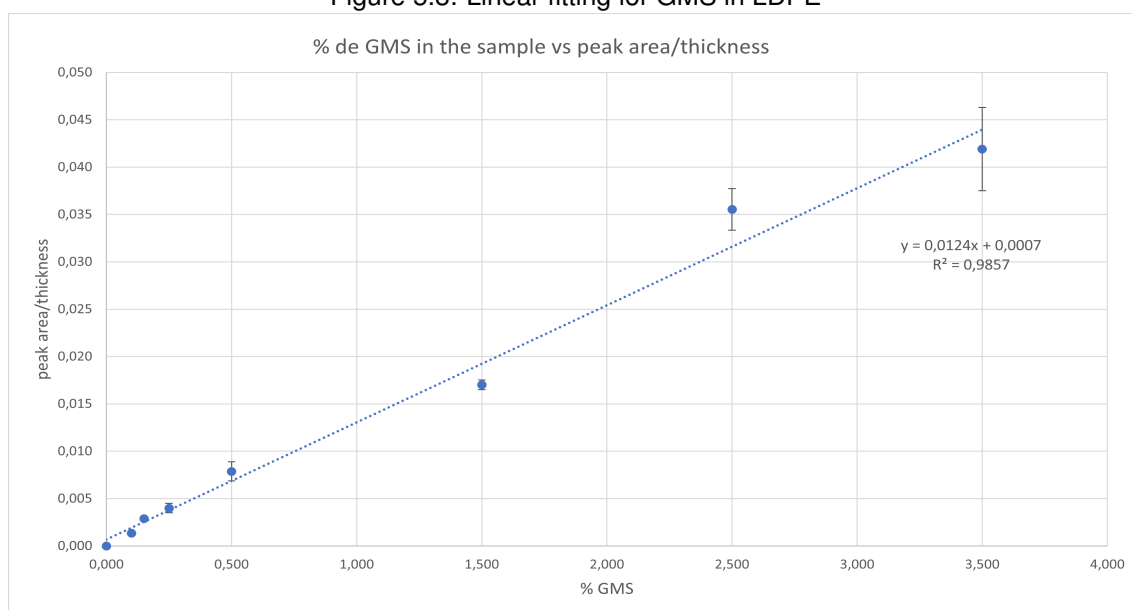
The data obtained for the samples described in Chapter 4 is presented in Appendix C.

In order to get a predictive model, linear fitting was performed. The correlation obtained is shown in figure 5.8 (R^2 of 0,9857). Equation 5.2 can be used to determine the percentage of GMS from the spectra of LDPE films containing this additive.

$$y = 0,124x + 0,0007; (R^2 = 0,9857) \quad (5.2)$$

The data above was used to create a Quality Control (QC) method for MB Antistatic, a 5% GMS concentrate on LDPE carrier manufactured by Poliversal.

Figure 5.8: Linear fitting for GMS in LDPE



Equation 5.2 was used for the determination of the GMS content in QC film samples (0,25% GMS + LDPE), obtained by diluting 5% of MB Antistatic with tubular film extrusion grade LLDPE (PE003), stored from different batches of MB Antistatic produced in 2021. Batch 099193, a 1033kg production batch; batch 100479, a 1672kg production batch; batch 103364, a 1018kg production batch and batch 103965, a 1672kg production batch. The results are presented in table 5.4.

Equation 5.2 was used to determine the approximate quantity of GMS present in the QC film (0,25% GMS + LDPE).

Table 5.4: Results from quality control samples of MB Antistatic

| Sample Identification (batch nr, production date, hour of QC) | Film Thickness (μm) | Peak Area | Peak Area/Thickness | wt% of GMS |
|--|-------------------------------|-----------|---------------------|------------|
| Batch 099193 (19/02/2021, 09h54) | 69,50 | 0,300 | 0,0043 | 0,29 |
| Batch 100479 (03/05/2021, 11h52) | 72,58 | 0,304 | 0,0038 | 0,25 |
| Batch 103364 (30/09/2021, 08h50) | 76,90 | 0,319 | 0,0042 | 0,28 |
| Batch 103965 (02/11/2021, 09h31) | 68,51 | 0,278 | 0,0041 | 0,27 |

The results in table 5.4 show values very close to the expected GMS content in the films, 0,25%.

Anti-UV Additive - HALS Tinuvin 622 and HALS Chimassorb 944

Figure 5.9 shows the normalised average spectra for films obtained from MB UV, MB Tinuvin and MB Chimassorb, evidencing that the higher the concentration of HALS Tinuvin 622 and HALS Chimassorb 944 in the film, the higher the absorbance value for the absorption band at 1728cm^{-1} and from 1527 to 1567cm^{-1} respectively.

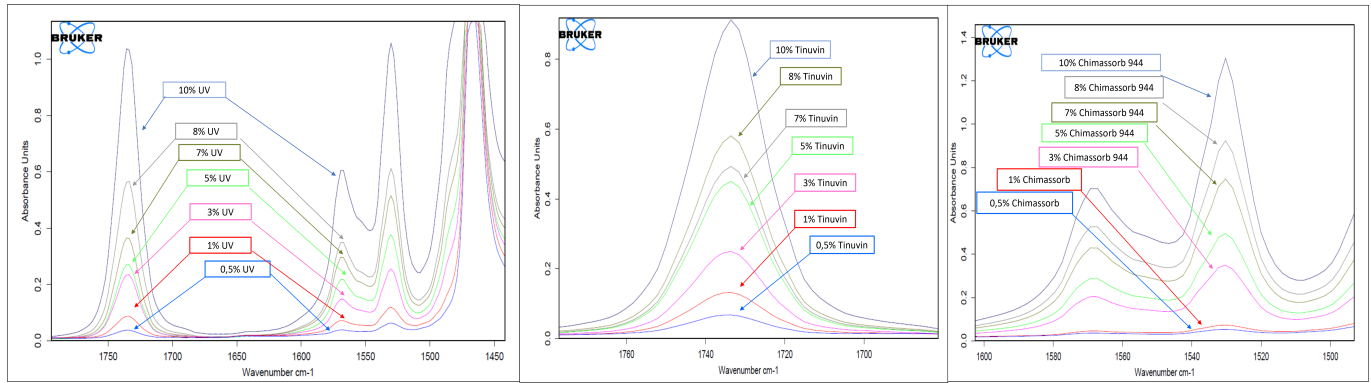


Figure 5.9: FTIR spectra for MB UV (left), HALS Tinuvin 622 (centre) and HALS Chimassorb 944 in LDPE using transmission mode FTIR

The data obtained for the samples described in Chapter 4 is presented in Appendix D (for films made from MB UV), E (for films made from MB Tinuvin) and F (for films made from MB Chimassorb).

In order to get a predictive model, linear fitting was performed, shown in figure 5.10.

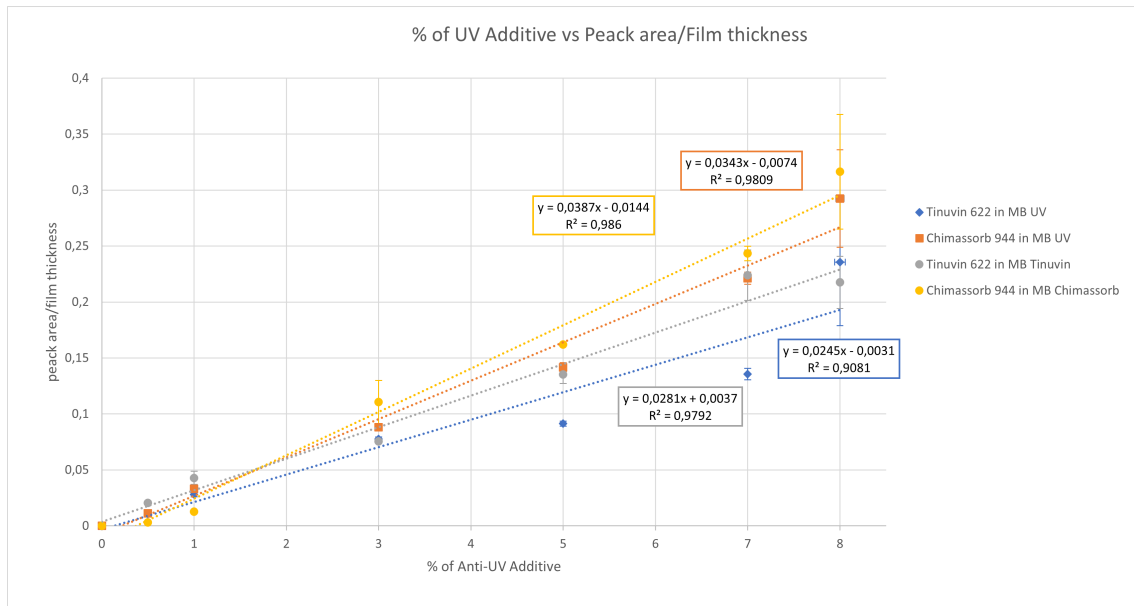


Figure 5.10: Linear fitting for UV additives

Following are the equations for each fitting curve later used for the determination of the concentration of UV additive.

- Equation 5.3 - linear fitting from the data obtained for HALS Tinuvin 622 out the MB UV.

$$y = 0,0245x - 0,0031; R^2 = 0,9081 \quad (5.3)$$

- Equation 5.4 - linear fitting from the data obtained for HALS Chimassorb 944 out of MB UV.

$$y = 0,0343x - 0,0074; R^2 = 0,9809 \quad (5.4)$$

- Equation 5.5 - linear fitting from the data obtained for HALS Tinuvin 622 from MB Tinuvin.

$$y = 0,0281x + 0,0037; R^2 = 0,9792 \quad (5.5)$$

- Equation 5.6 - linear fitting from the data obtained for HALS Chimassorb 944 from MB Chimassorb.

$$y = 0,0387x + 0,0144; R = 0,9860 \quad (5.6)$$

For both anti-UV additives, HALS Tinuvin 622 and HALS Chimassorb 944, the best correlation is obtained using film the samples prepared with a single substance, equations 5.5 for HALS Tinuvin 622 and 5.6. for HALS Chimassorb 944.

When samples containing both additives (films made from MB UV) are used to obtain the calibration curves, the quality of the fitting is different for the two additives. While for HALS Tinuvin 622 a worse fitting was obtained (0.9792 vs 0.9081), for HALS Chimassorb 944 the difference in the quality of the fitting is not relevant (0.9860 vs 0.9809). These results are probably related to the fact that less interactions are present when only one additive is present in the film sample.

The data above was used to create a Quality Control (QC) method for MB UV, a 10% HALS Tinuvin 622 + 10% HALS Chimassorb 944 concentrate on LDPE carrier not manufactured by Poliversal.

Equations 5.5 and 5.6 were used to determine the amount of both additives in film QC samples (5% HALS Tinuvin 622 and 5% HALS Chimassorb 944), obtained by diluting 50% of the MB UV with tubular film extrusion grade LLDPE (PE003).

Equations 5.5 and 5.6 were used for the determination of the HALS Tinuvin 622 and HALS Chimassorb 944 contents in QC samples stored from different batches of MB UV purchased in 2022. Batch 105129, batch 106003, and batch 107122. The results are presented in table 5.5.

Table 5.5: Results from quality control samples of MB UV

| Sample Identification (batch nr) | % of HALS Tinuvin 622 from equation 5.5 | % of HALS Chimassorb 944 from equation 5.6 |
|-------------------------------------|--|---|
| Batch 105129 | 7,0 | 5,1 |
| Batch 106003 | 7,4 | 5,7 |
| Batch 107122 | 7,4 | 5,3 |

It is safe to say that the MB consistently contains higher amount of the additives than expected, about 15% of HALS Tinuvin 622 and 11% of HALS Chimassorb 944.

The development of these novel quantification method give Poliversal the possibility to better perform QC on the MB with colourless additives.

5.3 Identification of the Detection Limit of Carbon Black and its Alternatives using NIR Spectroscopy

Figure 5.11 is the spectra for MB 81373 Black, T-17302/1/8, MB 81774 Black, T-16260/1/8, MB 7942 Brown and T-16270/2/7. For these samples it was not possible to identify the polymer of the injection moulding plaque because there is no characteristic bands found between 5950 and 5700cm⁻¹ [54].

Figure 5.12 is the spectra for MB 7810 Brown, T-13301/5/7, MB 62617 Blue, T-16266/4/6, MB 82521 Grey, T-16268/7/8, MB 7811 Brown, T-13302/4/7, MB 51939 Green, and T-16713/4/5. It is possible to see the characteristic bands for LDPE between 5950 and 5700cm⁻¹ [54].

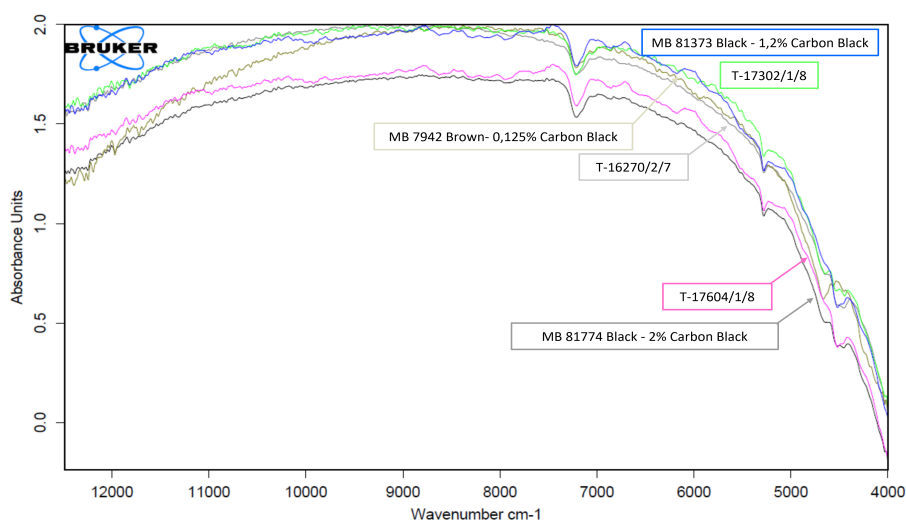


Figure 5.11: FT-NIR spectra for MB 81373 Black, T-17302/1/8, MB 81774 Black, T-17604/1/8, MB 7942 Brown and T-16270/2/7

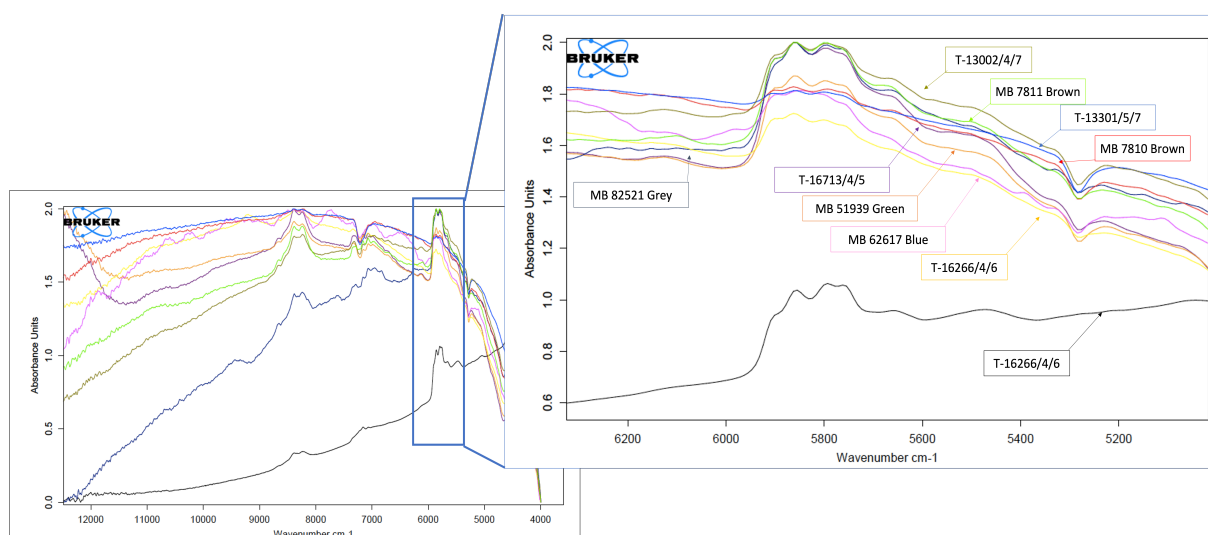


Figure 5.12: FT-NIR spectra for MB 7810 Brown, T-13301/5/7, MB 62617 Blue, T-16266/4/6, MB 82521 Grey, T-16268/7/8, MB 7811 Brown, T-13302/4/7, MB 51939 Green, and T-16713/4/5

In table 5.6, a summary of the obtained results is presented.

Table 5.6: Results for FT-NIR spectra analysis

| Sample | % of Carbon Black in end product | % of Black 11/Brown 29 in end product | Polymer Identification |
|----------------|-------------------------------------|--|------------------------|
| MB 81774 Black | 2 | - | Unsuccessful |
| T-17604/1/8 | - | 1 | Unsuccessful |
| MB 81373 Black | 1,2 | - | Unsuccessful |
| T-17302/1/8 | - | 1 | Unsuccessful |
| MB 7942 Brown | 0,125 | - | Unsuccessful |
| T-16270/2/7 | - | 0,95 | Unsuccessful |
| MB 7810 Brown | 0,041 | - | Successful |

| | | | |
|----------------|---------|-------|------------|
| T-13301/5/7 | - | 0,17 | Successful |
| MB 62617 Blue | 0,025 | - | Successful |
| T-16266/4/6 | - | 0,075 | Successful |
| MB 82521 Grey | 0,021 | - | Successful |
| T-16268/7/8 | - | 0,1 | Successful |
| MB 7811 Brown | 0,0076 | - | Successful |
| T-13302/4/7 | - | 0,04 | Successful |
| MB 51939 Green | 0,00165 | - | Successful |
| T-16713/4/5 | - | 0,005 | Successful |

From the results in the table above, it is clear that the maximum content of carbon black pigment present in a plastic part (final plastic product) that will allow polymer identification by NIR, is between 0,04 wt% and 0,1 wt%.

The samples made with an alternative pigment, Black 11, also showed that there is a limit of concentration of this pigment that can be used for polymer detection in a NIR sorting system, which was expected since this pigment is NIR absorbing. This pigment also absorbs in the NIR region but with lower intensity. With this pigment, plastic products may be coloured with concentrations higher than 0.1 wt% and still be detected by NIR. The maximum amount of pigment for a part to be detectable is in this case between 0,17 wt% and 0,95 wt%.

The tests performed with Pigment Brown 29 as an alternative to carbon black were not conclusive, as just one trial was made, and the amount of alternative pigment used revealed to be too high to allow polymer identification. This result was not expected because Pigment Brown 29 is an Inorganic NIR-reflecting pigment in which signal from the polymer should be clearly detected since reflection of IR is the dominant mechanism and NIR detection machines should be able to detect the signal. Further investigation is needed.

These results will contribute to define alternative formulations for plastic products containing carbon black, which will allow Poliversal to offer MB to customers looking for efficiently recyclable plastics. These will be detectable by NIR equipment used for plastic sorting in recycling plants.

This study was done to evaluate further use of IR spectroscopy on the plastic industry, other than the use of FTIR for plastic identification and additives determination, previously addressed.

Products available from the company range were used, aiming to evaluate the effect of the amount of carbon black on the effectiveness of NIR sorting of the coloured plastic parts.

The results obtained showed that also some of the alternative pigments used will have a maximum content that will allow detection. Further work will be needed, involving the preparation of more samples, to determine a more precise value for the maximum concentration of the pigments. This will allow Poliversal to develop alternative formulations for the colouration of plastic products detectable by NIR sorting in recycling plants.

Chapter 6

Conclusions and Future Work

6.1 Achievements

This work is aimed to develop a method to determine the quantity of uncoloured additive present in films and also the limit of detection of carbon black in the sorting step in a plastic waste management facility, i.e. the maximum amount of carbon black that can be present in a plastic compound, which still allows the base polymer identification by current NIR spectroscopy techniques used in recycling facilities.

A twin screw extruder was used to manufacture the MB with uncoloured additive, such as erucamide, GMS, HALS Tinuvin 622 and HALS Chimassorb 944, and the carrier polymer LDPE. Also, a blown film extruder was employed to produce the MB derived films displaying different quantities of additives mentioned in Chapter 4. These latter ones were obtained by diluting the previously obtained MB with virgin LDPE. Finally, for carbon black detection, plaques obtained by injection moulding were used.

FTIR spectroscopy was used to successfully identify polymers (and differentiate between grades of the same polymer namely PE) and additives. The quantification method for additives was created by producing a calibration curve of the area of the additive's characteristic peak over the film thickness versus the weight percentage of additive in the film and performing linear fitting of such data. After obtaining the quantification method, archived QC samples were tested, and the method was validated. Overall, for the four additives tested, it was possible to develop a successful quantification method for additives concentration in the range of 0,1 wt% to 10 wt%.

FT-NIR spectroscopy was used to estimate the detection limit of the pigment during the sorting process in a plastic waste management facility. It was possible to estimate that the carbon black maximum concentration where polymer identification by NIR is still possible is between 0,04 wt% and 0,1 wt% in the plastic part, and that for an alternative pigments to carbon black, namely Black 11 is between 0,17 wt% wt% and 0,95 wt% concentration in the final plastic part. NIR-reflecting Pigment Brown 29 showed to also have a detection limit, but this was not determined due to the lack of samples available.

6.2 Future Work

To obtain better results in the quantification of additives, a heated press to obtain a thin film with regular thickness could be used.

In the present work, in order to assure the amount of additive in the developed MB, these were developed in the pilot production line and then used to create the calibration curved. For a more accurate quantification of additive in the manufactured MB, using solvent extraction to separate the polymer and the additive could be done, in a laboratory that specialises in this type of analysis.

The determination of the detection limit of carbon black could be improved by analysing samples with concentrations of carbon black between 0,04 and 0,1%. Improving results is even more important to determine the limit of detection for alternative pigments to carbon black such as Black 11.

Bibliography

- [1] G. Faraca and T. Astrup, "Plastic waste from recycling centres: Characterisation and evaluation of plastic recyclability," *Waste Management*, vol. 95, pp. 388–398, 2019.
- [2] G. G. Pritchard, "Plastics additives : an A-Z reference," in *Plastics Additives: an A-Z reference* (G. Pritchard, ed.), pp. 485–498, Amsterdam: IOS Press, 1998.
- [3] D. Becker, *Color Trends and Selection for Product Design*, vol. 1. Oxford: William Andrew, 1 ed., 2016.
- [4] Markets and Markets, "Masterbatch Market."
- [5] "New moves in black and white.," *Compounding World*, no. November, 2021.
- [6] R. J. Young and P. A. Lovell, *Introduction to Polymers*, vol. 3. Florida: CRP Press, 3 ed., 2011.
- [7] O. T. Baur E. and R. N., *Plastics Handbook - The Resource for Plastics Engineers*. Hanser Publishers, 1 ed., 2018.
- [8] John Murphy, "Additives for Plastics Handbook," tech. rep., Oxford, 2001.
- [9] T. A. Osswald and G. Menges, *Material Science of Polymers for Engineers*. Hanser Publishers, 3 ed., 2012.
- [10] P. Barnes, "Determining Migration of GMS Antistat in Polypropylene," *Journal of Vinyl and Additive Technology*, vol. 3, no. 1, pp. 70–76, 1997.
- [11] Croda - Polymer Additives, "Atmer anti-static," 2013.
- [12] C. Maier and T. Calafut, *Polypropylene - The Definitive User's Guide and Databook*. Norwich, NY: William Andrew, 1998.
- [13] R. M. R. H. S. Davand, R., "Theoretical and experimental assessment of UV resistance of high-density polyethylene: Screening and optimisation of hindered amine light stabilizers, year = 2021," *Journal of Applied Polymer Science*, pp. 1–13.
- [14] R. E. Day, "The Role of Titanium Dioxide Pigments in the Degradation and Stabilisation of Polymers in the Plastics Industry," tech. rep., 1990.
- [15] R. A. H. e. . . i. . . m.-g. . T. p. . J. t. . C. y. . . Holtzen, D.A.
- [16] R. Dvorak, E. Kosier, and L. Moody, "Development of NIR Detectable Black Plastic Packaging," Tech. Rep. March, WRAP - Material chang for a better environment, 2011.
- [17] J. Chen, J. Li, T. Hu, B. Walther, and B. Walther, "Fundamental study of erucamide used as a slip agent Fundamental study of erucamide used as a slip agent," *JVSTA - Journal of Vacuum Science Technology A*, vol. 25, no. 2007, pp. 886–892, 2013.

- [18] P. C. Painter and M. M. Coleman, *Essentials of Polymer Science and Engineering*. Lancaster, Pennsylvania: DEStech Publications, Inc., 1 ed., 2009.
- [19] Leistritz Extrusionstechnik GmbH, "Masterbatch Production - Extruders and Extrusion Lines," 2021.
- [20] J. C. G. B. Ramos, *Composição de concentrados de aditivos anti-UV em base polimérica. Avaliação do efeito de variáveis do processo nas propriedades dos compostos*. PhD thesis, Universidade de Lisboa - Faculdade de Ciências, Departamento de Química e Bioquímica, 2019.
- [21] J. Vlachopoulos and N. D. Polychronopoulos, *Understanding Rheology and Technology of Polymer Extrusion*. Dundas, ON, Canada: Polydynamics inc, 1 ed., 2019.
- [22] S. Ebnesajjad, *Applied Plastics Engineering Handbook*. Oxford: William Andrew, 2 ed., 2017.
- [23] P. Inc, "The Advantages of Mid-IR Spectroscopy for Polymer Recycling," 2015.
- [24] "Mechanical and chemical recycling of solid plastic waste," *Waste Management*, vol. 69, pp. 24–58, 2017.
- [25] The Association of Plastic Recyclers, "Near Infrared (NIR) Sorting in the Plastics Recycling Process," *The Association of Plastics Recyclers*, no. Res-SORT-2, 2018.
- [26] P. Inc, "The Advantages of Mid-IR Spectroscopy for Polymer Recycling," *Perkin Elmer - Application Note*, 2015.
- [27] Y. Leng, *MATERIALS CHARACTERIZATION Introduction to Microscopic and Spectroscopic Methods*. John Wiley Sons, 1 ed., 2008.
- [28] C. Wang, J. Kim, C. T. Jin, P. H. Leong, and A. McEwan, "Review: Near infrared spectroscopy in optical coherence tomography," *Journal of Near Infrared Spectroscopy*, vol. 20, no. 1, pp. 237–247, 2012.
- [29]
- [30] J. Jalvandi, *Novel chemical and physical approaches for sustainable drug release from biodegradable electrospun nanofibres Novel Chemical and Physical Approaches for Sustainable*. PhD thesis, RMIT University, 2016.
- [31] V. Spatari, "Fourier-Transform Spectroscopy Instrumentation Engineering," tech. rep., 2003.
- [32] L. Barbes, C. Radulescu, and C. Stihl, "Atr - ftir spectrometry characterisation of polymeric materials," *Romanian Reports in Physics*, vol. 66, 06 2014.
- [33] D. A. Burns and E. W. Ciurczak, *Handbook of Near-Infrared Analysis*. f: Tayloe Francis Group, LLC, 3 ed., 2007.
- [34] M. Blanco and I. Villarroya, "NIR spectroscopy: A rapid-response analytical tool," *TrAC - Trends in Analytical Chemistry*, vol. 21, no. 4, pp. 240–250, 2002.
- [35] Bruker, "Why FT-NIR Spectroscopy."
- [36] B. M. Nicolaï, K. Beullens, E. Bobelyn, A. Peirs, W. Saeys, K. I. Theron, and J. Lammertyn, "Non-destructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review," *Postharvest Biology and Technology*, vol. 46, no. 2, pp. 99–118, 2007.

- [37] H. Lobo and J. W. Bonilla, *Handbook of Plastics Analysis*. Boca Raton: Marcel Dekker, Inc., 1 ed., 2003.
- [38] R. P. D. Amelia, S. Gentile, W. F. Nirode, and L. Huang, "Quantitative Analysis of Copolymers and Blends of Polyvinyl Acetate (PVAc) Using Fourier Transform Infrared Spectroscopy (FTIR) and Elemental Analysis (EA)," *World Journal of Chemical Education*, vol. 4, no. May, pp. 25–31, 2016.
- [39] M. R. Jung, F. D. Horgen, S. V. Orski, V. Rodriguez C., K. L. Beers, G. H. Balazs, T. T. Jones, T. M. Work, K. C. Brignac, S. J. Royer, K. D. Hyrenbach, B. A. Jensen, and J. M. Lynch, "Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms," *Marine Pollution Bulletin*, vol. 127, pp. 704–716, 2018.
- [40] M. Cherif Lahimer, N. Ayed, J. Horriche, and S. Belgaied, "Characterization of plastic packaging additives: Food contact, stability and toxicity," *Arabian Journal of Chemistry*, vol. 10, pp. S1938–S1954, 2013.
- [41] N. B. Joshi and D. E. Hirt, "Evaluating bulk-to-surface partitioning of erucamide in LLDPE films using FT-IR microspectroscopy," *Applied Spectroscopy*, vol. 53, no. 1, pp. 11–16, 1999.
- [42] S. Y. Sankhe, A. V. Janorkar, and D. E. Hirt, "Characterization of Erucamide Profiles in LLDPE Films: Depth-profiling Attempts using FTIR Photoacoustic Spectroscopy and Raman Microspectroscopy," *Journal of Plastic Film and Sheeting*, vol. 19, no. 1, pp. 16–29, 2003.
- [43] S. M. Eid, S. S. Soliman, M. R. Elghobashy, and O. M. Abdalla, "Atr-ftir coupled with chemometrics for quantification of vildagliptin and metformin in pharmaceutical combinations having diverged concentration ranges," *Vibrational Spectroscopy*, vol. 106, p. 102995, 2020.
- [44] K. M. Kelani, M. R. Rezk, H. H. Monir, M. S. Elsherbiny, and S. M. Eid, "FTIR combined with chemometric tools (fingerprinting spectroscopy) in comparison to HPLC: Which strategy offers more opportunities as a green analytical chemistry technique for pharmaceutical analysis," *Analytical Methods*, vol. 12, no. 48, pp. 5893–5907, 2020.
- [45] S. Weigel, M. Gehrke, C. Recknagel, and D. A. Stephan, "Identification and quantification of additives in bituminous binders based on FTIR spectroscopy and multivariate analysis methods," *Materials and Structures*, vol. 1, pp. 1–9, 2021.
- [46] J.-L. Xu, K. V. Thomas, Z. Luo, and A. A. Gowen, "Ftir and raman imaging for microplastics analysis: State of the art, challenges and prospects," *TrAC Trends in Analytical Chemistry*, vol. 119, p. 115629, 2019.
- [47] X. Song, "Comparison of ATR/transmittance FTIR combined with Beer's law and PLS to determine fipronil in matrine formulation," *Analytical Methods*, vol. 5, no. January, pp. 4790–4797, 2013.
- [48] A. Gardouh, "Design and Characterization of Glyceryl Monostearate Solid Lipid Nanoparticles Prepared by High Shear Homogenization," *British Journal of Pharmaceutical Research*, vol. 3, no. 3, pp. 326–346, 2013.
- [49] E. S. Aquino, Katia Aparecida S.; Araujo, "Effects of a Jomdered Amine Stabilizer (HAS) on Radiolytic and Thermal Stability of Poly(methyl methacrylate)," *Journal of Applied Polymer Science*, vol. 116, pp. 401–407, 2008.
- [50] M. Scoponi, S. Cimmino, and M. Kaci, "Photo-stabilisation mechanism under natural weathering and accelerated photo-oxidative conditions of LDPE films for agricultural applications," *Polymer*, vol. 41, no. 22, pp. 7969–7980, 2000.

- [51] D. L. from Ferro, ““Leveraging pigments’ NIR reflecting properties to overcome the challenge of sorting recyclable black plastics”,” 2022.
- [52] BRUKER OPTIK GmbH, *OPUS Reference Manual*. No. 8, 2019.
- [53] J. V. Gulmine, P. R. Janissek, H. M. Heise, and L. Akcelrud, “Polyethylene characterization by FTIR,” tech. rep., 2002.
- [54] H. Masoumi, S. Safavi, and Z. Khani, “Identification and Classification of Plastic Resins using Near Infrared Reflectance,” *Waset.Ac.Nz*, vol. 6, no. 5, pp. 213–220, 2012.

Appendix A

Spectra Evaluation Tools

A.1 Spectrum Search / Library Search [52]

An unknown spectrum is compared with spectra stored in a library. The spectra from the library that show distinct similarities to the unknown spectrum are detected and displayed in the search report.

In this search, it is possible to either use the whole spectra range to perform the search, or define particular spectral ranges for spectrum search.

To perform a spectrum search, the search parameters are decided by the user:

- In a *standard* spectrum search, all pieces of band information are reflected in the hit quality. The information contains the position, relative intensity and half-width of each band. A library spectrum band is considered to be identified in the measured spectrum if the spectrum contains a band which position does deviate from the position in the library spectrum by less than the half-widths or relative intensities is less than factor 2. The *standard* search algorithm provides further setting options:

One main component: adequate for a pure substance or when looking for only 1 main component.


Several components: if the samples analysed is a compound.

- The *Mixture analysis*: search is used to analyze spectra which have been acquired from mixtures. Mixture sample spectra contain bands of different substances and may not be interpreted by a one single library spectrum.

A.2 Normalizing Spectra [52]

Normalizing spectra allows to bring their peaks to comparable level.

A.2.1 Setting up normalization method

1. In the *Manipulate* menu, select the *Normalization*  icon.
2. In the *Normalization* window, it is possible to select the normalization method that is considered more appropriate.

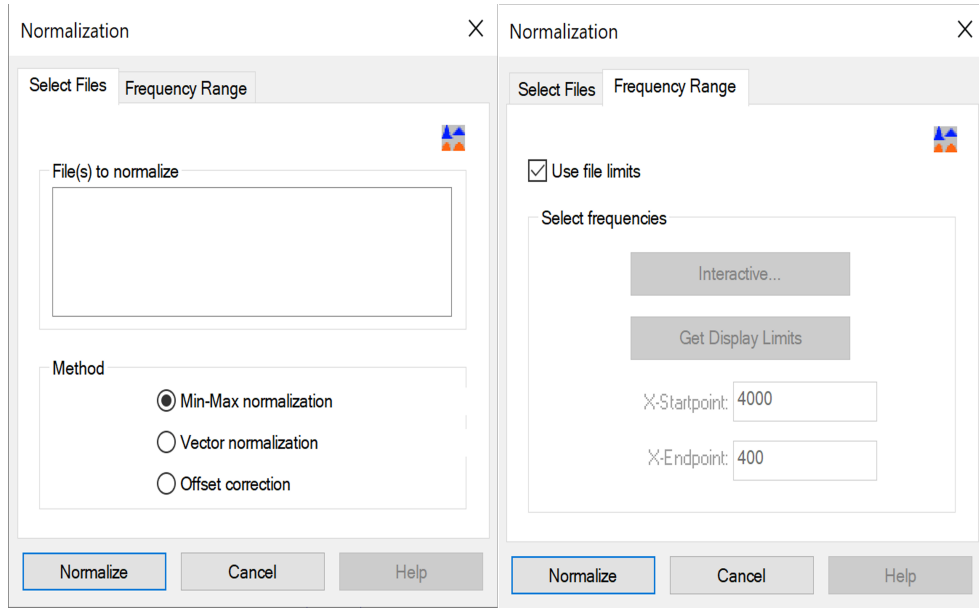


Figure A.1: Normalisation options window

- (a) **Min-Max normalization**: used with spectra which optical layer thickness substantially varies, to be able to compare these spectra with each other. The spectra are shifted linearly such that the minimum y-value equals to zero. Then, the spectra are expanded in y-direction such that the maximum y-value equals 2 absorbance units.
- (b) **Vector normalization**: calculates the average y-value of the spectrum. The calculation only considers the data points in the frequency ranges selected. The average value is subtracted from the spectrum. The subtraction decreases the mid-spectrum to $y=0$. Then, the sum of the squares of all y-values is calculated and the spectrum is divided by the square root of this sum. The vector norm of the result spectrum is 1:

$$\sum_{i=1}^{NPT} (x_i)^2 = 1 \quad (\text{A.1})$$

with x_i being the intensity of the data point i .

- 3. **Offset correction**: shifts the spectrum intensities to the effect that the minimum absorbance until will be 0.

The frequency range of the normalization function can be altered in the *Frequency Range* tab of the *Normalization* window. For the present work, the option *Use file limits* was always selected.

A.3 Layer Thickness [52]

Layer thickness determination is based on interferences which were caused by multiple reflection. It is possible to determine the layer thickness from the sub-m range to mm-range.

It is possible to determine the layer thickness for both homogeneous samples as well as coated samples, if the reflection or transmission spectrum contains meaningful interferences.

The algorithm determines the thickness d from the mean distance (Δf) of the interference maxima within the selected frequency range, and from the refraction index n of the measured layer:

$$d = \frac{1}{2 * n * \Delta f} \quad (\text{A.2})$$


The distance of the interference maxima decreases all the more, the thicker the layer and the greater the refraction index is.

To perform the layer thickness quantification, a presence of meaningful thickness interference is important and even more is the refraction index that is defined by the user.

A.4 Integration [52]

Integration functions allows to integrate peaks as well as calculate peaks highs.

A.4.1 Setting up an integration method

1. On the *Evaluate* menu, select *Integration* function by clicking on the  icon.
2. In the new window, on the *Select Files* tab, select *Setup Method...*

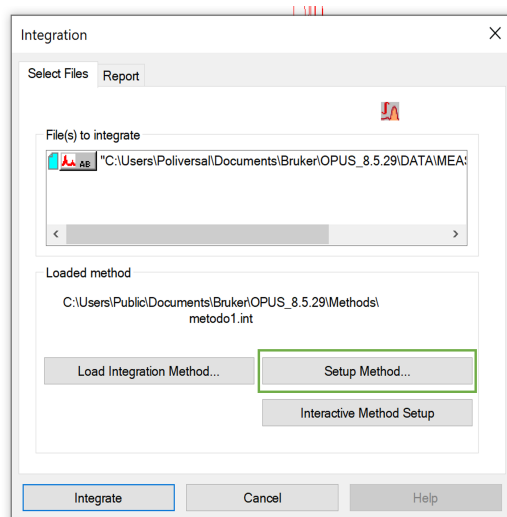


Figure A.2: Integration options window

3. In the new pop-up window, the integration method is set-up:
 - (a) In section 1 the integration mode is selected from a drop-down list. The two most used integration modes in the present work were mode B and K. In mode B a straight line is drawn between the peaks of the two frequency limits defines, the area above this line is integrated. In mode K, peak intensity relative to the local baseline is determined.
 - (b) In 2, the integration area is selected. Depending on the integration method selected, the left and right limits are chosen. This can be done by inserting the values of the limits directly or by using *Interactive* mode, that allows to set the limits interactively by opening a view of the spectra and move the frequency ranges to the desired wavenumber.
 - (c) In 3, the number of integration area is indicated, by clicking the arrow buttons to switch between the single areas.
 - (d) In 4, the chosen settings are deleted and , by default, the integration mode is reset to type A.

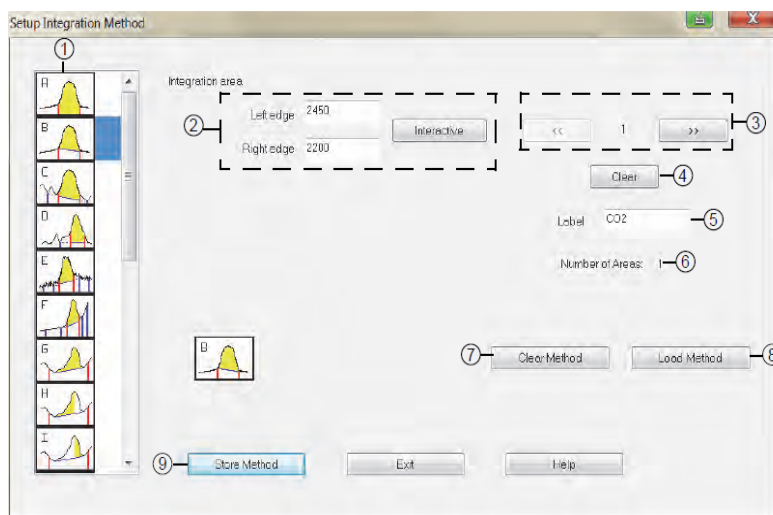


Figure A.3: Setup Integration Method window

- (e) In 5, an individual label has to be defined for each integration area.
- (f) In 6, the number of integration areas defined is indicated.
- (g) In 7, it resets all areas and the related settings.
- (h) In 8, an already existent integration method can be loaded.
- (i) In 9, the created method can be stored. Integration methods have the file extension *.int.

After the integration method configured and saved, we *Exit* from the *Setup Integration Method*.

4. Back in the *Integration* window, the integration is performed by clicking in the *Integrate* button.

Appendix B

Additive Quantification - Experimental Results from MB Slip

Table B.1: Experimental Results from MB Slip films

| | | thickness (μm) | area after normalisation | area/thickness |
|-------------------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,1% erucamide in LDPE film | sample 1 | 97,02 | 0,172 | 0,0018 |
| | sample 2 | 75,29 | 0,153 | 0,0020 |
| | sample 3 | 93,83 | 0,104 | 0,0011 |
| | sample 4 | 81,99 | 0,110 | 0,0013 |
| | sample 5 | 80,33 | 0,149 | 0,0019 |
| | sample 6 | 80,85 | 0,114 | 0,0014 |
| | sample 7 | 77,71 | 0,095 | 0,0012 |
| | sample 8 | 71,97 | 0,086 | 0,0012 |
| | sample 9 | 74,72 | 0,074 | 0,0010 |
| | sample 10 | 68,84 | 0,056 | 0,0008 |
| | average | 80,26 | 0,111 | 0,0014 |
| | std deviation | 8,54 | 0,035 | 0,0004 |
| 0,15% erucamide in LDPE film | sample 1 | 53,15 | 0,139 | 0,0026 |
| | sample 2 | 49,78 | 0,175 | 0,0035 |
| | sample 3 | 49,54 | 0,033 | 0,0007 |
| | sample 4 | 49,95 | 0,146 | 0,0029 |
| | sample 5 | 46,36 | 0,179 | 0,0039 |
| | sample 6 | 60,81 | 0,144 | 0,0024 |
| | sample 7 | 43,10 | 0,031 | 0,0007 |
| | sample 8 | 45,49 | 0,175 | 0,0038 |
| | sample 9 | 50,85 | 0,143 | 0,0028 |
| | sample 10 | 48,83 | 0,173 | 0,0035 |
| | average | 49,79 | 0,134 | 0,0027 |
| | std deviation | 4,58 | 0,053 | 0,0011 |
| | sample 1 | 58,60 | 0,275 | 0,0047 |
| | sample 2 | 67,63 | 0,194 | 0,0029 |

| | | | | |
|------------------------|----------------------|--------------|--------------|---------------|
| 0,25% erucamide | sample 3 | 50,48 | 0,223 | 0,0044 |
| | sample 4 | 53,96 | 0,302 | 0,0056 |
| in LDPE film | sample 5 | 39,94 | 0,171 | 0,0043 |
| | sample 6 | 54,00 | 0,141 | 0,0026 |
| | sample 7 | 44,37 | 0,171 | 0,0039 |
| | sample 8 | 50,02 | 0,246 | 0,0049 |
| | sample 9 | 83,74 | 0,323 | 0,0039 |
| | sample 10 | 56,76 | 0,236 | 0,0042 |
| | average | 55,95 | 0,228 | 0,0041 |
| | avg deviation | 12,38 | 0,060 | 0,0009 |
| 0,5% erucamide | sample 1 | 43,03 | 0,341 | 0,0079 |
| | sample 2 | 63,37 | 0,790 | 0,0125 |
| | sample 3 | 63,37 | 0,966 | 0,0152 |
| | sample 4 | 70,51 | 0,577 | 0,0082 |
| | sample 5 | 49,79 | 0,422 | 0,0085 |
| | sample 6 | 48,09 | 0,647 | 0,0135 |
| | sample 7 | 64,69 | 0,752 | 0,0116 |
| | sample 8 | 42,57 | 0,588 | 0,0138 |
| | sample 9 | 51,05 | 0,703 | 0,0138 |
| | sample 10 | 51,65 | 0,545 | 0,0106 |
| | average | 54,81 | 0,633 | 0,0116 |
| | std deviation | 9,35 | 0,172 | 0,0025 |
| 1,5% erucamide | sample 1 | 59,43 | 2,012 | 0,0339 |
| | sample 2 | 60,86 | 2,124 | 0,0349 |
| | sample 3 | 60,05 | 2,246 | 0,0374 |
| | sample 4 | 63,96 | 2,249 | 0,0352 |
| | sample 5 | 69,92 | 2,362 | 0,0338 |
| | sample 6 | 57,13 | 2,103 | 0,0368 |
| | sample 7 | 63,82 | 2,237 | 0,0351 |
| | sample 8 | 64,29 | 2,212 | 0,0344 |
| | sample 9 | 53,57 | 1,971 | 0,0368 |
| | sample 10 | 68,59 | 2,299 | 0,0335 |
| | average | 62,16 | 2,18 | 0,0352 |
| | std deviation | 4,74 | 0,12 | 0,0013 |
| 2,5% erucamide | sample 1 | 60,10 | 1,864 | 0,0310 |
| | sample 2 | 49,09 | 2,544 | 0,0518 |
| | sample 3 | 57,35 | 2,506 | 0,0437 |
| | sample 4 | 45,54 | 1,799 | 0,0395 |
| | sample 5 | 58,81 | 2,578 | 0,0438 |
| | sample 6 | 48,49 | 2,048 | 0,0422 |
| | sample 7 | 52,55 | 2,203 | 0,0419 |
| | sample 8 | 64,17 | 2,505 | 0,0390 |
| | sample 9 | 55,49 | 2,181 | 0,0393 |
| | sample 10 | 51,11 | 1,831 | 0,0358 |
| | average | 54,27 | 2,206 | 0,0408 |
| | std deviation | 5,59 | 0,297 | 0,0052 |

| | | | | |
|--|----------------------|--------------|--------------|---------------|
| 3,5% erucamide in LDPE film | sample 1 | 55,54 | 4,317 | 0,0777 |
| | sample 2 | 113,30 | 4,391 | 0,0388 |
| | sample 3 | 70,47 | 3,902 | 0,0554 |
| | sample 4 | 49,13 | 3,893 | 0,0792 |
| | sample 5 | 56,72 | 4,794 | 0,0845 |
| | sample 6 | 99,98 | 4,147 | 0,0415 |
| | sample 7 | 55,49 | 4,411 | 0,0795 |
| | sample 8 | 77,50 | 4,556 | 0,0588 |
| | sample 9 | 69,88 | 4,299 | 0,0615 |
| | sample 10 | 68,13 | 4,647 | 0,0682 |
| | average | 71,62 | 4,336 | 0,0645 |
| | std deviation | 19,59 | 0,280 | 0,0153 |
| 4% erucamide in LDPE film | sample 1 | 85,97 | 4,201 | 0,0489 |
| | sample 2 | 35,28 | 3,648 | 0,1034 |
| | sample 3 | 67,06 | 4,259 | 0,0635 |
| | sample 4 | 71,15 | 4,519 | 0,0635 |
| | sample 5 | 121,11 | 4,457 | 0,0368 |
| | sample 6 | 73,47 | 4,650 | 0,0633 |
| | sample 7 | 36,38 | 3,405 | 0,0936 |
| | sample 8 | 49,72 | 4,282 | 0,0861 |
| | sample 9 | 35,31 | 3,481 | 0,0986 |
| | sample 10 | 82,20 | 4,512 | 0,0549 |
| | average | 65,77 | 4,14, | 0,0713 |
| | std deviation | 26,10 | 0,436 | 0,0215 |

Appendix C

Additive Quantification - Experimental Results for MB Antistatic

Table C.1: Experimental Results from MB Antistatic films

| | | thickness (μm) | area after normalisation | area/thickness |
|------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,1% GMS in LDPE film | sample 1 | 66,35 | 0,102 | 0,0015 |
| | sample 2 | 52,32 | 0,066 | 0,0013 |
| | sample 3 | 64,59 | 0,083 | 0,0013 |
| | sample 4 | 66,65 | 0,080 | 0,0012 |
| | sample 5 | 58,37 | 0,132 | 0,0023 |
| | sample 6 | 50,93 | 0,215 | 0,0042 |
| | sample 7 | 41,11 | 0,201 | 0,0049 |
| | sample 8 | 65,00 | 0,146 | 0,0022 |
| | sample 9 | 52,26 | 0,086 | 0,0016 |
| | sample 10 | 59,88 | 0,253 | 0,0042 |
| | average | 57,74 | 0,136 | 0,0025 |
| | std deviation | 8,00 | 0,062 | 0,0013 |
| 0,15% GMS in LDPE film | sample 1 | 62,49 | 0,135 | 0,0022 |
| | sample 2 | 64,84 | 0,160 | 0,0025 |
| | sample 3 | 57,23 | 0,242 | 0,0042 |
| | sample 4 | 52,42 | 0,047 | 0,0009 |
| | sample 5 | 69,60 | 0,194 | 0,0028 |
| | sample 6 | 69,66 | 0,212 | 0,0030 |
| | sample 7 | 66,28 | 0,186 | 0,0028 |
| | sample 8 | 77,13 | 0,194 | 0,0025 |
| | sample 9 | 50,09 | 0,165 | 0,0033 |
| | sample 10 | 61,97 | 0,054 | 0,0009 |
| | average | 63,17 | 0,159 | 0,0025 |
| | std deviation | 7,84 | 0,061 | 0,0010 |
| | sample 1 | 72,00 | 0,214 | 0,0030 |
| | sample 2 | 72,43 | 0,323 | 0,0045 |

| | | | | |
|-------------------------------|----------------------|--------------|---------------|---------------|
| 0,25% GMS in LDPE film | sample 3 | 66,04 | 0,095 | 0,0014 |
| | sample 4 | 71,29 | 0,241 | 0,0034 |
| | sample 5 | 73,92 | 0,223 | 0,0030 |
| | sample 6 | 67,68 | 0,172 | 0,0025 |
| | sample 7 | 67,48 | 0,169 | 0,0025 |
| | sample 8 | 70,46 | 0,326 | 0,0046 |
| | sample 9 | 70,98 | 0,280 | 0,0039 |
| | sample 10 | 70,99 | 0,241 | 0,0034 |
| average | 70,33 | 0,228 | 0,0032 | |
| std deviation | 2,36 | 0,068 | 0,0009 | |
| 0,5% GMS in LDPE film | sample 1 | 102,10 | 0,248 | 0,0024 |
| | sample 2 | 41,37 | 0,203 | 0,0049 |
| | sample 3 | 47,74 | 0,374 | 0,0078 |
| | sample 4 | 40,42 | 0,120 | 0,0030 |
| | sample 5 | 47,56 | 0,433 | 0,0091 |
| | sample 6 | 48,61 | 0,323 | 0,0066 |
| | sample 7 | 44,09 | 0,250 | 0,0057 |
| | sample 8 | 49,33 | 0,248 | 0,0050 |
| | sample 9 | 48,61 | 0,228 | 0,0047 |
| | sample 10 | 55,15 | 0,415 | 0,0075 |
| | average | 52,50 | 0,284 | 0,0057 |
| | std deviation | 17,01 | 0,096 | 0,0020 |
| 1,5% GMS in LDPE film | sample 1 | 55,55 | 0,898 | 0,0162 |
| | sample 2 | 62,14 | 1,016 | 0,0163 |
| | sample 3 | 64,79 | 0,986 | 0,0152 |
| | sample 4 | 61,11 | 1,044 | 0,0171 |
| | sample 5 | 60,65 | 1,066 | 0,0176 |
| | sample 6 | 53,52 | 0,950 | 0,0178 |
| | sample 7 | 69,25 | 0,945 | 0,0136 |
| | sample 8 | 76,13 | 1,044 | 0,0137 |
| | sample 9 | 56,64 | 0,871 | 0,0154 |
| | sample 10 | 69,04 | 1,066 | 0,0154 |
| | average | 62,88 | 0,989 | 0,0158 |
| | std deviation | 6,68 | 0,067 | 0,0014 |
| 2,5% GMS in LDPE film | sample 1 | 55,56 | 1,854 | 0,0334 |
| | sample 2 | 73,87 | 2,399 | 0,0325 |
| | sample 3 | 47,72 | 1,893 | 0,0397 |
| | sample 4 | 71,14 | 2,312 | 0,0325 |
| | sample 5 | 44,11 | 1,503 | 0,0341 |
| | sample 6 | 71,03 | 2,598 | 0,0366 |
| | sample 7 | 37,31 | 1,505 | 0,0403 |
| | sample 8 | 72,63 | 2,725 | 0,0375 |
| | sample 9 | 60,57 | 1,598 | 0,0264 |
| | sample 10 | 68,23 | 2,397 | 0,0351 |
| | average | 60,22 | 2,078 | 0,0348 |
| | std deviation | 12,66 | 0,438 | 0,0039 |

| | | | | |
|------------------------------|----------------------|--------------|--------------|---------------|
| 3,5% GMS in LDPE film | sample 1 | 48,60 | 2,191 | 0,0451 |
| | sample 2 | 69,94 | 3,207 | 0,0459 |
| | sample 3 | 49,71 | 2,232 | 0,0449 |
| | sample 4 | 76,11 | 2,973 | 0,0391 |
| | sample 5 | 49,91 | 2,222 | 0,0445 |
| | sample 6 | 72,46 | 3,247 | 0,0448 |
| | sample 7 | 72,93 | 2,603 | 0,0357 |
| | sample 8 | 71,31 | 3,224 | 0,0452 |
| | sample 9 | 57,68 | 2,283 | 0,0396 |
| | sample 10 | 88,36 | 3,249 | 0,0368 |
| | average | 3,25 | 2,743 | 0,0421 |
| | std deviation | 12,77 | 0,456 | 0,0037 |

Appendix D

Additive Quantification - Experimental Results for MB UV

D.1 Tinuvin 622

Table D.1: Experimental Results from MB UV films - Tinuvin 622 additive

| | | thickness (μm) | area after normalisation | area/thickness |
|---------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,5% Tinuvin in LDPE film | sample 1 | 54,05 | 0,598 | 0,0111 |
| | sample 2 | 79,13 | 0,711 | 0,0090 |
| | sample 3 | 60,21 | 0,693 | 0,0115 |
| | sample 4 | 54,40 | 0,616 | 0,0113 |
| | sample 5 | 40,59 | 0,532 | 0,0131 |
| | sample 6 | 52,90 | 0,433 | 0,0082 |
| | sample 7 | 53,99 | 0,514 | 0,0095 |
| | sample 8 | 58,93 | 0,731 | 0,0124 |
| | sample 9 | 50,31 | 0,486 | 0,0097 |
| | sample 10 | 58,60 | 0,653 | 0,0111 |
| | average | 56,31 | 0,597 | 0,0107 |
| | std deviation | 9,26 | 0,097 | 0,0015 |
| 1% Tinuvin in LDPE film | sample 1 | 69,20 | 1,737 | 0,0251 |
| | sample 2 | 62,53 | 1,945 | 0,0311 |
| | sample 3 | 64,70 | 1,793 | 0,0277 |
| | sample 4 | 48,16 | 1,380 | 0,0287 |
| | sample 5 | 61,44 | 1,630 | 0,0265 |
| | sample 6 | 58,77 | 1,400 | 0,0238 |
| | sample 7 | 63,02 | 1,665 | 0,0264 |
| | sample 8 | 68,73 | 1,793 | 0,0261 |
| | sample 9 | 68,80 | 1,760 | 0,0256 |
| | sample 10 | 48,15 | 0,945 | 0,0196 |
| | average | 61,35 | 1,605 | 0,0261 |

| | | | | |
|--------------------------------|----------------------|--------------|---------------|---------------|
| | std deviation | 7,36 | 0,276 | 0,0029 |
| 3% Tinuvin in LDPE film | sample 1 | 67,46 | 5,466 | 0,0810 |
| | sample 2 | 63,30 | 4,526 | 0,0715 |
| | sample 3 | 69,65 | 5,331 | 0,0765 |
| | sample 4 | 55,45 | 4,176 | 0,0753 |
| | sample 5 | 50,28 | 5,607 | 0,1115 |
| | sample 6 | 48,88 | 3,506 | 0,0717 |
| | sample 7 | 68,93 | 5,346 | 0,0776 |
| | sample 8 | 47,27 | 3,628 | 0,0767 |
| | sample 9 | 55,98 | 4,461 | 0,0797 |
| | sample 10 | 56,72 | 4,417 | 0,0779 |
| | average | 58,39 | 4,646 | 0,0799 |
| | std deviation | 8,01 | 0,722 | 0,0109 |
| 5% Tinuvin in LDPE film | sample 1 | 47,17 | 4,323 | 0,0917 |
| | sample 2 | 51,23 | 4,844 | 0,0945 |
| | sample 3 | 47,37 | 4,742 | 0,1001 |
| | sample 4 | 48,55 | 4,359 | 0,0898 |
| | sample 5 | 53,52 | 4,775 | 0,0892 |
| | sample 6 | 50,82 | 4,589 | 0,0903 |
| | sample 7 | 54,01 | 4,774 | 0,0884 |
| | sample 8 | 93,96 | 7,629 | 0,0812 |
| | sample 9 | 94,96 | 7,133 | 0,0751 |
| | sample 10 | 76,36 | 7,061 | 0,0925 |
| | average | 61,80 | 5,423 | 0,0893 |
| | std deviation | 18,18 | 1,231 | 0,0065 |
| 7% Tinuvin in LDPE film | sample 1 | 48,47 | 6,745 | 0,1391 |
| | sample 2 | 44,64 | 5,890 | 0,1319 |
| | sample 3 | 45,68 | 6,473 | 0,1417 |
| | sample 4 | 46,43 | 6,300 | 0,1357 |
| | sample 5 | 41,61 | 6,664 | 0,1601 |
| | sample 6 | 47,04 | 7,083 | 0,1506 |
| | sample 7 | 63,56 | 10,884 | 0,1712 |
| | sample 8 | 45,55 | 7,881 | 0,1730 |
| | sample 9 | 63,47 | 9,874 | 0,1556 |
| | sample 10 | 52,83 | 7,115 | 0,1468 |
| | average | 49,93 | 7,491 | 0,1506 |
| | std deviation | 6,22 | 1,546 | 0,0136 |
| 8% Tinuvin in LDPE film | sample 1 | 43,49 | 10,461 | 0,2405 |
| | sample 2 | 71,11 | 16,780 | 0,2360 |
| | sample 3 | 62,25 | 18,535 | 0,2977 |
| | sample 4 | 61,51 | 15,278 | 0,2484 |
| | sample 5 | 69,11 | 13,490 | 0,1952 |
| | sample 6 | 45,70 | 9,302 | 0,2035 |
| | sample 7 | 88,33 | 9,931 | 0,1124 |
| | sample 8 | 65,54 | 10,537 | 0,1608 |

| | | | | |
|---------------------------------|----------------------|--------------|---------------|---------------|
| | sample 9 | 71,11 | 10,181 | 0,1432 |
| | sample 10 | 85,85 | 9,867 | 0,1149 |
| | average | 66,40 | 12,436 | 0,1953 |
| | std deviation | 13,81 | 3,171 | 0,0586 |
| 10% Tinuvin in LDPE film | sample 1 | 66,26 | 22,921 | 0,3459 |
| | sample 2 | 64,63 | 24,538 | 0,3797 |
| | sample 3 | 62,61 | 21,273 | 0,3398 |
| | sample 4 | 89,78 | 21,416 | 0,2385 |
| | sample 5 | 71,66 | 17,280 | 0,2411 |
| | sample 6 | 92,47 | 22,264 | 0,2408 |
| | sample 7 | 58,17 | 21,396 | 0,3678 |
| | sample 8 | 86,54 | 20,539 | 0,2373 |
| | sample 9 | 48,97 | 39,456 | 0,8058 |
| | sample 10 | 88,68 | 23,129 | 0,2608 |
| | average | 72,98 | 23,421 | 0,3552 |
| | std deviation | 14,29 | 5,951 | 0,1692 |

D.2 Chimassorb 944

Table D.2: Experimental Results from MB UV films - Chimassorb 944 additive

| | | thickness (μm) | area after normalisation | area/thickness |
|-------------------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,5% Chimassorb in LDPE film | sample 1 | 54,05 | 0,622 | 0,0115 |
| | sample 2 | 79,13 | 0,743 | 0,0094 |
| | sample 3 | 60,21 | 0,604 | 0,0100 |
| | sample 4 | 54,40 | 0,565 | 0,0104 |
| | sample 5 | 40,59 | 0,631 | 0,0155 |
| | sample 6 | 52,90 | 0,474 | 0,0090 |
| | sample 7 | 53,99 | 0,620 | 0,0115 |
| | sample 8 | 58,93 | 0,542 | 0,0092 |
| | sample 9 | 50,31 | 0,479 | 0,0095 |
| | sample 10 | 58,60 | 0,593 | 0,0101 |
| | average | 56,31 | 0,587 | 0,0106 |
| | std deviation | 9,26 | 0,075 | 0,0018 |
| 1% Chimassorb in LDPE film | sample 1 | 69,20 | 2,277 | 0,0329 |
| | sample 2 | 62,53 | 2,349 | 0,0376 |
| | sample 3 | 64,70 | 2,059 | 0,0318 |
| | sample 4 | 48,16 | 1,336 | 0,0277 |
| | sample 5 | 61,44 | 1,761 | 0,0287 |
| | sample 6 | 58,77 | 1,714 | 0,0292 |
| | sample 7 | 63,02 | 2,104 | 0,0334 |
| | sample 8 | 68,73 | 1,891 | 0,0275 |
| | sample 9 | 68,80 | 1,817 | 0,0264 |

| | | | | |
|-----------------------------------|----------------------|--------------|---------------|---------------|
| | sample 10 | 48,15 | 1,393 | 0,0289 |
| | average | 61,35 | 1,870 | 0,0304 |
| | std deviation | 7,36 | 0,322 | 0,0033 |
| 3% Chimassorb in LDPE film | sample 1 | 67,46 | 6,197 | 0,0919 |
| | sample 2 | 63,30 | 5,282 | 0,0834 |
| | sample 3 | 69,65 | 6,148 | 0,0883 |
| | sample 4 | 55,45 | 4,838 | 0,0872 |
| | sample 5 | 50,28 | 6,440 | 0,1281 |
| | sample 6 | 48,88 | 4,092 | 0,0837 |
| | sample 7 | 68,93 | 6,064 | 0,0880 |
| | sample 8 | 47,27 | 4,129 | 0,0873 |
| | sample 9 | 55,98 | 5,065 | 0,0905 |
| | sample 10 | 56,72 | 4,911 | 0,0866 |
| | average | 58,39 | 5,317 | 0,0915 |
| | std deviation | 8,01 | 0,816 | 0,0124 |
| 5% Chimassorb in LDPE film | sample 1 | 47,17 | 6,646 | 0,1409 |
| | sample 2 | 51,23 | 7,560 | 0,1476 |
| | sample 3 | 47,37 | 7,412 | 0,1565 |
| | sample 4 | 48,55 | 6,748 | 0,1390 |
| | sample 5 | 53,52 | 7,409 | 0,1384 |
| | sample 6 | 50,82 | 7,076 | 0,1392 |
| | sample 7 | 54,01 | 7,372 | 0,1365 |
| | sample 8 | 93,96 | 12,022 | 0,1279 |
| | sample 9 | 94,96 | 11,253 | 0,1185 |
| | sample 10 | 76,36 | 11,123 | 0,1457 |
| | average | 61,80 | 8,462 | 0,1390 |
| | std deviation | 18,18 | 1,998 | 0,0099 |
| 7% Chimassorb in LDPE film | sample 1 | 46,47 | 10,693 | 0,2301 |
| | sample 2 | 47,64 | 9,514 | 0,1997 |
| | sample 3 | 45,68 | 10,423 | 0,2282 |
| | sample 4 | 46,43 | 10,217 | 0,2200 |
| | sample 5 | 41,61 | 10,727 | 0,2578 |
| | sample 6 | 47,04 | 11,358 | 0,2414 |
| | sample 7 | 63,56 | 17,951 | 0,2824 |
| | sample 8 | 60,87 | 13,093 | 0,2151 |
| | sample 9 | 64,33 | 15,324 | 0,2382 |
| | sample 10 | 62,83 | 11,684 | 0,2514 |
| | average | 52,65 | 12,098 | 0,2364 |
| | std deviation | 8,55 | 2,515 | 0,0224 |
| 8% Chimassorb in LDPE film | sample 1 | 43,49 | 12,255 | 0,2818 |
| | sample 2 | 71,11 | 19,610 | 0,2758 |
| | sample 3 | 62,25 | 21,583 | 0,3467 |
| | sample 4 | 61,51 | 17,852 | 0,2903 |
| | sample 5 | 69,11 | 15,746 | 0,2278 |
| | sample 6 | 45,70 | 10,861 | 0,2376 |
| | sample 7 | 88,33 | 11,567 | 0,1309 |

| | | | | |
|------------------------------------|----------------------|--------------|---------------|---------------|
| | sample 8 | 65,54 | 12,247 | 0,1869 |
| | sample 9 | 71,11 | 11,857 | 0,1667 |
| | sample 10 | 85,85 | 11,485 | 0,1338 |
| | average | 66,40 | 14,506 | 0,2278 |
| | std deviation | 13,81 | 3,703 | 0,0685 |
| 10% Chimassorb in LDPE film | sample 1 | 66,26 | 24,825 | 0,3747 |
| | sample 2 | 64,63 | 26,403 | 0,4085 |
| | sample 3 | 62,61 | 22,949 | 0,3665 |
| | sample 4 | 89,78 | 23,192 | 0,2583 |
| | sample 5 | 97,09 | 22,835 | 0,2352 |
| | sample 6 | 71,66 | 18,579 | 0,2593 |
| | sample 7 | 92,47 | 24,197 | 0,2617 |
| | sample 8 | 58,17 | 23,521 | 0,4043 |
| | sample 9 | 86,54 | 22,327 | 0,2580 |
| | sample 10 | 48,97 | 41,897 | 0,8556 |
| | average | 88,68 | 25,026 | 0,2822 |
| | std deviation | 75,17 | 25,068 | 0,3682 |

Appendix E

Additive Quantification - Experimental Results for MB Tinuvin

Table E.1: Experimental Results from MB Tinuvin films

| | | thickness (μm) | area after normalisation | area/thickness |
|----------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,5% Tinuvin in LDPE film | sample 1 | 68,87 | 1,121 | 0,0163 |
| | sample 2 | 55,24 | 1,335 | 0,0242 |
| | sample 3 | 63,76 | 1,044 | 0,0164 |
| | sample 4 | 50,22 | 1,125 | 0,0224 |
| | sample 5 | 52,12 | 0,941 | 0,0181 |
| | sample 6 | 49,88 | 1,055 | 0,0211 |
| | sample 7 | 28,71 | 1,202 | 0,0419 |
| | sample 8 | 58,87 | 1,181 | 0,0201 |
| | sample 9 | 60,82 | 1,011 | 0,0166 |
| | sample 10 | 54,95 | 1,247 | 0,0227 |
| | average | 54,35 | 1,126 | 0,0220 |
| | std deviation | 10,31 | 0,112 | 0,0072 |
| 1% Chimassorb in LDPE film | sample 1 | 56,13 | 2,272 | 0,0405 |
| | sample 2 | 66,16 | 2,541 | 0,0384 |
| | sample 3 | 62,43 | 2,249 | 0,0360 |
| | sample 4 | 64,22 | 2,655 | 0,0413 |
| | sample 5 | 55,99 | 2,096 | 0,0374 |
| | sample 6 | 50,22 | 2,561 | 0,0510 |
| | sample 7 | 73,35 | 3,056 | 0,0417 |
| | sample 8 | 50,75 | 2,046 | 0,0403 |
| | sample 9 | 62,39 | 2,652 | 0,0425 |
| | sample 10 | 68,97 | 2,886 | 0,0418 |
| | average | 61,06 | 2,501 | 0,0411 |
| | std deviation | 7,26 | 0,315 | 0,0039 |
| | sample 1 | 61,65 | 4,132 | 0,0657 |
| | sample 2 | 72,96 | 6,231 | 0,0854 |

| | | | | |
|-----------------------------------|----------------------|--------------|---------------|---------------|
| 3% Chimassorb in LDPE film | sample 3 | 55,76 | 4,219 | 0,0757 |
| | sample 4 | 70,32 | 5,479 | 0,0779 |
| | sample 5 | 51,70 | 3,975 | 0,0769 |
| | sample 6 | 68,80 | 6,015 | 0,0874 |
| | sample 7 | 49,95 | 3,700 | 0,0741 |
| | sample 8 | 73,28 | 5,411 | 0,0738 |
| | sample 9 | 70,44 | 5,368 | 0,0762 |
| | sample 10 | 96,95 | 4,053 | 0,0418 |
| | average | 67,18 | 4,939 | 0,0735 |
| | std deviation | 12,95 | 0,900 | 0,0120 |
| 5% Chimassorb in LDPE film | sample 1 | 83,71 | 6,982 | 0,0834 |
| | sample 2 | 65,81 | 9,453 | 0,1436 |
| | sample 3 | 63,64 | 9,206 | 0,1447 |
| | sample 4 | 64,12 | 7,995 | 0,1247 |
| | sample 5 | 76,77 | 11,489 | 0,1497 |
| | sample 6 | 94,14 | 8,254 | 0,0877 |
| | sample 7 | 45,28 | 7,798 | 0,1722 |
| | sample 8 | 71,74 | 9,520 | 0,1327 |
| | sample 9 | 62,43 | 8,533 | 0,1367 |
| | sample 10 | 74,38 | 10,576 | 0,1422 |
| 7% Chimassorb in LDPE film | average | 70,20 | 8,981 | 0,1318 |
| | std deviation | 12,65 | 1,284 | 0,0259 |
| 7% Chimassorb in LDPE film | sample 1 | 56,36 | 11,930 | 0,2117 |
| | sample 2 | 86,29 | 15,146 | 0,1755 |
| | sample 3 | 65,55 | 11,549 | 0,1762 |
| | sample 4 | 67,84 | 14,398 | 0,2122 |
| | sample 5 | 86,62 | 12,061 | 0,1392 |
| | sample 6 | 45,73 | 14,774 | 0,3230 |
| | sample 7 | 54,08 | 11,069 | 0,2047 |
| | sample 8 | 68,14 | 13,904 | 0,2041 |
| | sample 9 | 55,62 | 14,212 | 0,2555 |
| | sample 10 | 115,79 | 10,272 | 0,0887 |
| 8% Chimassorb in LDPE film | average | 70,20 | 12,932 | 0,1991 |
| | std deviation | 19,75 | 1,651 | 0,0598 |
| | sample 1 | 89,14 | 12,075 | 0,1355 |
| | sample 2 | 45,16 | 9,383 | 0,2078 |
| | sample 3 | 56,52 | 10,527 | 0,1863 |
| 8% Chimassorb in LDPE film | sample 4 | 41,20 | 8,043 | 0,1952 |
| | sample 5 | 56,65 | 10,741 | 0,1896 |
| | sample 6 | 49,69 | 9,243 | 0,1860 |
| | sample 7 | 42,47 | 10,606 | 0,2497 |
| | sample 8 | 69,97 | 12,127 | 0,1733 |
| | sample 9 | 81,93 | 9,783 | 0,1194 |
| | sample 10 | 67,20 | 11,309 | 0,1683 |
| | average | 59,99 | 10,384 | 0,1811 |
| | std deviation | 15,79 | 1,229 | 0,0344 |

| | | | | |
|-----------------------------|----------------------|--------------|---------------|---------------|
| 10% Chimassorb in LDPE film | sample 1 | 45,08 | 21,537 | 0,4778 |
| | sample 2 | 44,85 | 19,757 | 0,4405 |
| | sample 3 | 44,13 | 25,380 | 0,5752 |
| | sample 4 | 44,54 | 23,330 | 0,5238 |
| | sample 5 | 44,75 | 20,626 | 0,4609 |
| | sample 6 | 44,84 | 20,700 | 0,4616 |
| | sample 7 | 44,61 | 21,852 | 0,4898 |
| | sample 8 | 44,72 | 22,140 | 0,4951 |
| | sample 9 | 44,01 | 20,789 | 0,4724 |
| | sample 10 | 44,38 | 20,729 | 0,4671 |
| | average | 44,58 | 21,633 | 0,4855 |
| | std deviation | 0,34 | 1,630 | 0,0384 |

Appendix F

Additive Quantification - Experimental Results for MB Chimassorb

Table F.1: Experimental Results from MB Chimassorb films

| | | thickness (μm) | area after normalisation | area/thickness |
|------------------------------|----------------------|-----------------------------|--------------------------|----------------|
| 0,5% Chimassorb in LDPE film | sample 1 | 68,99 | 0,365 | 0,0053 |
| | sample 2 | 68,87 | 0,485 | 0,0070 |
| | sample 3 | 67,69 | 0,494 | 0,0073 |
| | sample 4 | 61,66 | 0,203 | 0,0033 |
| | sample 5 | 63,09 | 0,284 | 0,0045 |
| | sample 6 | 61,45 | 0,100 | 0,0016 |
| | sample 7 | 49,88 | 0,214 | 0,0043 |
| | sample 8 | 28,71 | 0,361 | 0,0126 |
| | sample 9 | 68,76 | 0,340 | 0,0049 |
| | sample 10 | 80,79 | 0,170 | 0,0021 |
| | average | 61,99 | 0,302 | 0,0053 |
| | std deviation | 13,36 | 0,125 | 0,0030 |
| 1% Chimassorb in LDPE film | sample 1 | 62,98 | 0,775 | 0,0123 |
| | sample 2 | 172,58 | 0,791 | 0,0046 |
| | sample 3 | 67,69 | 0,796 | 0,0118 |
| | sample 4 | 55,55 | 0,719 | 0,0129 |
| | sample 5 | 59,46 | 0,875 | 0,0147 |
| | sample 6 | 51,78 | 0,581 | 0,0112 |
| | sample 7 | 64,57 | 0,928 | 0,0144 |
| | sample 8 | 78,30 | 1,072 | 0,0137 |
| | sample 9 | 50,42 | 0,701 | 0,0139 |
| | sample 10 | 60,32 | 0,957 | 0,0159 |
| | average | 72,37 | 0,820 | 0,0125 |
| | std deviation | 34,28 | 0,135 | 0,0030 |
| | sample 1 | 70,11 | 6,525 | 0,0940 |
| | sample 2 | 56,49 | 5,157 | 0,0913 |

| | | | | |
|----------------------------|----------------------|--------------|---------------|---------------|
| 3% Chimassorb in LDPE film | sample 3 | 102,62 | 8,842 | 0,0862 |
| | sample 4 | 61,61 | 8,477 | 0,1376 |
| | sample 5 | 77,35 | 9,136 | 0,1181 |
| | sample 6 | 101,09 | 8,585 | 0,0849 |
| | sample 7 | 68,76 | 6,537 | 0,0951 |
| | sample 8 | 80,79 | 7,244 | 0,0897 |
| | sample 9 | 66,72 | 6,616 | 0,0992 |
| | sample 10 | 75,64 | 6,589 | 0,0871 |
| | average | 76,12 | 7,465 | 0,0983 |
| | std deviation | 14,57 | 1,278 | 0,0159 |
| 5% Chimassorb in LDPE film | sample 1 | 48,42 | 8,279 | 0,1710 |
| | sample 2 | 51,78 | 8,680 | 0,1676 |
| | sample 3 | 64,57 | 10,519 | 0,1629 |
| | sample 4 | 15,80 | 10,878 | 0,6885 |
| | sample 5 | 65,83 | 10,527 | 0,1599 |
| | sample 6 | 22,36 | 12,596 | 0,5633 |
| | sample 7 | 63,37 | 10,211 | 0,1611 |
| | sample 8 | 65,90 | 10,687 | 0,1622 |
| | sample 9 | 91,49 | 13,486 | 0,1474 |
| | sample 10 | 74,50 | 11,526 | 0,1547 |
| | average | 56,40 | 10,739 | 0,2539 |
| | std deviation | 21,78 | 1,493 | 0,1882 |
| 7% Chimassorb in LDPE film | sample 1 | 65,40 | 14,516 | 0,2220 |
| | sample 2 | 75,82 | 18,321 | 0,2417 |
| | sample 3 | 57,61 | 13,889 | 0,2411 |
| | sample 4 | 79,56 | 14,610 | 0,1836 |
| | sample 5 | 45,58 | 19,570 | 0,4294 |
| | sample 6 | 60,30 | 15,152 | 0,2513 |
| | sample 7 | 88,13 | 18,492 | 0,2098 |
| | sample 8 | 63,38 | 15,414 | 0,2432 |
| | sample 9 | 19,27 | 18,175 | 0,9431 |
| | sample 10 | 62,28 | 14,669 | 0,2355 |
| | average | 61,73 | 16,281 | 0,3201 |
| | std deviation | 18,20 | 1,993 | 0,2169 |
| 8% Chimassorb in LDPE film | sample 1 | 62,32 | 21,387 | 0,3432 |
| | sample 2 | 62,50 | 15,023 | 0,2404 |
| | sample 3 | 60,36 | 22,872 | 0,3789 |
| | sample 4 | 61,27 | 15,528 | 0,2535 |
| | sample 5 | 39,36 | 14,178 | 0,3602 |
| | sample 6 | 61,66 | 19,519 | 0,3165 |
| | sample 7 | 63,09 | 21,229 | 0,3365 |
| | sample 8 | 38,60 | 15,351 | 0,3977 |
| | sample 9 | 271,56 | 19,946 | 0,0735 |
| | sample 10 | 58,28 | 21,314 | 0,3657 |
| | average | 77,90 | 18,635 | 0,3066 |
| | std deviation | 65,17 | 3,087 | 0,0915 |

| | | | | |
|------------------------------------|----------------------|--------------|---------------|---------------|
| 10% Chimassorb in LDPE film | sample 1 | 58,02 | 34,687 | 0,5978 |
| | sample 2 | 57,62 | 23,510 | 0,4080 |
| | sample 3 | 58,16 | 32,893 | 0,5656 |
| | sample 4 | 58,72 | 33,252 | 0,5663 |
| | sample 5 | 58,60 | 32,245 | 0,5503 |
| | sample 6 | 58,72 | 21,434 | 0,3650 |
| | sample 7 | 58,50 | 31,734 | 0,5424 |
| | sample 8 | 59,41 | 25,731 | 0,4331 |
| | sample 9 | 57,96 | 26,401 | 0,4555 |
| | sample 10 | 59,77 | 32,567 | 0,5449 |
| | average | 58,55 | 29,445 | 0,5029 |
| | std deviation | 0,63 | 4,463 | 0,0759 |