Universitat Rovira i Virgili

Escola Tècnica Superior d’Enginyeria Química

Dow Chemical Company

Greenhouse films properties model: From 3 to 5 layers

Master thesis presented by

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to obtain the Master’s degree in Chemical Engineering
from the Universitat Rovira i Virgili

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SUMMARY

Current plastic films used for greenhouses have multilayer structures (3-7 layers) containing materials such as LDPE, LLDPE, EVA (Ethylene vinyl acetate), EBA (Ethylene butyl acrylate) and certain types of additives to absorb IR rays or prevent condensation. The use of all these materials distributed in the different layers helps to comply with the mechanical, optical and thermal properties set in this case by the European Norm for greenhouse plastics.

This study deals with the development of a predictive model for the properties of 5-layer greenhouse films whose methodology was already established in another project for 3-layer structures. Based on the results of that model, which includes four materials, it has been extended to nine materials in order to propose different alternatives both in terms of economics and properties. These alternatives include materials that ensure processability during film extrusion or reduce the cost of the final product while maintaining its properties. One of the main motivations has been to replace or reduce the use of EVA in this sector due to the shortage in the European market. For this purpose, two different options have been employed: the use of LLDPE with an inorganic additive to absorb infrared radiation or the use of EBA.

The model used to predict the properties uses linear or parabolic correlations from the results of monolayer films to apply them to multilayer films, correcting possible errors with a final validation with results from extruded and characterized multilayer films. The methodology for developing such a model is detailed in the report as well as its limitations and the results achieved. Looking to the future, recommendations have been suggested with the aim of improving predictive models for properties of plastic films.

ACKNOWLEDGEMENTS

First of all, I would like to dedicate this work to my family, for once again giving me their support and help with the decisions I have made in my academic life. Undoubtedly, you are my clear reference for the future professional I want to become.

Secondly, to the entire Dow Pack Studios Tarragona department, especially my two tutors Pere Puig and Antoni Cabello as well as the technicians and engineers who have participated in this project. It has been a pleasure to be able to do my internship in a team like this and in a company like Dow Chemical. I will never forget these nine months of experiences and learning.

Finally, to my friends, master’s colleagues and other students in the Dow I2C program, this is also for you, for the moments we have experienced and all the help you have given me. Thank you for everything.

FIGURES AND TABLES

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NOMENCLATURE

BUR: Blow-up ratio

CD: Cross direction

DDI: Dart Drop Impact

EBA: Ethylene Butyl Acrylate

EVA: Ethylene Vinyl Acetate

HDPE: High-Density Polyethylene

HPC: High Pressure Copolymer

IR: Infrared

LDPE: Low-Density Polyethylene

LLDPE: Linear Low-Density Polyethylene

MD: Machine direction

MFR: Melt Mass-Flow Rate

PE: Polyethylene

PVC: Polyvinylchloride

TS&D: Technical Service and Development

UV: Ultraviolet

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1. PROLOGUE

The main motivation to carry out this project remains into applying all the knowledge in polymer and materials science as well as in programming and modelling achieved during the master’s and bachelor’s degree in Chemical Engineering. In the world we live in, it is important to keep in mind the importance and benefits of plastics in comparison with other materials, and that is a good argument against the global plastic controversy. Related with that, it is important to know how a company like Dow Chemical develops this research and development projects, always following the scientist methodology and considering all the necessary tools like statistics for example.

In a parallel way, the agricultural sector generates an extra motivation due to the coincidence of being born and raised in a family of farmers. Then, the fact to be so close with the topic allows to create a boost with the project as well as to have more applied ideas about the impact of the greenhouse’s properties in the growing of crops.

2. INTRODUCTION

Following the global tendency around the world, agriculture is one more sector which has been benefited from the introduction of plastics in several types of applications such as silage, mulch or greenhouses. Nowadays, plastic films use in this field is very common around the world and depending on the application, materials need certain properties and requirements to fulfil. The most common technique to produce this type of films is the blown extrusion, for that reason some of the raw materials require certain properties for good processability.

This project is related with multilayer greenhouse films and this part of the report is going to introduce a general idea of the state of art as well as the suggested problem to solve for this application.

2.1. Plastic film extrusion

Plastic extrusion is a commonly used manufacturing process that involves melting plastic material and then forcing it through a die to create a specific shape or profile. This process is widely used in the production of a huge number of plastic products, from simple toys and household items to more complex components used in automotive and aerospace industries. (1)

One of the most commonly used plastics in the extrusion process is polyethylene, or PE. PE is a thermoplastic polymer that is widely used due to its low cost, good mechanical properties, and ease of processing. There are several types of PE, including low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE), each with their own unique properties and applications. The extrusion process for PE typically involves feeding the plastic material into a hopper and then heating it to the melting temperature in a screw-type extruder. The molten plastic is then forced through a die, which determines the final shape of the extruded product depending on the final product. The next Figure 2.1 shows an example of the schematic view of an extruder.

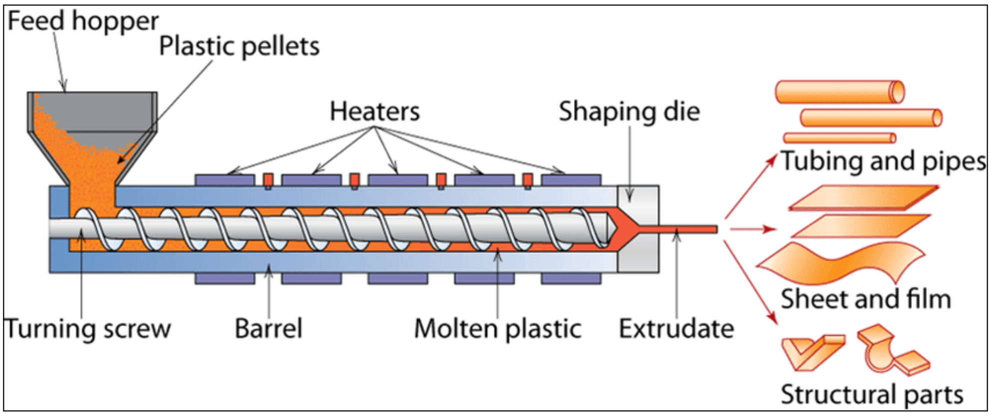


Figure 2.1. Schematic view of a general plastic extrusion machine. (11)

The question now is how plastic films are created from a molten mass of plastic. Several techniques exist but the most important ones in terms of producing films are the blown and cast extrusion. In the case of the blown extrusion, once the melt polymer has passed through the annular die is subsequently expanded in vertical and horizontal directions using compressed air forming a plastic bubble that is cooled by an air ring as well. The bubble is stabilized by a bubble cage, collapsed into lay flat tubing, and wound as a roll (tube or slit sheet) as it can be seen in Figure 2.2 The previous procedure can be done for monolayer films, in this case only one extruder is required, or for multilayer films, which can use a minimum of one extruder per layer. Blown extrusion offers several advantages over other types of extrusion processes, including greater flexibility in film thickness and improved mechanical properties. It is widely used in the production of a variety of products, including packaging films, agricultural films, and construction materials. However, it also presents some challenges, such as controlling the uniformity of the film thickness and preventing defects such as air bubbles and wrinkles. Various techniques have been developed to overcome these challenges, including the use of advanced control systems and specialized dies.

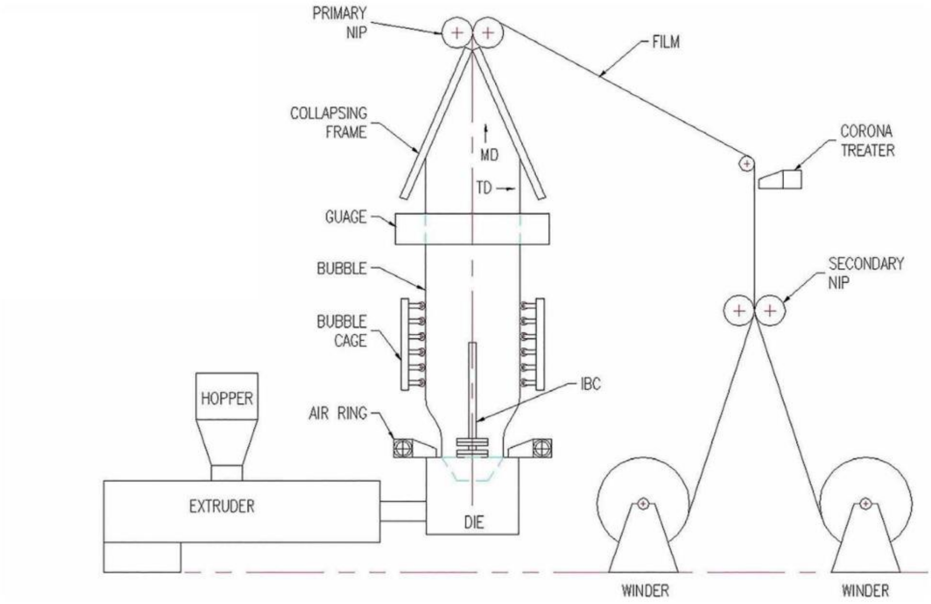


Figure 2.2. Schematic view a monolayer blown film process. (1)

Unlike blown extrusion, the cast extrusion process does not involve inflating the plastic, which makes it more suitable for producing thin films with very precise thicknesses. This process extrudes the molten plastic through a flat die, which is then cooled on a chill roll to create flat sheet or film, meaning that in this technique the way of how the polymer falls in the chill roll is crucial for the final result, dropping from the die vertically or with a certain inclination angle. Figure 2.3 represents a schematic view of the process, which has multiple passes through different rollers to maintain the shape and tight it (1). Cast extrusion is widely used in the production of high-quality packaging films, such as those used in food packaging or industrial applications like stretch wrap.

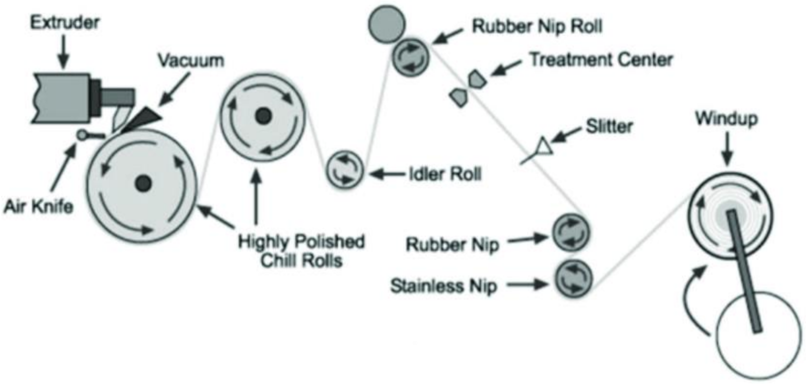


Figure 2.3. Schematic view of a cast film extrusion line. (12)

2.2. Greenhouse films

The application of plastics as coverings for agricultural greenhouses is a fairly new development, dating back to 1948 when cellulose hydrate replaced glass, only to be soon replaced itself by PE or PVC.

Since this replacement, greenhouses suppose and excellent cost-effective solution to grow crops due to, among other characteristics, the wide range of sizes and structures according to the needs and requirements for each of the areas around the world as it can be seen in Figure 2.4. In terms of global production, greenhouses were around the 46% of the 5.1 millions of tons produced during the last year, and the 27% of the 0.7 millions of tons produced in Europe, being Spain and Italy the principal producers and China the first one in the world. (2)

Figure 2.4. Low tunneling, high tunneling and industrial size building greenhouses. (14)

The use of a greenhouse also provides an important advantage by creating a warmer environment within the structure, primarily due to the thermicity effect. This allows crops to grow faster and more efficiently. When sunlight enters the greenhouse, it is absorbed by the plants and soil, which then emit heat energy as longer-wavelength infrared radiation. Properly designed greenhouse films prevent this heat from escaping through natural convection, resulting in a rise in internal temperature. This controlled environment also helps to regulate humidity, prevent pest infestations, and protect plants from harsh weather conditions such as wind or hail. Greenhouse films that block long-wavelength radiation are known as thermic films.

Today's greenhouses thermic films are basically made of combinations of low-density polyethylene (LDPE) and ethylene vinyl acetate (EVA) or ethylene butyl acrylate (EBA) because the necessities are focused in the optical and physical properties. LDPE is the most used one because is easy to extrude in the blown technique and is very resistant to the weather and the greenhouse structure conditions, having good toughness, lightweight and stiffness. Related with that, one of the problems is the tendency to crack due to the fact is not resistant to stress or impact. EVA and EBA are high pressure copolymers (HPC) that are known for their ability to absorb infrared radiation (thermicity) and maintain their flexibility and elasticity even at low temperatures. This characteristic has made EVA-rich films a popular choice in regions like Northern China, where temperatures can be very low. The reason why these ethylene copolymers can absorb the infrared radiation comes from its molecular structure, specifically from the double bond between the carbon and oxygen molecules as it can be seen in Figure 2.5.

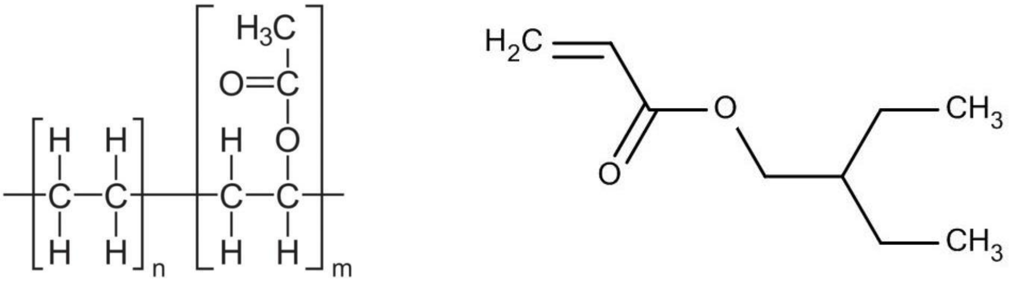


Figure 2.5. EVA and EBA molecular structures respectively. (4) (5)

However, following other industrial application changes, this ethylene copolymers are being displaced by the linear low-density polyethylene (LLDPE). This type of resins have good puncture, tear and impact resistance properties as well as high optics, because normally are very transparent. In addition, the thermicity effect can be provided by the use of inorganic thermic additives, but controlling the increase in the production and final cost of the film.

To conclude with the different materials used to produce the films for greenhouses, additives have a high importance in this sector. These new technologies make it possible to reduce or eliminate effects such as condensation or fogging or to protect PE from degradation caused by UV rays. One of the most interesting ones is the use of organic additives to increase the thermicity, maintain the light transmission, as well as increase the light diffusion through the film. Light diffusion is very important for the crops inside the greenhouse because the direct impact of the rays coming from the sun can cause damage to the flowers or the leaves. With the use of LLDPE or certain LDPE the diffused light is very low, and then these additives are needed to increase the haze of the film. Some of these properties such as light diffusion or drip effect are shown in the following Figure 2.6.

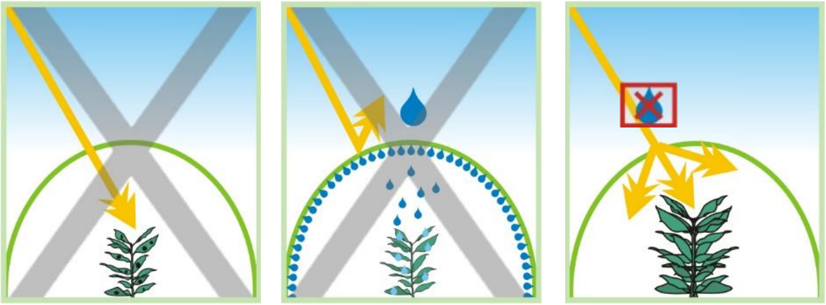


Figure 2.6. Light diffusion and drip effect explanation. (6)

2.3. Description of the problem

One of the main problems in industrial applications is the distribution of the different raw materials around the world, and in this case, the problem is related with the global use of EVA. Being one of the principal materials in the greenhouse films production, the usage of these materials varies widely across different regions, depending on local supply. Additionally, the prices of these resins are subject to significant fluctuations based on demand and production levels.

Latin America faces availability issues with EVA due to its reliance on a single local producer, which primarily supplies the Brazilian market. As a result, EVA usage in the region is limited, accounting for only up to 5% of total consumption in 2019. In contrast, EVA is widely used in Asia, particularly in high-end greenhouses, with levels of up to 60% thanks to the material's easy availability and production. North America and Europe fall somewhere in the middle, with EVA accounting for around 10% to 20% of greenhouse film production and a lack of a local source here in Europe. The next graph shows the capacity for each of the regions explained before.

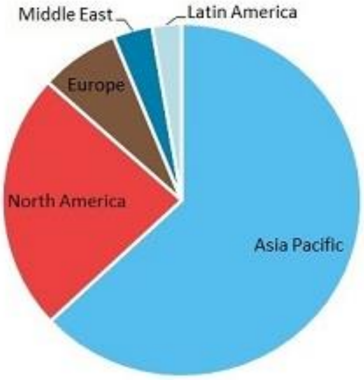


Figure 2.7. Global ethylene vinyl acetate (EVA) capacity by region. (7)

Regarding with the price of this replacement or reduction, the proposed solution should not increase so much the cost of the fabricated films for this sector to maintain the competence in the market, and a variety of different price materials can be a call for the customers.

2.4. Solution

The solution for the proposed problem is to reduce or replace this EVA, widely used in the market, with other materials maintaining the necessary properties to fulfil de requirements of greenhouses. Based in the results of other projects, this replacement can be done with LLDPE resins plus the use of an IR additive or with EBA, which is a high-pressure copolymer potentially more available in the European market.

In order to demonstrate that this replacement is possible, the other part of the solution is the construction of a properties predictive model for 5-layer greenhouse films. This model will help in comparing the properties of the different alternatives for the replacement done and provide certain guidance for customers.

Otherwise, this predictive model can consider the use of a wide variety of products for each of the layers, taking into account the price for example, and then be very useful to study the different requirements depending on the area or the conditions where the greenhouse is located.

3. SCOPE OF THE PROJECT

The scope of this project is based in the expansion of 3-layer film properties predictive model done in 2017 into a 5-layer one applied in greenhouses for agricultural applications. Following with that, the model will be expanded with new variables as well, considering the implementation of additional PE materials and blends for the different layers of the film. Related with the materials extension, one of the requirements of the project is to study the reduction or replacement of a widely used high-pressure ethylene copolymer: EVA, taking into account that the use of LLDPE has a good performance in this issue. This substitution will introduce the use of certain additive to supply the crucial properties of the ethylene copolymers or HPC in this specific agricultural sector.

Due to the regulations applied by the European Government in the greenhouses field, the model needs to compare the predicted results with the *European Norm for GH AG films 13206 2017+A1* standards in order to fulfil it as well as satisfy the client requirements for the different existing necessities in agriculture and plastic films production.

Considering the industrial trends in this area, the same methodology could be applied to build a predictive model for the novel 7-layers films with more materials or additives included, but this is a hypothetical extension of the project carried out.

3.1. Objectives

The objectives of the thesis are the next ones:

- Expand the designed 3-layers predictive model for the current 5-layers coextruded films used for greenhouses in agricultural applications.
- Replace or reduce the Ethylene-vinyl acetate (EVA), widely used in this sector.
- Introduce the use of Linear Low-density Polyethylene plus IR Additive or another high-pressure ethylene copolymer like the Ethylene Butyl Acrylate (EBA) as substitutes.
- Include the resins used in the 3-layers model plus new Dow Polyethylene (PE) products specific for this type of application.
- Predict and compare the film properties with the European Norm for Greenhouse films to provide guidance for the department and the customers.

3.2. Hypotheses

During the project realization, an experimental plan will be developed to verify the three principal hypotheses of this thesis:

1. The 3-layers model methodology will work for the 5-layers predictive model.
2. This procedure allows the introduction of new materials as alternatives.
3. Multilayer film properties prediction from monolayers raw data is the option to pursue.

Regarding the first one, some potential conflicts can appear considering the change in the film properties when the number of layers is increased from 3 to 5. This will be validated with the extrusion and characterization of 5-layers films.

Having a look at the second one, it is interesting to see different alternatives for the materials used. As an example, the use of a “low cost” LLDPE alternative needs to be verified to check if film properties are maintained, although some studies show non appreciable differences. The expansion of the materials and formulations for the model can provide a multiple-choice option for consulting the properties of the different films and formulations available for the customers and the market. For this reason, the design should consider the most common practiced distributions as a limitation, which means to put inside of each layer a specific type of material or blends.

Finally, the third hypothesis is related with the potential error accumulation and difficulties when the layers are incremented. In this case, is important to consider how the methodology reacts from 3 to 5 layers films, regarding with the new trends in the sector and the search of new tools for properties predictions.

4. STUDENT'S ROLE IN COMPANY

One of the principal purposes of doing the final master's thesis in a company is to create a bonding between the University and the companies to develop the future employees of the sector in the real assignments, projects and methodologies, practical knowledge difficult to learn only in University subjects. For this reason, is important to know the company and its goals and how the student matches with it by completing the different tasks during the internship.

4.1. Description of the company

The Dow Chemical Company is an American multinational chemical corporation among the world's leading suppliers of chemical, plastics, synthetic fibers and agricultural products. With the Headquarters in Midland, Michigan, it was founded in 1897 by chemist Herbert Henry Dow to supplement the Midland Chemical Company (1890) and the Dow Process Company (1895). Created in part because Dow required a bleach plant to use the wastes from the bromine extraction processes performed by Midland Chemical, the new company also began extracting other chemicals such as chlorides, magnesium and calcium from Michigan's plentiful brine deposits. In 1900, Dow Chemical was incorporated, combining all of Dow's Midland properties. Although the company initially produced bromide, after 1920 it turned to the production of phenol and magnesium, initially for use in World War I munitions.

Nowadays, Dow Chemical Company employs 35.700 people worldwide with a presence in about 175 countries. More than 7.000 products families of the company are fabricated in 104 placed in 31 countries around the world, producing an annual revenue of 55.000 million US$ in 2021.

One of the European subsidiaries is Dow Chemical Ibérica, introduced in Spain in 1960 in Bilbao. In 1966 Dow established itself in Tarragona, where over time the Low-Density Polyethylene, High-Density Polyethylene, Polyols, Polyglycols and Octene plants were built and began operations, along with the Ethylene cracker. Now, Dow has three centers in Spain (Tarragona, Ribaforada and Tudela) besides its headquarters in Madrid, representing the 3% of the global corporation.

As an important part of the company, since 2020 part of the Dow Packaging and Specialty Plastics is done in Pack Studios Tarragona, the 10th in a global network of Pack Studios sites helping customers address packaging sustainability by providing a testing platform to shorten development cycles for new formats and load stability innovation.

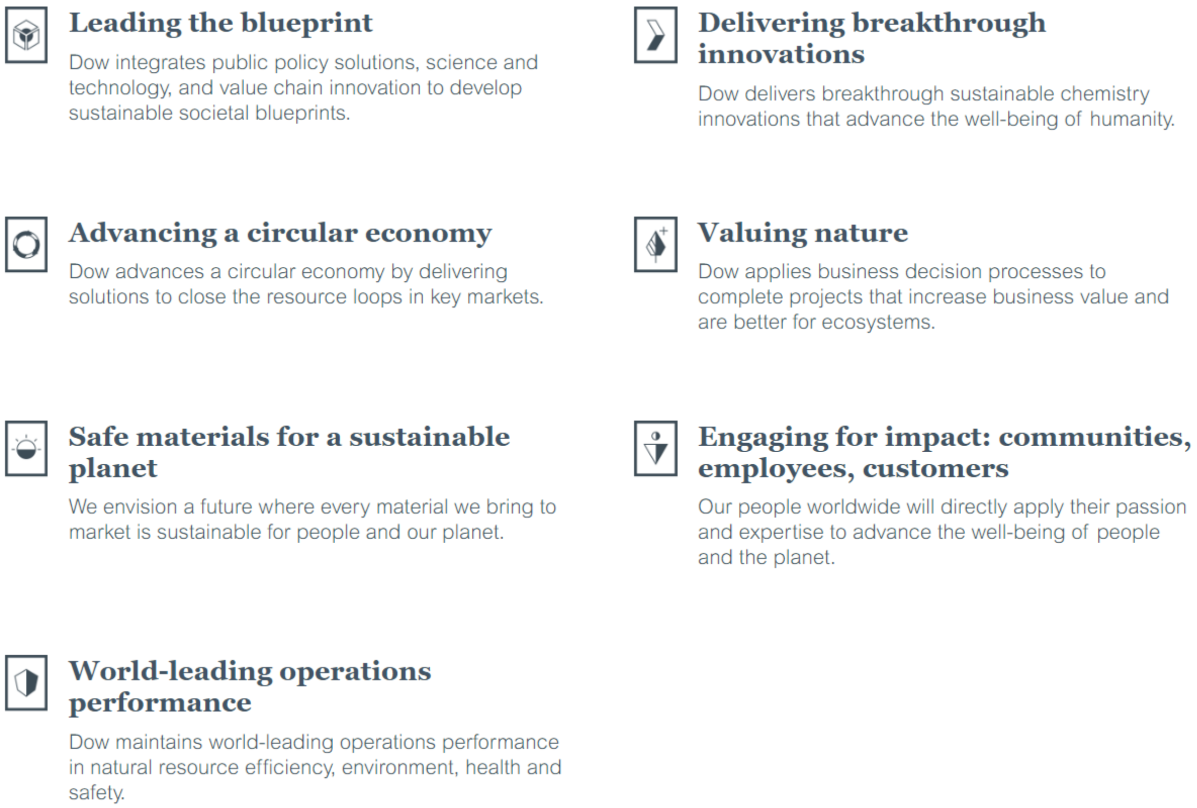
4.2. Goals and products of the company

Dow Chemical is a materials science leader committed to delivering innovative and sustainable solutions for customers in packaging, infrastructure, and costumer care, with a clear ambition:

"We want to be the most innovative, customer-centric, inclusive and sustainable materials science company in the world"

For that reason, the company develops the *2025 Sustainability Goals* keeping in mind the collaboration with like-minded partners to create a stronger future together through a more sustainable planet and society.

The seven goals are the next ones:



Leading the blueprint

Dow integrates public policy solutions, science and technology, and value chain innovation to develop sustainable societal blueprints.

Delivering breakthrough innovations

Dow delivers breakthrough sustainable chemistry innovations that advance the well-being of humanity.

Advancing a circular economy

Dow advances a circular economy by delivering solutions to close the resource loops in key markets.

Valuing nature

Dow applies business decision processes to complete projects that increase business value and are better for ecosystems.

Safe materials for a sustainable planet

We envision a future where every material we bring to market is sustainable for people and our planet.

Engaging for impact: communities, employees, customers

Our people worldwide will directly apply their passion and expertise to advance the well-being of people and the planet.

World-leading operations performance

Dow maintains world-leading operations performance in natural resource efficiency, environment, health and safety.

Figure 3.1. Dow 2025 Sustainability Goals. (8)

With these goals, Dow is trying to accelerate its sustainability strategy as well as the global one. Another important issue is the values of the company, which are Integrity, Respect for People and Protecting the planet. So, it is trying to promote the globalization with the employees by combining different cultures and countries to create a diverse work environment and become a forward company in this matter inside the chemical sector.

Regarding with the products of the company, Dow is usually called the “chemical companies” chemical company, as its sales are to other industries rather than directly to end-use consumers, meaning that is it a business-to-business transaction. According to that, Dow is providing a high level of raw materials related with the next technologies:

- Adhesives and Sealants
- Polyethylene
- Polyurethanes
- Silicones, Silicone-Organic Hybrids and Silanes
- Elastomers and Plastomers
- Amines and Chelates

All this product technologies are enabling the company to have a huge number of market opportunities, being the top ones:

- Building, Construction and Infrastructure
- Chemical Manufacturing and Industrial
- Mobility
- Films, Tapes and Release Liners
- Packaging
- Agriculture, Feed and Animal Care

In the case of the Iberian part, it is more centered in the development of low and high-density polyethylene resins, investigation and development of plastic film technologies or in the commissioning of polyurethanes systems among other technologies and applications.

Related with that, the Tarragona Pack Studios segment facilitates world leading innovation within food and industrial packaging while also serving global label customers with innovative adhesives solutions. The center is equipped with state-of-the-art film production and testing capabilities for primary, secondary and tertiary packaging applications to keep the customers in contact and collaborate with them. Then, the basic idea of this department is to create, test, innovate and consult all the client specifications as well as the new market trends to continuously improve in the sector, keeping in mind the next sentence:

"The future of packaging starts with collaboration"

4.3. Specific tasks of the student

Greenhouse predictive model project

In the case of the developed project, it allows to have a multiple task internship in the company, which lets the student to improve and obtain multiple abilities in different sectors but in the same field. The student can work in an autonomous way and prepare step by step the different parts of the project, following the industrial and the company's methodology. This allows being conscious about the importance of the timing, scheduling, raw materials availability, customer requirements, market pressure, machines failing, or many problems related with this type of industrial capabilities.

The Pack Studios investigation and innovation center here in Tarragona is the corresponding part of Dow to do these types of projects. Then, in this project the specific tasks are divided in three types:

- Fabrication
- Testing
- Modelling

Each of the parts are going to be detailed and explained below.

Fabrication

The tasks to develop in the fabrication line are basically related with the production of the plastic films to extract the necessary data for the project. In this case, the project needs two different machines: blown extrusion for monolayers films and a multilayer one for 5 layers. On the one hand, the monolayer machine can be used by the own student after completing the correspondent training, which shows you how to manage the machine, start and stop the production and act in an emergency.

On the other hand, the multilayer blown extrusion machine requires working with an operator trained for the task. Here, the student can manage the different parts of the extruder as well as preparing the raw materials, but always with the supervision of a company's worker.
Related with that type of task, in the initial part of the internship there were a couple of weeks to work as an operator for other projects to start manipulating some of the machines and know some of the rules and dynamics in the fabrication line, previously studied by different mandatory learnings provided by the multinational.

Testing

Once the samples are extruded in the fabrication line, it is time to analyze and collect the data. All the necessary tests are available in the three different labs of the center. For this project, only two of it are required, the mechanical laboratory (Lab-G) and the chemistry one (LACAT).

The tasks to develop there are basically the different methods and trials. Previously to work by your own with the tools, the required training and supervisor agreement is necessary. Then, it is necessary to work with some samples to test from other projects. Finally, all the suggested tests for the project are done following a priority order with other projects.

Modelling

The last task of the project is done in the office provided to the students. This part takes the data files and the modelling program necessary to produce the predictive model. During this stage, it is important to keep in contact with the some of the data analysts of the department to obtain good ideas and a certain guidance of how to manage some of the possibilities of creating the model. The modelling shows you the tendency of some of the materials, extrusion conditions or film properties, which is an important part for the application of the project.

Innovating tool for blown extrusion machines project

During the 9 months internship in the company a total of a 20% of the time needs to be invested in one of the backbones of the department: generating innovation. This proposal tries to get a more representative idea of how projects are developed with the collaboration of the multiple parts inside Pack Studios: technicians, engineers and clients. With this time investment, all the new ideas coming from the next generations can be applied to some of the new internal projects or necessary improvements.

Then, considering the blown extrusion knowledge acquired during the different extruded samples for the own studies, a team of three students decided to get part of one project that was created years ago and need the push with new ideas and time. Due to confidential issues, not all the information can be described, but the project is related with the measurement of one of the characteristics of the blown extrusion technique using artificial intelligence. After an exhaustive search for similar ways to measure the property, only one technology exists, meaning that the idea can suppose an opportunity in the sector.

The tasks done represent the entire development of the tool: from the construction of the prototype to the final analysis. The first step was to take the decision of which machine is the first one in use this technology, and once it was decided, the prototype was designed and created with simplicity and effectiveness regarding the necessities. The next stage included the application implementation, which requires the known calculation methodologies in addition to the programming skills of one the technicians linked with the project. Finally, after the preliminary design of the prototype and the application, the tool was tested with multiple samples and diverse materials to see the different characteristics like the sensitivity. Obviously, several modifications were developed to enhance the measurement and correct operation of the system as well as a statistical analysis of the results.

The project will keep on movement after the internship in order to be part of the digitalization transition for the department and the opportunity that can suppose in the market.

Laboratory Gantt scheduling project

Keeping in mind the percentage of innovation suggested, the amount of working hours done in the lab and the lack of a visualization tool for the management of tasks, another project started.

With the same student's team as in the last project, the idea now is to improve the current lab scheduling tool with the use of visual solutions like a Gantt diagram. The reason why it is needed is related with the number of projects that are continuously being entered in the system and the necessity to be able to predict an estimated end date for the studies, which is one of the most useful values for the lab clients (TS&D engineers and customers).

Having all the information about the studies in the system and the clear objectives to achieve, the tasks to develop were directly to create these diagrams for the different three sectors of the laboratory: fabrication, testing and packaging. This last part is very important to adapt the tool to the needs and requirements of each coordinator. Apart from that, the diagram needs to be automatic with the selection variable like the number of study or the date when it was created. Successfully, the result was helpful for the team with the task management and future recommendations were created to continue with the optimization of the studies and the prediction of the end dates, probably, with the use of machine learning techniques.

4.4. Internship report

During the nine months internship in Dow Chemical, a global leader in the chemical industry with a focus on sustainability, innovation and integrity, I gained valuable experience working with various teams and contributing to the company's goals and objectives for the present and the future. In this report, I will try to explain how my internship matches with these goals by the different experiences and projects done.

In terms of sustainability, Dow Chemical is committed to advancing a circular economy, which aims to eliminate waste and promote the efficient use of resources as well as leading the blueprint for a sustainable future. During my internship, I participated in various sustainability initiatives and programs that aimed to reduce the company's environmental footprint. I also attended workshops and training sessions on sustainability and learned about Dow's sustainability goals and initiatives. Additionally, I had the opportunity to participate in some presentations to develop sustainable packaging solutions using Dow's circular economy expertise. In the middle of the controversy with plastics, the company is using the current packaging practices and proposing solutions that are aligned with the principles of this model. One example is the use of predictive models to avoid the extrusion repetition and waste of raw materials for the characterization of the plastic films.

Regarding with innovation, the North American multinational is known for its innovative products and solutions linked with its world-leading operations performance, which includes operational excellence, cost optimization and innovation. I had personally experienced to work with different teams and learn about Dow's operations performance strategies. I also participated in various process development projects and analyzed data to identify areas for improvement, collaborating with a team of engineers and scientists to conduct research and experiments, and we successfully developed a prototype of the product or the tool. All the projects in which I contributed during these nine months were inside the same strategy: the digitalization of the department. Various indicators demonstrate this: select different areas to develop prediction tools, automate the tests of the laboratory or the use of artificial intelligence. All the procedures and innovation proposals go together with the importance of the safety of the employees under the slogan: “safety first”.

Another important goal for Dow is upholding the integrity and inclusion in all aspects of its business, including ethical behavior, compliance with laws and regulations, and responsible governance. I learned about Dow's values and ethical standards, and I was expected to uphold them in all my work. I also participated in compliance training sessions and learned about Dow's policies and procedures for maintaining integrity. As part of the I2C program that includes students from all over the world, you can open your mind and know more about different cultures, working methodologies and life experiences. Regarding with that, it is remarkable the way that people of the entire department allow you the integration in the team and helps you with your different tasks, always maintaining the respect for the people and the collaboration. I can also take into account all the proposals that the company offers to interact with your co-workers outside the work environment, with different team sports activities, typical food events in the area or healthy breakfasts. Things like that create a good work environment to develop the objectives of the company.

In conclusion, my internship at Dow Chemical gives me the opportunity to growth in a professional, personal and technical way as a chemical engineer. During the nine months in Tarragona Pack Studios I had the chance to know more of the Dow’s culture day by day, the good practices in terms of environmental health and safety, collaboration and self-employment, establishing the beginning of a hopefully desired professional career.

5. METHODOLOGY AND EXPERIMENTAL PLAN

Referring to the project again, one of the most important things to consider when a project like that is done, in this case a predictive model based on experimental data, is to have a clear methodology, which means to follow step by step the different parts of the experimental plan with the same criteria and “modus operandi”. For this reason, the followed methods to carry out the project are going to be explained next.

Regarding with the first hypothesis, the idea is to use a stablished methodology to, in this case, predict the properties of a multilayer film composed of 5 layers. The base of the practice is to take the properties data from monolayer films with the materials and blends used for this sector and then use the data to give values for the properties of 5-layer films. The reason why it is done this way is easy to explain. In the case of monolayer films there are only two variables: the thickness and the composition of the blend (usually only two materials are mixed, so with one percentage value the other one is known as well), so the possibility to predict the desirable properties via correlations is feasible as long as the values are tightly adjusted. Considering a multilayer film, the number of variables starts to increase exponentially with the number of layers. For a 5 layers film, the variables are: the layers distribution (volumetric % of each layer), the total thickness and the composition of each layer. So, it is clear that the prediction starts to be inviable with correlations.

Assuming the last explanation, the idea then is to treat a multilayer film as the combination of monolayer films. The procedure of the project then is the next one:

- Extrude monolayer samples with the blends of materials that are going to be used.
- Characterize and collect the properties data from these films.
- Create the model with the data collected.
- Validate it with 5-layer films extruded and adjust the deviations with corrective factors.

Broadly speaking, these are the steps to follow and then the methodology of the project is adapted with the objectives proposed. Then, due to the diversion of techniques to develop the final model, the experimental plan is divided in three different parts that will be detailed below.

5.1. Part 1: Old project data verification

As it is stated in the scope of the project, the thesis is based in the expansion of a properties predictive model for 3-layer films. Bearing in mind that, it is necessary to collect all the data of this project and then propose the new tool.

The predictive model for the 3-layer films of the last project done in 2017 collect the data or film properties from the 64 samples extruded, considering blends of maximum two different materials that are specified in Table 5.1. The blends are done with two different variables: the mass percentage of each material plus (or not) the additive and the thickness (from 100 to 200µm).

Table 5.1. Products used in the 3 layers model and its relevant properties for extrusion. (Own source)

Product	Density (g/cm^3)	MFR (g/10 min)
LDPE-1	0.921	0.25
LLDPE-1	0.905	0.80
EVA	0.941	0.70
IR-Add	1.580	-

This collected data needs to be the base of the new materials addition and for this reason needs to be verified. But, a verification of the results needs to be done.

In this case, several reasons drive to do a previous verification. Firstly, the *Extrusion Blown – Collin 30 mm*, showed in Figure 5.1, was the machine used for this monolayer samples. This machine has suffered different modifications and adjustments during the last five years, probably, due to the required maintenance or possible breakdowns, meaning that the extruded films can have differences. Secondly, the materials produced or not for the company are supposedly inside the quality margins, but the blends not, so it could be interesting to check it. Thirdly, the possible human errors done during the entire process (extrusion and testing) need to be reviewed, in this case, because a different operator is working on that. So, all these points ordered from high to low influence can play an important role in the variance of the results.

Figure 5.1. Extrusion Blown – Collin 30 mm similar to the Tarragona Pack Studios one. (9)

According to that, the decided way to develop the verification is to take fourteen of the total of samples and repeat the tests which data is collected. The selected samples are the ones that appear in Table AI.1 from Appendix I with the ID of verification, and the tests to evaluate are in the next Table 5.2. The tests are explained in Appendix II and in the next section 5.2.1.

Table 5.2. Tests to verify the last project data. (Own source)

Test name
DDI
Elmendorf
Creep
Tensile 23ºC
Haze
Transmittance
Thermicity

The basic idea once the data is compiled is analyze it and establish if there is any trend between the values of the old project and the new ones, and then updated it or not for the new model.

5.2. Part 2: New samples data collection

5.2.1. Samples definition

Once the results of the samples of the last project are validated, the next step is including the new materials that are going to be part of the model and then create a design of experiments in order to reduce the number of samples to extrude if it is necessary.

Basically, the new materials are variants of the PE structures and another HPC, in this case the EBA, as a replacement of the mostly used EVA. In the case of the LDPE, the new alternative material has been designed for the blown extrusion technique, having an excellent bubble stability and processability to large wide blown film applications such as agriculture. Regarding with the LLDPE, the new substance presents similar properties to the other linear polymer but with a lower price, remembering that both will be compared in terms of how good are replacing the EVA with the addition of the additive and if the cost of the film can be reduced or not.

In addition, two more materials will be added to the model only for the skins of the 5-layer films as it is commonly used in this type of solutions to improve the optics, generating a specialty option for the final model. These materials will be considered as a blend of LDPE and LLDPE in this case. The next Table 5.3 presents all the materials with its properties and the highlighted ones for the skins.

Table 5.3. New products to add in the model and its relevant properties for extrusion. (Own source)

Product	Density (g/cm^3)	MFR (g/10 min)
LDPE-2	0.921	0.25
LLDPE-2	0.918	0.85
EBA	0.924	1.50
*LDPE-3	0.923	0.75
*LLDPE-3	0.916	1.00

With the selected materials, the next step is to consider the specifications for the samples to extrude for the model. The main specifications are:

- Blends of maximum two different materials (with addition or not of the IR Additive).
- Thickness: 100, 150 or 200µm. For the EBA blends, the thickness of 200µm is replaced by 50-75µm.
- Percentage of mixture: 100-0%, 75-25%, 25-75% or 0-100%.
- Percentage of IR-Additive: 0%, 4% or 8%.

These values are quite similar to the ones used for the last 3-layers model, but reduced in order to limit the number of samples to be extruded. The blends to extrude are available in the next Table 5.4.

Table 5.4. Mixtures of the materials to extrude for the model. (Own source)

LDPE+LLDPE	EBA	Skins
LDPE-2/LLDPE-1 LDPE-2/LLDPE-2	EBA/LDPE-2 EBA/LLDPE-1 EBA/LLDPE-2	LDPE-3/LLDPE-3

The blends selected are the most frequent and interesting ones used for the application in the 5-layer films for greenhouses, so not all combinations will be predictable. This is one of the principal limitations of the model.

According to the number of blends and specifications, a total of 216 samples are calculated. Since this is a huge number of samples to extrude and characterize and for this reason different criteria are used to reduce it:

- Replications: pure samples (100-0%) that are repeated for the different blends and the case of LLDPE-1 which values are available from the old project. A total of 63 samples are neglected.
- Additive predictability: samples with IR Additive which optical and thermal properties are predictable and the mechanical properties are quite similar to the mixture without it. Only one sample for the different percentage of mixtures at one thickness. A total of 25 samples are neglected.
- Additive in EBA blends: the samples which have EBA will have less addition of additive but for some of it is interesting to see how both work together. A total of 35 samples are neglected.
- Additive in skins: the samples designed for the skins do not have additive because the main use is for having good optical properties. A total of 24 samples are neglected.

Finally, the total of samples to extrude is 69, available in the Table AI.2.

5.2.2. Extrusion and characterization

Having the samples chosen, the next parts are the extrusion and the characterization in the lab. The extrusion follows the same conditions as the verification samples, available in Table 5.5, in order to maintain the properties of the films and change only the materials. This consideration is very important because the orientation of the molecules once the film is extruded depends a lot on these conditions.

Table 5.5. Extrusion conditions during the production of monolayer blown films. (Own source)

Property	Value
Output rate (kg/h)	7
Screw (rpm)	50-70
Extrusion speed (m/min)	1.4-2.7
Die diameter (mm)	60
Die gap (mm)	1.20
Bubble diameter (mm)	150
Blow up ratio (BUR)	2.50
Film width (mm)	235
Temperature profile (^oC)	180-240

In the case of the testing, there are many important properties in a plastic film, but in the case of the greenhouse application the most important properties are defined by the European Norm for GH AG films 13206 2017 + A1. This European Norm says that agricultural films used in Europe should follow the requirements set on the standard *Plastics – Thermoplastic covering film for use in agriculture and horticulture – Requirements and test methods, conditions for installation, use and removal, EN 13206* specifying the requirements related to dimensional, mechanical, optical and thermal characteristics of films used for covering permanent or temporary greenhouses and tunnels. (3)

Then, the principal idea for the model is to get created to predict these normalized properties, which standards are available in the next Table 5.6 for films from 100 to 200µm.

Table 5.6. European Norm requirements for thermal clear films used in greenhouses. (3)

Characteristics	Units	Nominal thickness		
	µm	100[1]	150[2]	≥ 200
Dimensional				
Tolerance of average thickness	%	5%		
Mechanical				
Tensile stress at break (MD[3], CD[4])	MPa	≥ 20		
Tensile strain at break (MD, CD)	%	≥ 400	≥ 450	≥ 550
Impact resistance (flat area)	g	≥ 350	≥ 500	≥ 650
Elongation under a steady load (MD)	%	≤ 30		
Optical				
Visible light transmission	%	≥ 90	≥ 88	≥ 88
Haze	%	≤ 25	≤ 30	≤ 30
IR effectiveness	%	≥ 55	≥ 65	≥ 75
Comments [1] 100µm ≤ nominal thickness < 150µm. [2] 150µm ≤ nominal thickness < 200µm. [3] MD refers to the direction of the film equal to the extrusion one. [4] CD refers to the perpendicular direction of the extrusion one of the film.				

According to that, the selected tests for the 69 samples are: Tensile, Dard Drop Impact, Creep, Elmendorf, Light Transmission, Haze and Thermal effect. All the tests are detailed and explained in Appendix II.

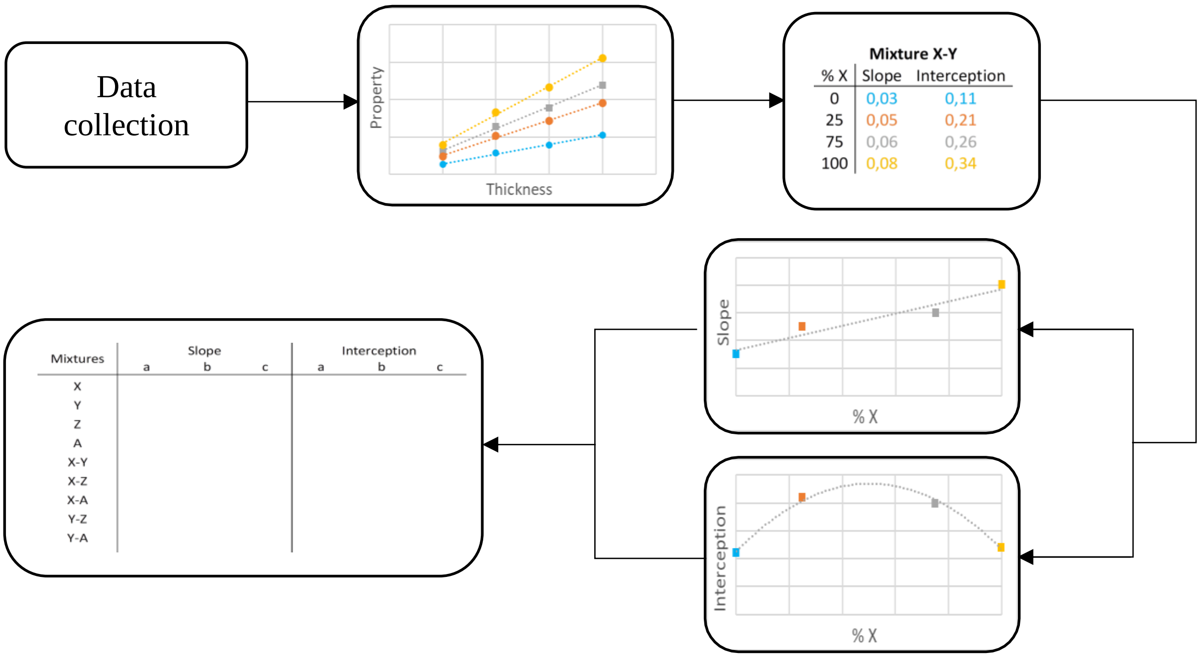
5.3. Part 3: Model construction and final validation

5.3.1. Model construction

All generated data is separated by the different properties measured, some of them depending on the direction of the film (MD or CD). So, the next step of the project is to extract the necessary information from this data and make it useful to build the model, based principally in correlations.

As mentioned before, the % of each component in the mixture and the thickness are the two principal variables of the tested samples. To predict the properties for these mixtures at a certain thickness is necessary to do a double correlation, one for each variable, and it is important to decide which the first one is. In this case, the first one is the thickness, because in most of the tests is measured and there is a certain discrepancy with the theoretical value due to the extrusion process and the cooling of the film in the bubble. Conversely, the mass percentage of each material in the mixture is very difficult to measure and usually is considered as very exact due to good mixing practices.

Once the thickness has been decided to be the first variable to correlate, the procedure follows the next steps for each property, as it is shown in the next Figure 5.2 (the values are not related with the graphs):



Mixture X-Y

% X	Slope	Interception
0	0,03	0,11
25	0,05	0,21
75	0,06	0,26
100	0,08	0,34

Mixtures	Slope			Interception		
	a	b	c	a	b	c
X						
Y						
Z						
A						
X-Y						
X-Z						
X-A						
Y-Z						
Y-A						

Figure 5.2. Flow diagram that represents the data analysis steps to predict the properties. (Own source)

1. Correlate the results with the thickness at the same percentage of mixture using a linear method. This will generate a slope and interception in the origin values for each percentage.
2. The slopes and the interception points will be correlated with the % of this mixture independently, using a lineal or parabolic method (necessary for not linear cases). Consequently, two functions that depend on the % of mixture are available, one for the slope and the other one for the interception point.
3. Finally, the coefficient results are tabulated for the different blends and the pure components.

Then, it is important to define how the model will predict the different properties of the films with the correlations detailed previously. Basically, the 5-layer films will be treated as films composed by 5 monolayers and each layer will contribute in each of the properties, calculating first the values for each layer and then doing the total sum. This additive way to predict the model is based on the total thickness of the film and the layer distribution (volumetric percentage for each layer) as well as the mixture selected. The next Equation 5.1 gives an example of how the layer properties are calculated.

$$Property_{layer\ 1} = (slope \cdot thickness_{total} + interception) \cdot \%_{layer\ 1} \qquad \text{Equation 5.1.}$$

According to that, the prediction requirements to make the model work are (the order is not mandatory because of the automatization of the Excel software):

- Define the blends by filling the percentage of each one to a total 100%. The model will alert if the two-material blend introduced plus or not the additive is predictable or not (depending on whether the samples are extruded or not). This step will automatically generate a line equation with the slope and the origin point interception predicted by the correlation commented before and available in Equation 5.1.
- Introduce the layer distribution desired. Usually this is a symmetric parameter and a clear example is 10/20/40/20/10 in volumetric %.
- Establish the total thickness of the film. With the line equation produced by the % of the materials in the mixture, the model calculates the property result in these conditions.

Once the parameters are completed, the model calculates each of the properties for the hypothetical film as it has been said: using an additive method based in the sum for each layer. Apparently, and the 3-layer model designed shows it, this method accuracy depends on the property predicted, considering that in this case an increase in the possible errors is inside the capabilities of the methodology.

5.3.2. Final validation

Having the model created and ready to predict, the best way to check that these supposed predictions for the properties are coherent in comparison with the real properties of the films is with the extrusion and characterization of a certain number of 5-layer films. This validation will contain samples with the materials used in the model and then the final comparison of the prediction and the measured values for these formulations. With a final evaluation of the model for the different properties of the films, some possible corrections can be considered.

Following with that, it is important to keep in mind the reproducibility of the model, related with the mixtures and characteristics of the monolayer films or the extrusion conditions used to build it. For these reasons, several considerations in both parts must be taken in order to cover the wider area of validation possible with the multilayer films.

Regarding with the characteristics of the monolayers, the considerations that are going to be explained below are attached to the number of 5-layer films decided to extrude and characterize, which structure is available in Figure 5.3.

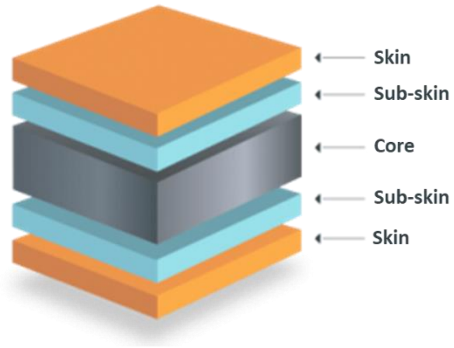


Figure 5.3. Structure and layer distribution of a 5 layer film. (Own source)

In this case, a total of 20 samples will be necessary: 10 different formulations at two different thicknesses. One of the considerations is related with the materials and distribution among the layers. It is explained with the different parts:

- Skins: mixtures rich in LDPE with LLDPE. The IR additive is not used.
- Sub-skins: mixtures of LDPE and LLDPE to increase the elasticity and flexibility of the film. The IR additive is not commonly used but can be added.
- Core: use of the HPC or the LLDPE (or mixtures of both) plus the IR additive to maintain good mechanical properties and have the necessary thermicity for greenhouses.

The priority for the validation is the variety of materials used in the core. The first purpose was the distribution of the materials in the core: 3 mixtures have EVA, 3 more have EBA and the 4 remainder have the IR additive with LLDPE. Due to logistics and planning problems, the IR additive was not able for the extrusion of these samples and then the distribution in the core is the next one: 3 mixtures have EVA, 5 have EBA and the 2 remainder have pure LDPE or LLDPE.

Other considerations are:

- Layer distribution: the most used volumetric distribution is 10/20/40/20/10, but sometimes the alternative of 15/30/10/30/15 is used, and 2 formulations have this one. The other 8 are maintaining the first one.
- Skin specialty: the special materials only for the skins are used in 3 of the formulations and the 7 remainder are using the rest of the detailed materials.
- Asymmetry between skins and sub-skins: is an alternative in some applications and for this reason 3 asymmetric formulations are included. The other 7 are symmetric.

- Thickness: the most common range in European regions is around 150 and 200µm, so these are the thicknesses used in each formulation.

All the considerations are used to create the different samples for the validation available in the Table AI.3.

In the case of the extrusion conditions, the importance remains in adjusting the parameters to the scale-up of the machine used. In this case, the selected machine is the *Coextrusion Blown – Collin 9L*, working in a 5 layers mode, represented in Figure 5.4, which is the directly next stage in blown extrusion machines because can produce lab scale samples at higher output rates with more than one extruder (multilayer structures).

Figure 5.4. Coextrusion Blown – Collin 9L similar to the Tarragona Pack Studios one. (10)

To make the model reproducible, it is essential to maintain the proportionality of the monolayer films done in a smaller machine with the multilayers ones and this is adjusted by the blow-up ratio, which contemplates both properties of the machine and the extruded bubble. Then, this value is maintained at 2.5 which is the mostly used in the agricultural sector. Taking into account this consideration, the other conditions are adjusted following the necessities of the samples: layers distribution, materials, etc. The values are available in the next Table 5.7.

Table 5.7. Extrusion conditions during the production of multilayer blown films. (Own source)

General Property	Value
Total output rate (kg/h)	22
Extrusion speed (m/min)	2.3-2.7
Die diameter (mm)	100
Die gap (mm)	2.2
Bubble diameter (mm)	250
Blow up ratio (BUR)	2.50
Film width (mm)	398
Skin Layer Extruders (x2)	**Value**
Output rate (kg/h)	2.2
Screw (rpm)	50
Temperature profile (^oC)	200-240
Sub-skin Layer Extruders (x2)	**Value**
Output rate (kg/h)	4.4
Screw (rpm)	100
Temperature profile (^oC)	200-240
Core Layer Extruders (x3)	**Value**
Output rate (kg/h)	2.9
Screw (rpm)	130
Temperature profile (^oC)	200-220

As it can be seen, the biggest differences remain in the use of different extruders. The machine has nine and in this case seven are used: 2 for the skins, 2 for the sub-skins and 3 for the core (considering the 10/20/40/20/10% layer distribution). Another important point is the temperature profile, adapted for each of the densities and melt index of the materials of the blends, for this reason the value is given as a range.

With the extrusion done, the samples are ready to be characterized in the laboratory with the same tests as the monolayers and then collect the data for the validation. This validation will allow the model to be trained with raw data and ready to predict properties at these conditions with a certain error margin.

6. RESULTS AND DISCUSSION

This section presents the results obtained from the characterization of the monolayer films, the multilayer films, and the final results for the predictive model. For this reason, it is structured in three different parts following the experimental plan procedure. The most important observations and comments for the results obtained will be mentioned, and then all the rest of the data will be available in Appendix III.

6.1. Monolayer films

In the case of the monolayer films there are two different things to check. On the one hand, it is important to verify the data from the 3-layers project in order to include it in the new model of 5-layers. On the other hand, it is necessary to comment the results obtained with the new materials used as well as to compare it with the ones that are replacing as alternatives.

6.1.1. Old project data verification

As it is introduced in the methodology, 14 of the 64 monolayer samples for the 3-layers project were extruded and characterized again to check and verify if there are important changes in the results and update them if it is necessary. Basically, the idea is to compare both results and try to find different tendencies between them.

For the comparison, the tests shown as example are Elmendorf, Creep elongation, Total Haze and Thermal effect. As it was suggested previously, the different factors considered during the extrusion process and the characterization have a clear impact in most of the results for the selected tests. In the next Figures 6.1, 6.2, 6.3 and 6.4 the results are shown, and different comments are extracted from them.

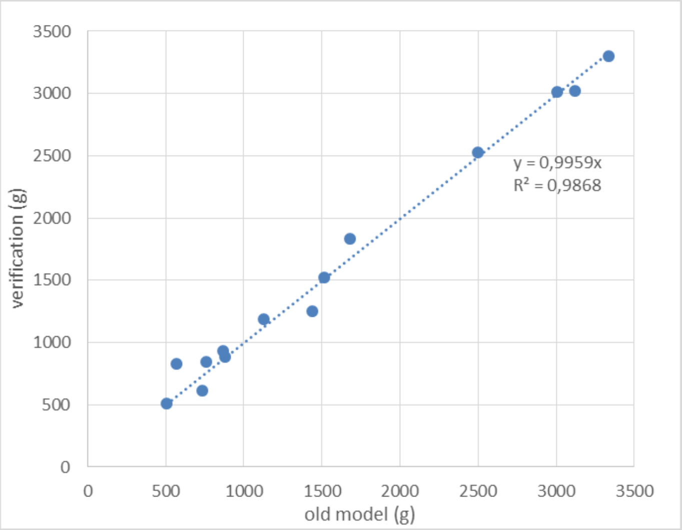


Figure 6.1. Elmendorf Tear in CD results comparison for the 3-layers (old model) and the new 5-layers project (verification).

For the Elmendorf Tear the results are practically the same as it is shown in the slope for the linear correlation, in fact, together with some of the optical and tensile properties, is the one with the highest similarity. According to that, the data collected for these properties can be used directly for the new model. Another example with high similarity is the Creep elongation shown next.

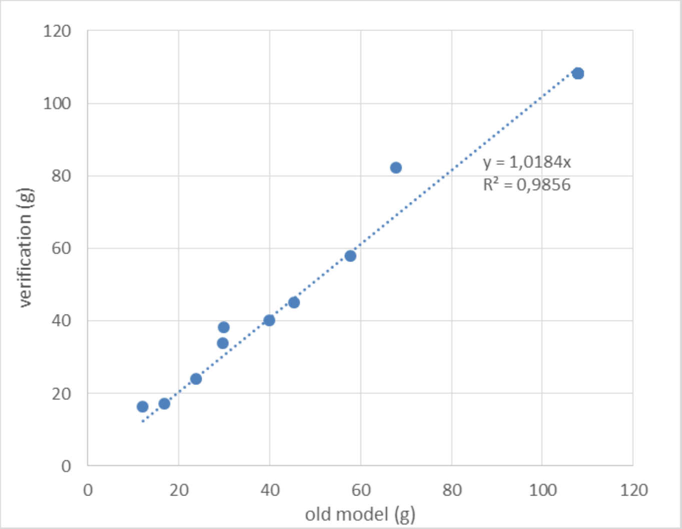


Figure 6.2. Creep elongation results comparison for the 3-layers (old model) and the new 5-layers project (verification).

Again, the slope shows a 1.84% of change between both projects, meaning that the values are very similar.

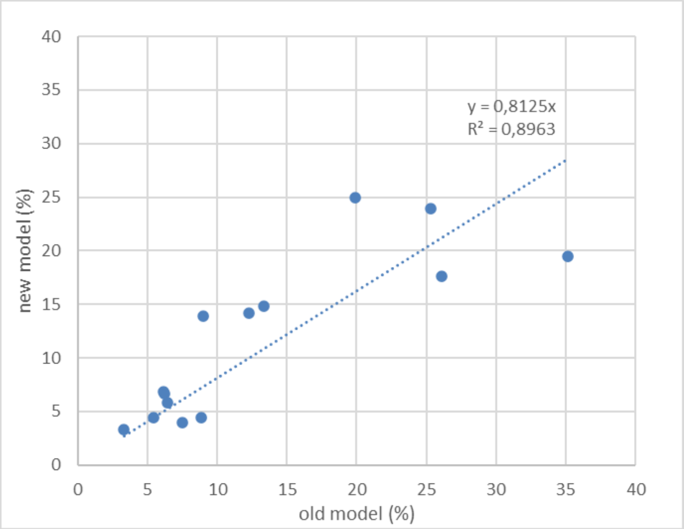


Figure 6.3. Total Haze results comparison for the 3-layers (old model) and the new 5-layers project (verification).

Following with the optical properties, the Total Haze offers a high discrepancy between the results of both projects. Whereas the other properties are showing differences within an expected range (± 5%), this property and the DDI have not the same behavior. Considering the fact that the haze is very sensitive to the extrusion parameters and the conditions of the die, the reasons for the discrepancy of the results can be related with some irregularities in the internal or external face of the extruded films, and the same applies to the impact resistance (DDI). Even though, the new results have a tendency with the old ones and it can be used to update and include them in the model.

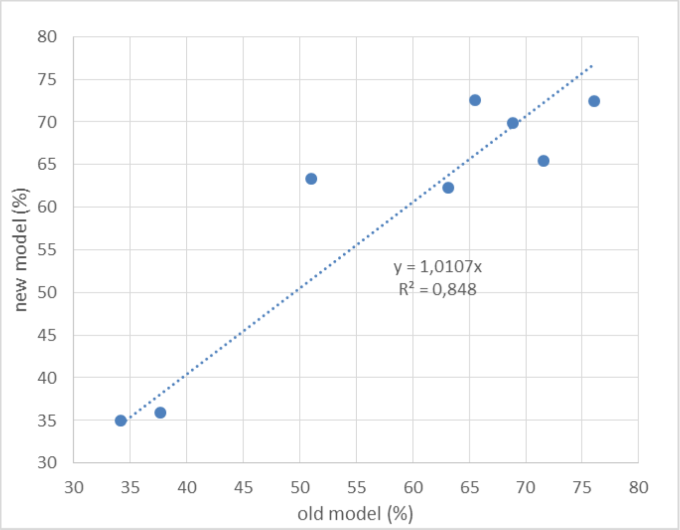


Figure 6.4. Thermal effect results comparison for the 3-layers (old model) and the new 5-layers project (verification).

The last property to verify is the Thermal effect. In this case, although there is an existing difference between the 8 samples selected, the ones with the materials that have more influence in this property like EVA or the IR-Add, the values are inside the variability range expected. In this case, the samples with the IR additive show bigger errors than the other materials, assuming that the thickness has a high influence in this property.

After the necessary verification of the results and understanding where the differences between the values come from, the next step is to update the collected data and then include it in the new model to use it for the prediction of the multilayer films properties. The next Table 6.1 shows the corrective factors (slopes of the linear correlations) used in the 3-layers data to renew the results.

Table 6.1. Corrective factors used to update the 3-layers model data (old model).

Property	**Stress at Break MD**	**Stress at Break CD**	**Strain at Break MD**	**Strain at Break CD**	**Dart Drop Impact**	**Creep**
Corrective factor	1.0163	1.0895	0.9692	1.0032	1.2585	1.0184

Property	**Transmittance**	**Haze**	**Thermal effect**	**Elmendorf tear MD**	**Elmendorf tear CD**
Corrective factor	1.0146	0.8125	1.0107	1.0137	0.9959

Considering the same assumption for the different tests, in general the variation is not surpassing the 10% except for the DDI and the Haze as it has been said before. After the modification, the data is ready to be part of the model.

6.1.2. New samples data collection

The second part of the analysis of results for the monolayers considers the new resins to be included in the model as well as the different blends made between them. The discussion of these results will focus on comparing the values of the main properties measured for the different alternatives proposed, both to replace EVA and the new options of LDPE and LLDPE. To have a better perspective of what will be all the options available in the model, the resins used in the previous model (3-layers one) are included in the different attached graphs.

Mechanical properties

Taking mechanical properties as the starting point, it is important to remember the high performance of LLDPE-1 and EVA in terms of elasticity, flexibility and resistance to the impact and the tear. Mentioning the impact resistance, the results shown in Figure 6.5 below show how each resin responds to this test at the same value of thickness.

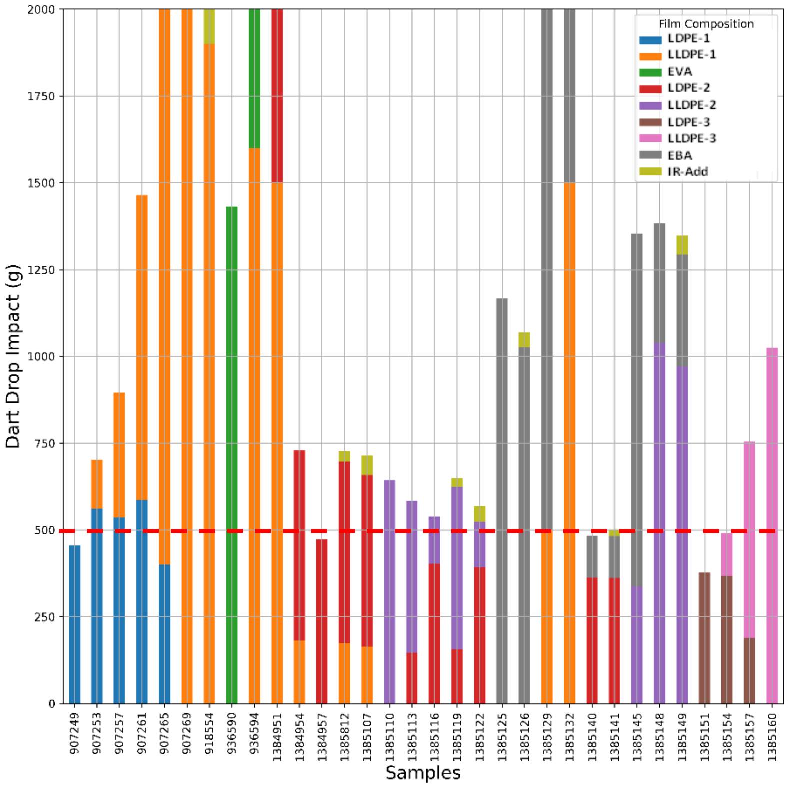


Figure 6.5. Dart drop impact in the flat area results for the different monolayer samples at 150μm. The dashed line shows the value of the standard.

As expected, the difference between comparing pure LLDPE-1 and LLDPE-2 is quite large, but if they are mixed with other materials, the difference is reduced. In the case of LLDPE-1, its value can reach the limit of 2000g that allows the test both in pure state and mixed with other materials such as any LDPE or HPC. On the other hand, LLDPE-2 is not able to reach the requirement of the standard of 500g when pure, however, if it is mixed with a certain percentage of an elastomer such as EBA, its resistance can exceed twice the value.

Comparing the EVA with EBA, the first one has better results but they are not very different from those of the second one, besides, both meet the suggested limit.

Finally, if the samples which have the IR Additive in the formulation are compared with the ones that do not have it (same blends and the same %), results are practically unchanged, suggesting the idea that in the model the percentage of additive added will have no impact in the mechanical properties. In fact, the same conclusion can be extracted for the creep or the tensile tests.

Continuing with the tear resistance, in this case the assumption of evaluating only the samples without IR-Add was taken. The next Figure 6.6 gives the results for this property in the MD at the same thickness.

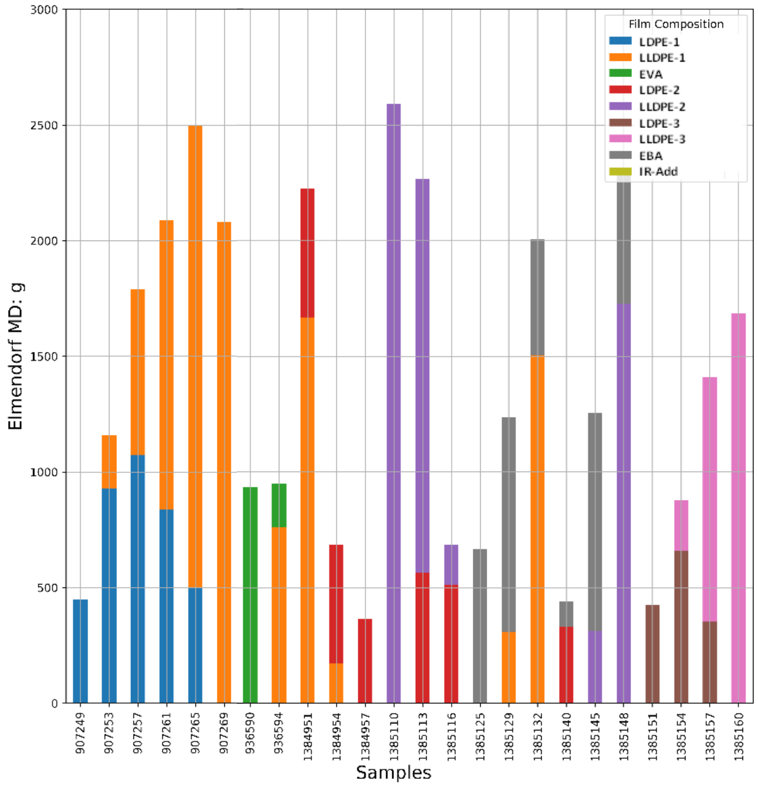


Figure 6.6. Elmendorf tear in MD results for the different monolayer samples at 150µm.

For this property, the difference between LLDPE-1 and LLDPE-2 is not very large, with the second having greater resistance in this case. In fact, in this case LLDPE-2 is also better if mixed with other materials, as the main peaks in the graph belong to blends with this resin. One of them is EBA, which, if blended with either LLDPE can reach higher values than EVA blends.

As for LDPE, both LDPE-1 and LDPE-2 show very similar results, since their density and melt index are the same. Therefore, in terms of mechanical properties it does not matter to use one or the other. According to that, the alternatives suggested may represent a new option for multilayer films applied to greenhouses, remembering that other variables such as cost may play a determining role in the materials choice.

Optical properties

Related to the optical properties, while for Light transmission all resins or blends offer quite similar values, with the IR additive being the most affected but not below the limit established by the European Norm, the property that changes the most is the Total haze. The following Figure 6.7 shows the results for this property at a thickness of 100 microns.

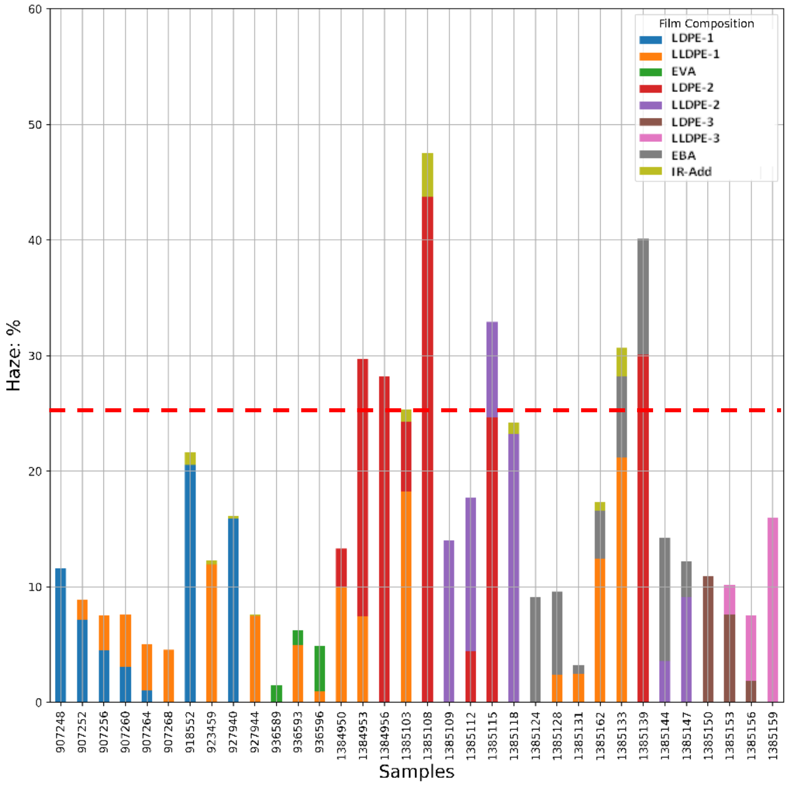


Figure 6.7. Total haze results for the different monolayer samples at 100µm. The dashed line shows the value of the standard.

Without any doubt, as the graph shows, the most determinant material for this property is LDPE-2. Of the six samples that exceed the stipulated limit for this thickness, five of them contain it and the other one exceeds it due to a high percentage of IR additive in its formulation. Although this material is known for its high processability and ability to stabilize the bubble during extrusion, it is also known to generate significant irregularities on the film surface, which leads to higher light diffusion values. Knowing this particularity, the option of using blends between LDPE-3 and LLDPE-3 was proposed, because is currently the best alternative to improve the optical properties of multilayer films as demonstrated by their results in the last four bars of the graph.

As far as the IR-Add is concerned, it is able to increase the light diffusion through the film but in general without exceeding the limit, which is clearly what is most desired. It should be remembered that light diffusion is one of the most interesting properties of a greenhouse depending on its location, since light does not impact directly on the crops.

Thermal properties

Last but not least, the results obtained for the Thermal effectiveness, available in Figure 6.8 below, should be analyzed.

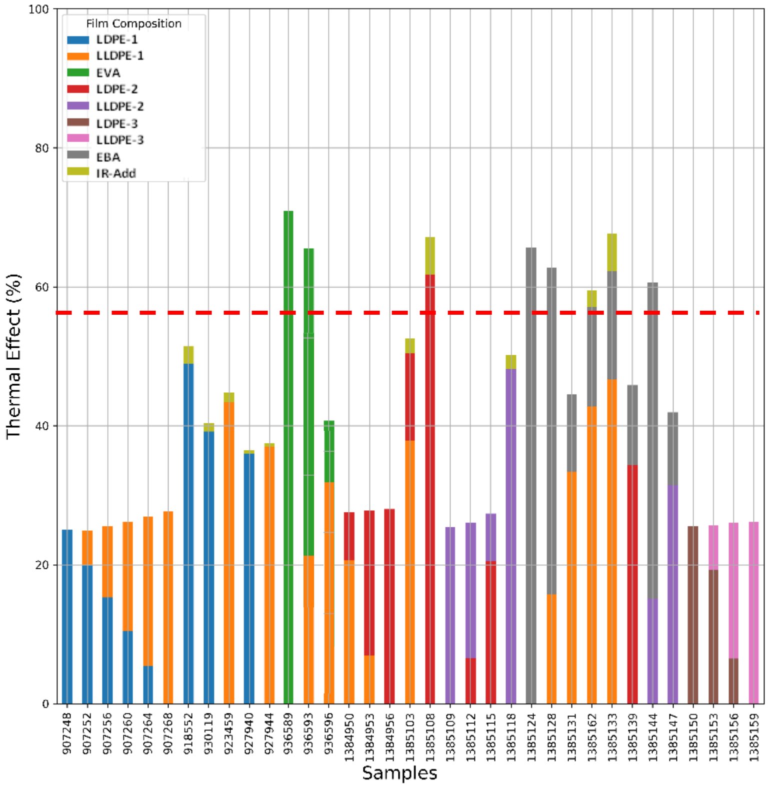


Figure 6.8. Thermal effect results for the different monolayer samples at 100µm. The dashed line shows the value of the standard.

As expected, the results are totally dependent on the level of EVA, EBA or IR Additive contained in the blends, as for LDPE or LLDPE they are practically the same due to the fact that they are two variants of polyethylene.

Comparing EVA with EBA, the first one shows slightly higher values, but both can fulfill the EN requirement for the thermicity at 100µm even if they are blended with other PE resins, having at least the 50% of the mass composition. In the case of the IR additive, its impact is very satisfactory, since with an 8% it is possible to exceed the limit established for 100µm films, which in general are narrower than those used on the market. Therefore, and as can be seen in the results tables, for thicker films (150-200 microns) its impact is even more effective.

Again, it is shown that the materials proposed to replace the use of EVA in one of its most relevant properties work well and should therefore be considered for multilayer films.

6.2. Multilayer films

After performing the characterization of the monolayer films, the next step is to perform the same analysis for the multilayers. In this case, considering that the formulations of these films are a mixture of those made for the monolayers, the most important comments and observations will be extracted from the results, depending on the fact of putting one material or the other in the core or in the skins, for example.

Mechanical properties

Starting with the mechanical properties, more specifically with the tensile, it can be interesting to check the results for the Stress at break and the Strain at break properties in the MD of the film, because normally for greenhouse films in this direction the values are lower and for this reason it is the limiting one. The results for both properties are available in the next Figure 6.9.

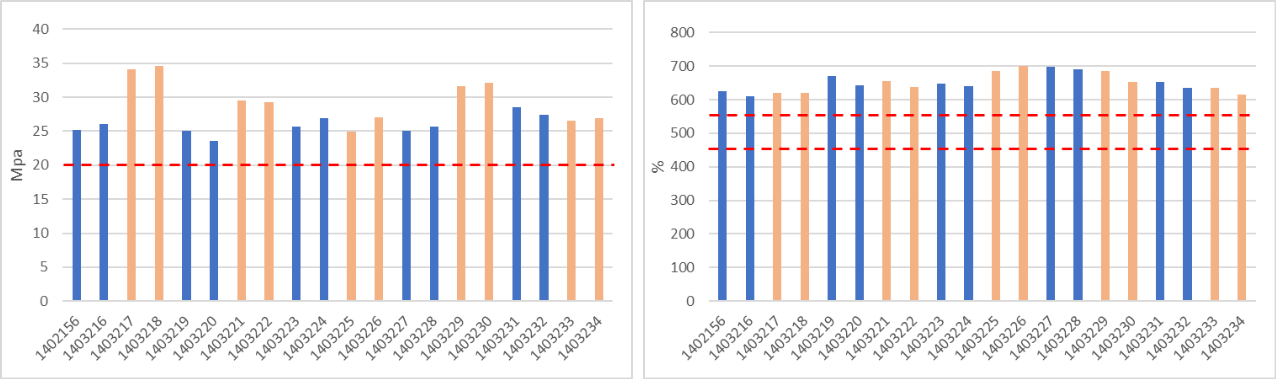


Figure 6.9. Stress at break and Strain at break results in MD for the multilayer films. The dashed lines show the value of the standard at different thicknesses.

As it is represented and considering that for the different formulations the thickness difference has not a high impact in these two properties, in general, all the samples are above the limits required. In terms of materials, samples with more LLDPE-1 have greater values for Stress at break than the samples with LLDPE-2 or EBA, which tend to have higher elongation values at break. This higher elongation can have a direct impact in the Creep results, available in the next Figure 6.10.

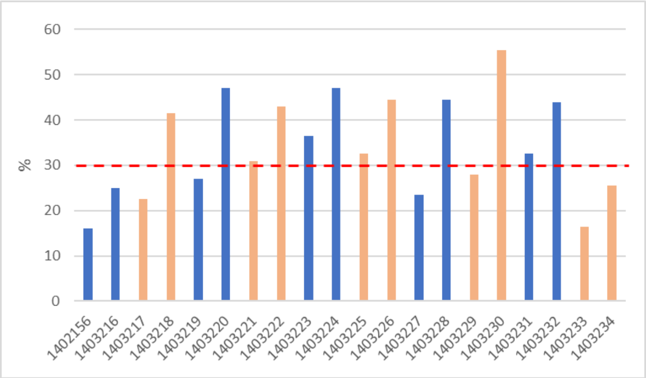


Figure 6.10. Elongation results for the creep test done for the multilayer films. The dashed line shows the value of the standard.

Considering that most of the samples with a thickness of less than 200µm are out of the European requirements for the proposed formulations, in general terms, samples which have a certain level of LLDPE in the different layers of the structure tend to rich the maximum value proposed by the European Norm. The clear examples are samples 1403223 and 1403224, which have a total of 12% of LLDPE-1 in the structure but a 20% in the skins and sub-skins, and for that reason, the values are higher than the maximum required like in sample 1403230 as well, with pure LLDPE-2 in the sub-skins. The best way to reduce this elongation is by the addition of a LDPE to the mixture, like in sample 1403227 for example.

Referring to the impact, and remembering the results obtained from the monolayers, in which the LLDPE-1 has the highest influence, it is time to check how the distribution of the materials affects this property, available in the next Figure 6.11.

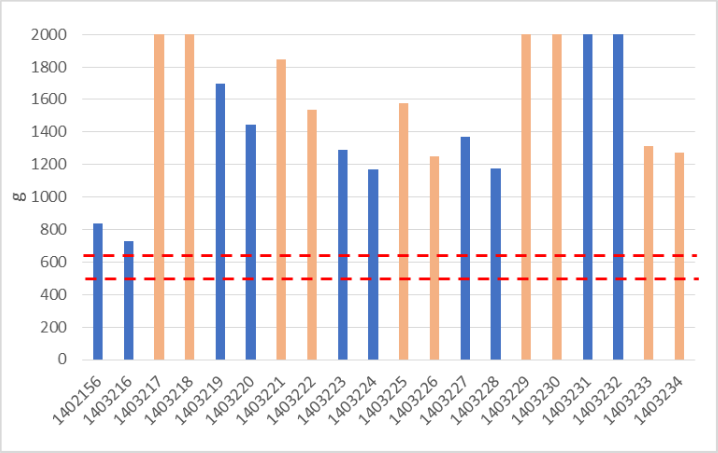


Figure 6.11. Dart drop impact in the flat area results for the multilayer films. The dashed lines show the value of the standard at different thicknesses.

As expected, samples with a layer of pure LLDPE-1 or samples with blends of this material or LLDPE-2 in their structure tend to reach or to be near the maximum 2000 g allowed by this test. However, samples with LLDPE-2 and EBA have lower values than the previous ones but are fulfilling the European Norm requirements as well, which means that can suppose a clear alternative to the firstly suggestion for the EVA replacement.

In reference to the previous comment, this effect can also be observed in the tearing property in both MD and CD directions. Once again, the fact of having these two materials in the same sample increases its resistance values, especially if the EBA is in the core of the film. The next Figure 6.12 shows the results, with special emphasis on samples 1403219, 1403220 and 1403229, 1403230.

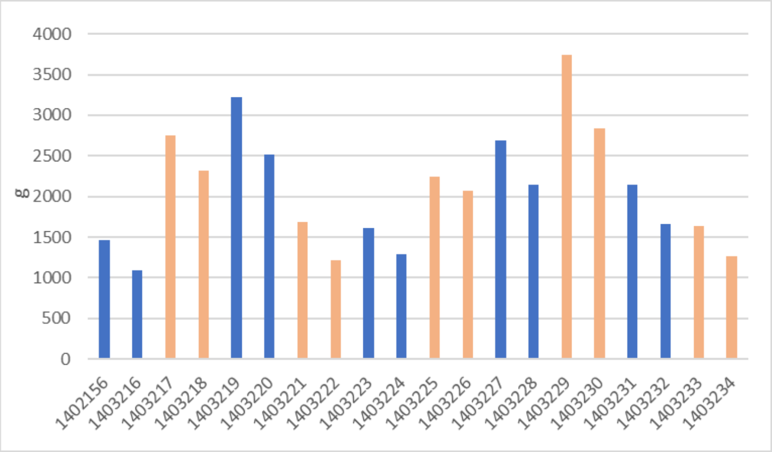


Figure 6.12. Elmendorf tear in MD results for the multilayer films.

Optical properties

Referring to the optical properties, it should be remembered that the requirements of the standard are for the thermal clear films group, which means having a high Light transmission value as well as a certain limit on diffusion. In the case of the light transmission, all the results are around the 90-91%, which is higher than the minimum required that in this case is 88%. According to that, the influence of the materials distributed in the different layers is practically the same for all the used ones. However, in the case of the Haze, there is a clear impact in the results depending on the resin used. The next Figure 6.13 presents the results to understand the previous explanation.

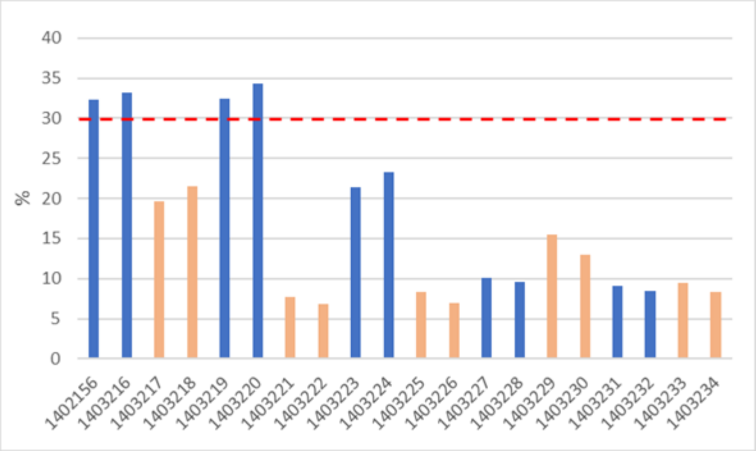


Figure 6.13. Total haze results for the multilayer films. The dashed line shows the value of the standard.

As shown in the graph, the samples with higher values of Haze, four of them surpassing the limit suggested, are the ones that have a blend containing LDPE-2 in the skins (1402156, 1403216, 1403217, 1403218, 1403219, 1403220, 1403223, 1403224). Therefore, although this resin helps in terms of the stability of the bubble, it is better not to use it for skins, and consider the LDPE-1option that is not producing irregularities in the surface.

In contrast, if for example the skins are composed of the blend of LDPE-3 with LLDPE-3 (1403221, 1403222, 1403225, 1403226, 1403227, 1403228), the results are much improved as expected, decreasing the light diffusion and creating a better option for this type of films.

Thermal properties

In the case of the thermal effectiveness of the films, remembering that the IR additive could not be used for these samples, the results are completely dependent on the percentage of HPC (EVA/EBA) they contain, as it is represented in the next Figure 6.14.

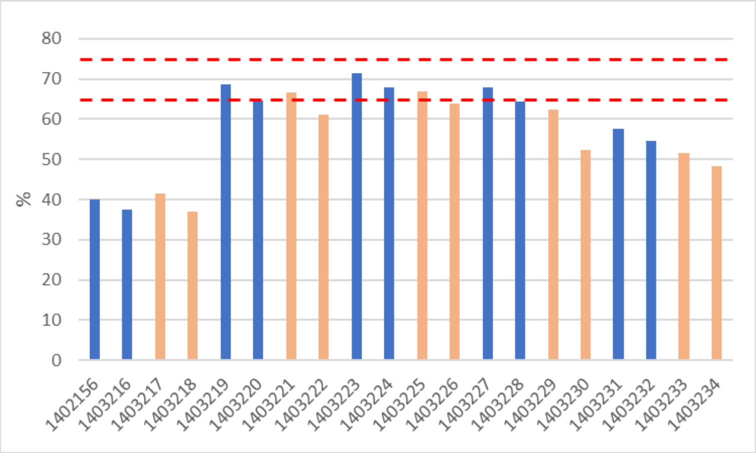


Figure 6.14. Thermal effect results for the multilayer films. The dashed lines show the value of the standard at different thicknesses.

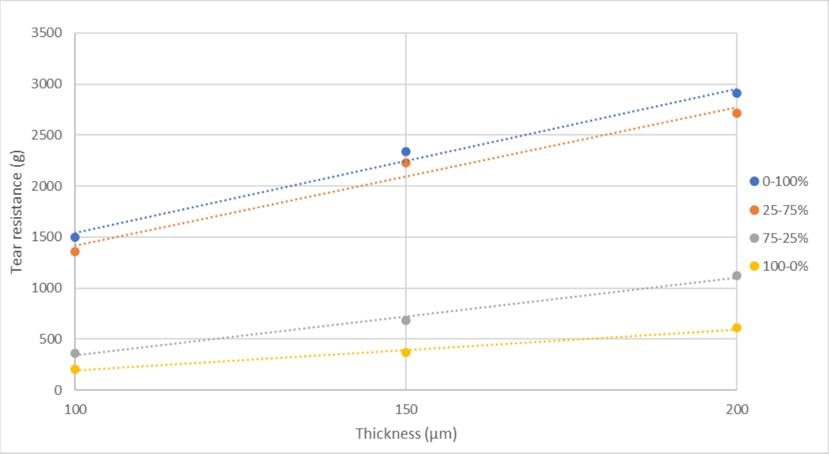
As expected, having more EVA or EBA provides higher thermal effectiveness, with EVA samples being slightly higher than EBA ones, as observed in the monolayers. Another important think to consider is that very few samples (thicknesses of 175µm) reach the value proposed by the standard, which means that the percentage of HPC in the formulation should probably be increased or the IR additive should be used in small percentages to guarantee the minimum required.

6.3. Predictive model and final validation

6.3.1. Model construction

Once the data of all the monolayers is analyzed and organized, is ready to start with the multivariable correlations. As it is stated in the methodology, the idea is to first correlate each of the properties of each blend with the thickness, and then, the results of the slopes and intercept point are correlated with the percentage of one of the materials.

After the previous explanation, the results will serve to better understand the methodology as well as the difference that exists for each of the properties. Two examples of properties will be discussed here, considering and the rest has the same procedure. The first example is for the Elmendorf tear in the MD. This property presents a high linearity when correlated with thickness, as can be seen in Figure 6.15 below, in this case for the blend of LDPE-2 with LLDPE-1.



% LDPE-2	Slope	Interception
0	15.70	-128.16
25	14.84	-149.00
75	5.73	-105.80
100	3.05	-47.17

Figure 6.15. Elmendorf tear MD correlation example with the thickness for the LDPE-2 and LLDPE-1 blend. The % of mixtures are following the previous order.

After checking that there is indeed a good linear correlation between the different values, the table on the right is created to have available the values of the slope and the point of interception. After this, the next step is to apply the second correlation, in this case with the percentage of LDPE-2 contained in the blend. The results for both values are available in Figures 6.16 and 6.17 below.

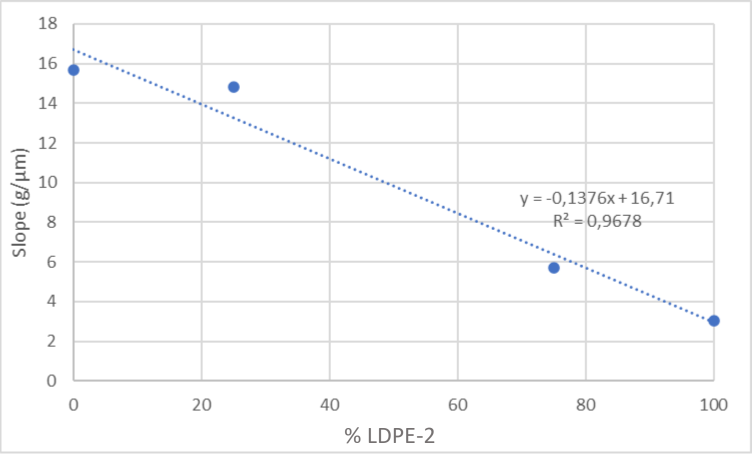


Figure 6.16. . Slope values for the correlation with the % of LDPE-2 of the LDPE-2 and LLDPE-1 blend.

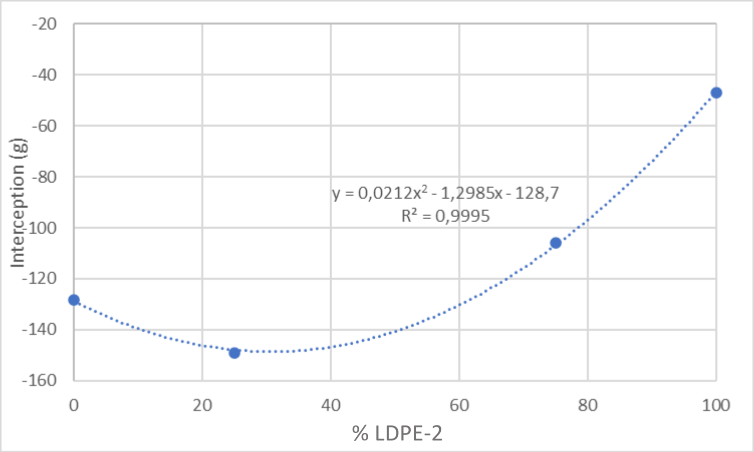
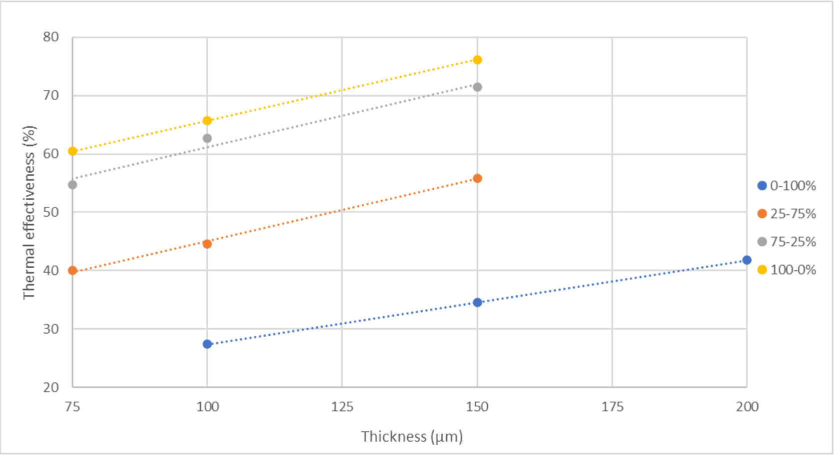
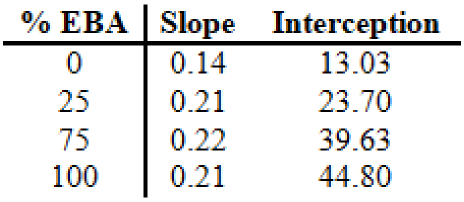


Figure 6.17. Interception values for the correlation with the % of LDPE-2 of the LDPE-2 and LLDPE-1 blend.

As can be seen, the slopes fit quite well to a straight line, while the interception points fit better to a second-degree polynomial. This is true for many of the properties analyzed, in fact, it is difficult to find a property that has two linear fits for slopes and interception points. As a second example, a property where exactly the opposite occurs is going to be proposed to verify the previous comment. Now, the property is the Thermal effectiveness for the EBA and the LLDPE-1 blend and the correlations are available in the next Figure 6.18.





% EBA	Slope	Interception
0	0.14	13.03
25	0.21	23.70
75	0.22	39.63
100	0.21	44.80

Figure 6.18. Thermal effect correlation example with the thickness for the EBA and LLDPE-1 blend. The % of mixtures are following the previous order.

As it was expected, the Thermal effect property shows a high linearity as well when is correlated against the thickness. In this case, the addition of EBA to the blend has a great impact, because the values are increasing in a proportional but not constant way, as can be seen in the distances of the different straight lines. Again, once the values that define the line equations are tabulated, the correlation with the % of EBA is done. The results for both values are available in Figures 6.19 and 6.20 below.

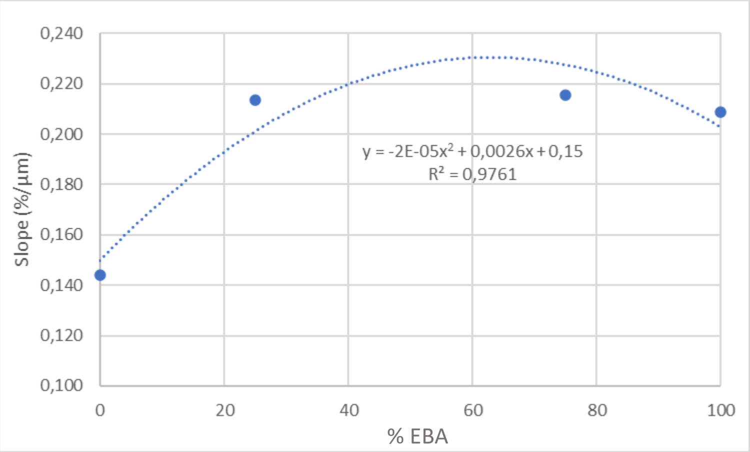


Figure 6.19. Slope values for the correlation with the % of EBA of the EBA and LLDPE-1 blend.

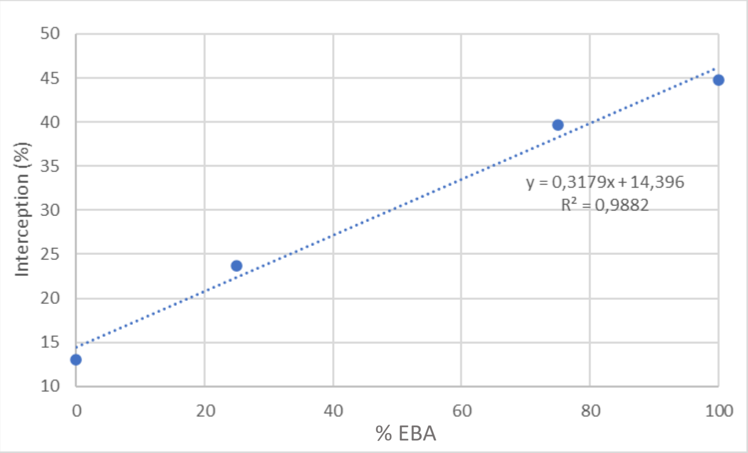


Figure 6.20. Interception values for the correlation with the % of EBA of the EBA and LLDPE-1 blend.

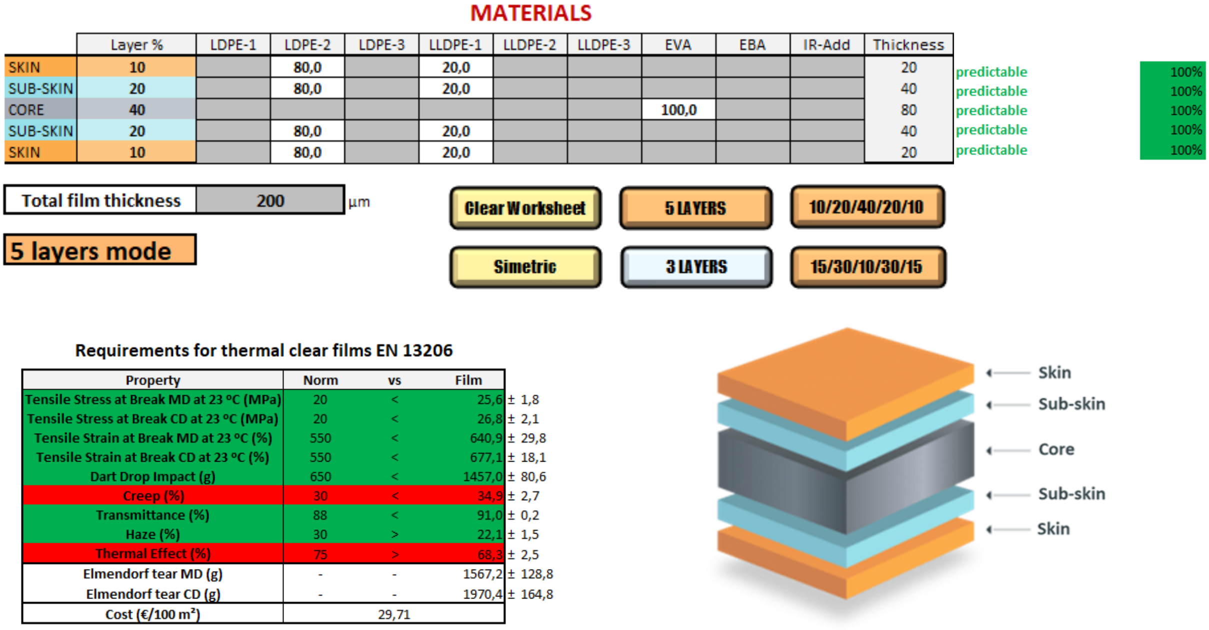
In this case, the slopes tend to have a more parabolic shape as shown in the first figure, and conversely, the interception points have a clearly linear trend. The idea then is to study the tendency that better adjusts both values for each property and blend. After performing all these correlations for each of the blends and properties, the results of the equations for the slopes and interception points must be tabulated for use in the predictive model.

It is necessary to consider that the effect of the IR Additive on the optical properties and the Thermal effect is separate in this case. By means of the monolayer samples containing it, it has been observed that its results are linear with the percentage added to each of the blends, therefore, the results of the slopes and the interception points with that percentage will be used in the same way.

Up to this point, the model already has all the necessary information to be able to predict the different properties for the multilayer films as explained in the methodology. In order to be able to predict, the following values must be introduced:

- Layer distribution, considering if it is 3 or 5-layers (% v/v).
- Composition in mass percentage of each of the layers.
- Total thickness of the multilayer (μm).

These values are entered in the worksheet on the top shown in Figure 6.21 below, which is a screenshot of the model interface.



MATERIALS

	Layer %	LDPE-1	LDPE-2	LDPE-3	LLDPE-1	LLDPE-2	LLDPE-3	EVA	EBA	IR-Add	Thickness		
SKIN	10		80,0		20,0						20	predictable	100%
SUB-SKIN	20		80,0		20,0						40	predictable	100%
CORE	40							100,0			80	predictable	100%
SUB-SKIN	20		80,0		20,0						40	predictable	100%
SKIN	10		80,0		20,0						20	predictable	100%

Total film thickness 200 µm

5 layers mode

Requirements for thermal clear films EN 13206

Property	Norm	vs	Film	
Tensile Stress at Break MD at 23 °C (MPa)	20	<	25,6	± 1,8
Tensile Stress at Break CD at 23 °C (MPa)	20	<	26,8	± 2,1
Tensile Strain at Break MD at 23 °C (%)	550	<	640,9	± 29,8
Tensile Strain at Break CD at 23 °C (%)	550	<	677,1	± 18,1
Dart Drop Impact (g)	650	<	1457,0	± 80,6
Creep (%)	30	<	34,9	± 2,7
Transmittance (%)	88	<	91,0	± 0,2
Haze (%)	30	>	22,1	± 1,5
Thermal Effect (%)	75	>	68,3	± 2,5
Elmendorf tear MD (g)	-	-	1567,2	± 128,8
Elmendorf tear CD (g)	-	-	1970,4	± 164,8
Cost (€/100 m^2)		29,71		

Figure 6.21. Interface of the properties predictive model designed in Microsoft Excel.

Once the above values have been specified, and after determining whether the properties for the blends introduced in each layer are predictable, the results for each of the properties as well as the cost of the film are automatically generated and compared with the standard in the table at the bottom left. Basically, by means of conditional formats of the Excel tool, the model can know the blend that exists in each of the layers to calculate a slope and interception point value that together with the hypothetical thickness of each layer, will allow the calculation of the layer property.

The above explanation can best be shown by giving an example of how the Light transmission has been calculated for sample 1403223, which is the one defined in the interface of the model. The next Figure 6.22 give a screenshot of the table used to calculate this property.

Transmittance			
Slope	Interception	Additive	Value
-0,01	*93,09*	*0,00*	9,08
-0,01	*93,09*	*0,00*	18,16
0,00	*92,87*	*0,00*	36,78
-0,01	*93,09*	*0,00*	18,16
-0,01	*93,09*	*0,00*	9,08
			91,25 %

Figure 6.22. . Table for the calculation of the Light transmission of the multilayer film based on the predicted values of each layer.

Remembering that for each property and blend there is an equation for the slope and another for the interception point that depend on the percentage of one of the materials, by means of the material composition of each of the layers, a slope and interception point value is automatically generated. In this case, for the sample used as example, the skins and sub-skins have the same blend, and for this reason the slope and the interception are the same as well, being the only change the core, that is composed of pure EVA. Then, after checking that there is no participation of the IR Additive in this case (Additive column), the value for each layer is calculated as stated in the methodology by the Equation 5.1. Finally, the sum of the values is the result for the property of the multilayer film.

The same method is used for all the other properties.

6.3.2. Final validation

After understanding how the model is developed with the monolayer results, the values it is able to predict so far must be validated in some way in order to admit them as good to give guidance. As has been seen, the method used can have several sources of error, such as those coming from the tests themselves or from the correlations, which, as has been shown, are not entirely accurate.

The idea then is to use the data from the multilayers analyzed to do this validation by the well known as train-test method. This method will allow to use the 80% of the samples (16 samples) for the training set, which will be used to compare the values and create corrective factors to reduce the possible error, and the remaining 20% for the testing set (4 samples), which will be used to compare how the model predicts after the adjustments done by the corrective factors. The samples for each of the sets have been taken randomly and are as follows:

- Training set: 1403216, 1403217, 1403218, 1403219, 1403220, 1403221, 1403222, 1403224, 1403225, 1403226, 1403227, 1403229, 1403230, 1403231, 1403233, 1403234.
- Testing set: 1402156, 1403223, 1403228, 1403232.

Then, three different examples will be taken to explain how the corrections are done for the Creep, the Haze and the Thermal Effect. The other examples will be available in Appendix III. The first step is to compare the results of the properties with the values of the training set samples, whose values are measured. Results are shown in Figures 6.23, 6.24 and 6.25 below.

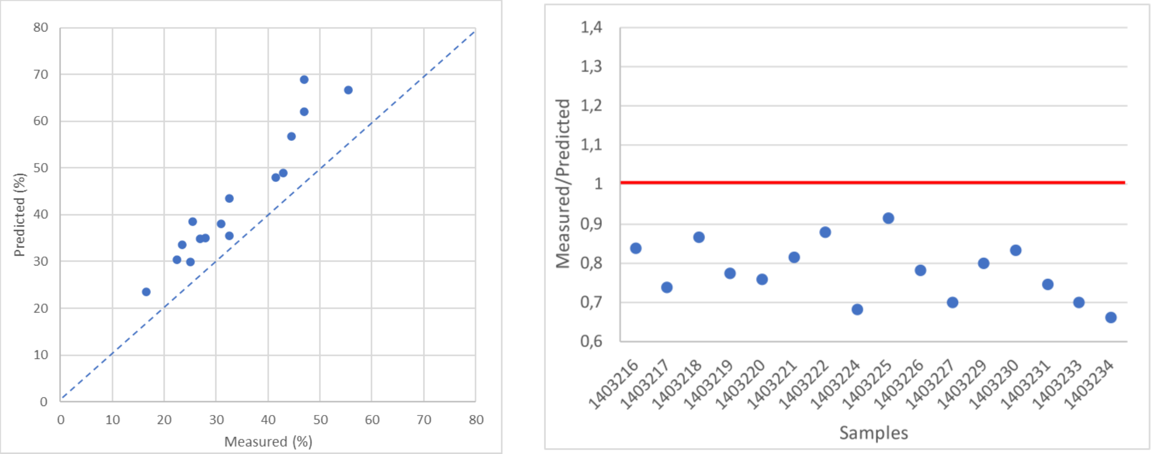


Figure 6.23. Creep results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

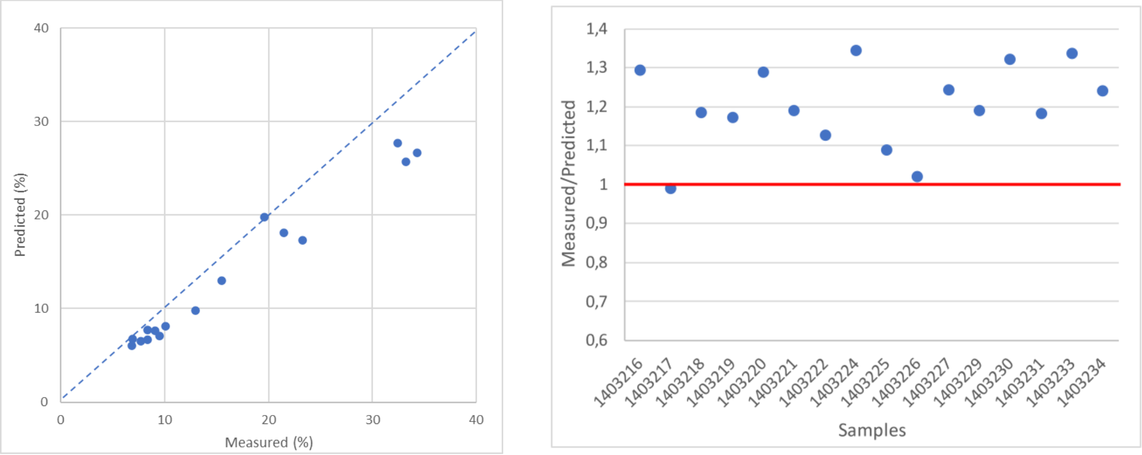


Figure 6.24. Haze results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

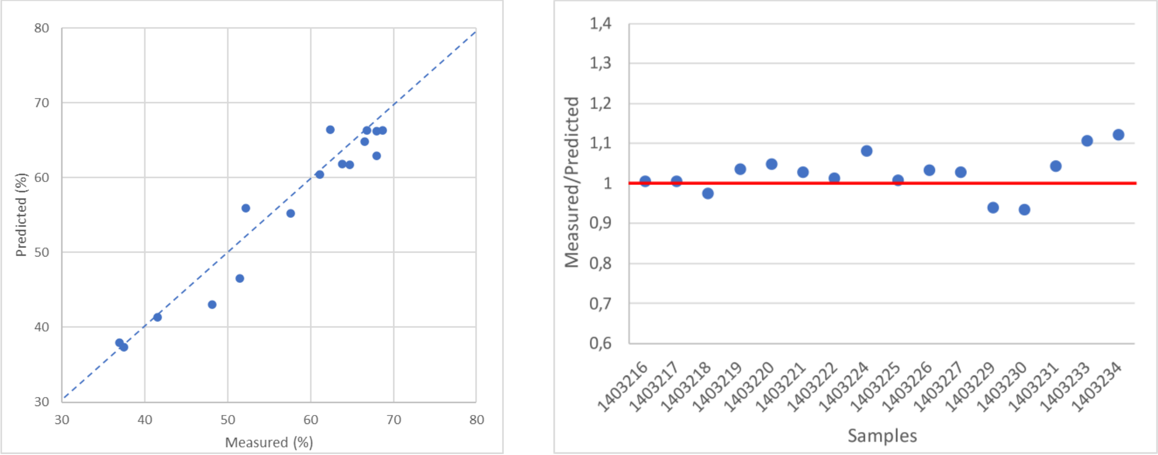


Figure 6.25. Thermal effect results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

As expected, the graphs show differences between predicted and measured values. What is important is that this trend is in the same direction for each property, i.e., they are either larger or smaller and in a similar proportion. In the proposed examples, it can be seen that in the case of Creep, the values are larger than expected while in Haze the values are smaller. The Thermal effect, on the other hand, presents much lower errors, fluctuating in both directions around the value of 1, which value means the “perfect prediction”. According to that, the first two examples are probably better to rectify because the adjustment goes always in the same direction.

After this, all the measured/predicted values are collected for each of the properties and then the average is going to be used as the corrective factor. Attached to this value, the average error is going to be used as well to give a certain range of uncertainty for the predicted value. Then, the next Table 6.2 gives all these values that are going to be directly applied to the model.

Table 6.2. Corrective factors and error values used to rectify the model prediction using the multilayers measured data.

Property	Stress at Break MD	Stress at Break CD	Strain at Break MD	Strain at Break CD	Dart Drop Impact	Creep
Corrective factor	1.1049	1.1039	1.0448	1.0761	1.1071	0.7804
Error (%)	6.92%	7.77%	4.64%	2.68%	5.53%	7.73%

Property	Transmittance	Haze	Thermal effect	Elmendorf tear MD	Elmendorf tear CD
Corrective factor	0.9970	1.2001	1.0244	1.0867	1.1298
Error (%)	0.26%	6.92%	3.64%	8.22%	8.36%

The corrective factors show the different error tendencies for each property, which after the modifications are theoretically corrected. In this case, the Creep and the Haze are the properties that were furthest away from the measured values, while the rest remain within the range of 10% difference, with Light transmission being the closest one.

With the modifications done and the corrective factors applied to the model, it is time to run the model for the testing set samples and see the results for the last three examples again. The test results are available in the next Figures 6.26, 6.27, and 6.28.

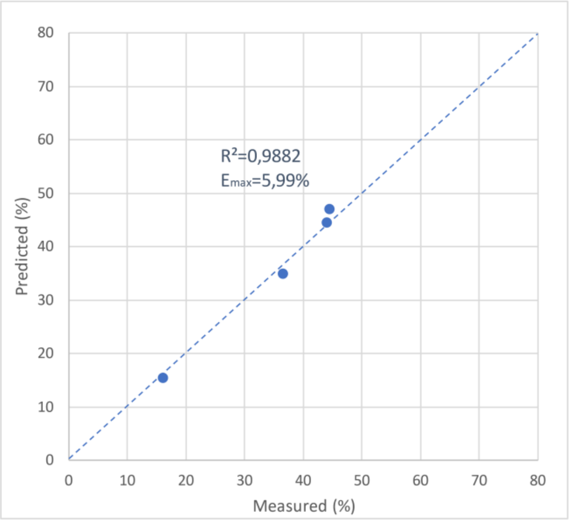


Figure 6.26. Test results for the Creep property showing the coefficient of determination and the maximum error achieved.

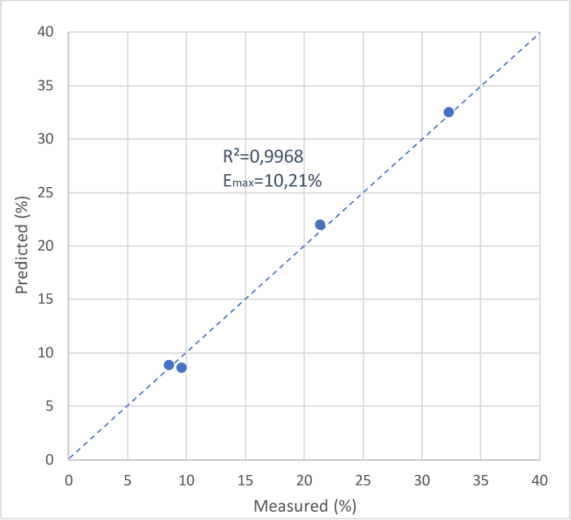


Figure 6.27. Test results for the Haze property showing the coefficient of determination and the maximum error achieved.

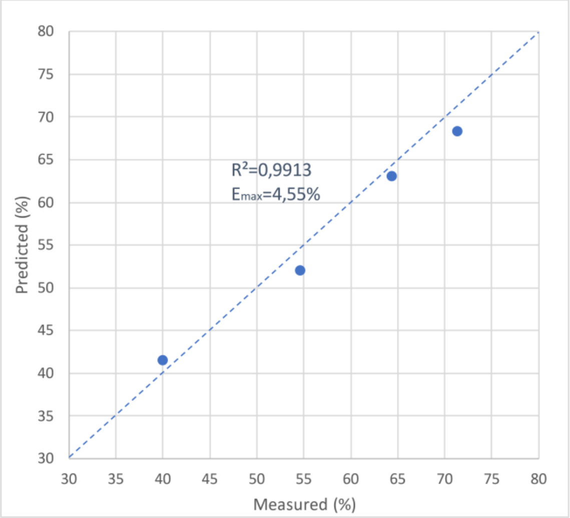


Figure 6.28. Test results for the Thermal effect property showing the coefficient of determination and the maximum error achieved.

In general, as the graphs show, the results for the test are quite satisfactory for the selected samples. The maximum error obtained is 17.38% for the Tensile Stress at break in CD property, therefore, the results can be said to be in general within a range of 15% with respect to the actual values of the multilayer films, which, considering the method used, demonstrates the range of uncertainty of predicting values for multilayers from monolayer films. The rest of the test results are available in Appendix III.

7. CONCLUSIONS

At this point in the project, several conclusions can be drawn from the results obtained.

On the one hand, it has been possible to verify that the same methodology used for the 3-layer model can indeed be used in the current 5-layer model. Knowing the possible impact of the expansion from 3 to 5 layers on the properties studied, by using linear and parabolic correlations it has been shown that values quite close to those that could be measured for multilayer films can be predicted. Although the method itself allows the accumulation of errors coming from multiple sources, these are reduced by the final validation, training the model with real data so that it rectifies the estimated values in the same direction.

However, although this reduction has been achieved, in some of the results of the model tests the errors are still high, exceeding 15% in the case of the Tensile Stress at break in CD. In the rest of properties the errors can be considered valid for this type of model. Accepting these values, it has been possible to design an interactive tool using Microsoft Excel to estimate the properties related to multilayer films applied to greenhouses with its EN regulations.

On the other hand, it has been demonstrated that the model is also capable of adding new materials to generate different multilayer film structures. In fact, the new resins proposed generate an alternative for one of the main objectives of the project: to reduce the use of EVA in greenhouse films. The two main materials proposed for this purpose are LLDPE and EBA.

In the case of LLDPE, knowing its good performance in previous projects, a low-cost alternative has been suggested (LLDPE-2). Despite having poorer optical properties and lower impact resistance, its tearing behavior and lower cost compared to the principal resin used (LLDPE-1) make it a clear low-cost alternative for this type of film, since by using the IR additive its thermicity value can reach the value required by the standard.

In relation to EBA, although the results for monolayers seemed to put it below EVA in both mechanical and thermal properties, when used in the core of multilayers its results for properties such as tearing, impact or creep elongation have improved a lot. However, its thermal effect levels are still lower compared to EVA, a fact that could be discouraged by increasing its percentage in the formulations or by using IR Additive.

Referring to the alternative for LDPE (LDPE-2) its excellent bubble stability during extrusion of both monolayers and multilayers should be highlighted, a factor that makes it perfect for the type of films needed for agricultural applications. However, it has been shown that its use in the skins of multilayer films causes the haze value to increase too much, exceeding the values suggested by the European Norm. It is in these cases where the proposed special blend suggested for the skins comes into action, improving the optics by reducing the haze and maintain the light transmission without altering the rest of the properties.

Finally, it would be interesting to highlight the expected good performance offered by the IR additive. Although it could not be used for the extrusion of multilayer films, its ability to increase the haze and thermal effect as well as its low influence on the mechanical properties and light transmission makes it again a good alternative when mixed with other products such as LLDPE.

8. RECOMMENDATIONS

In order to improve the work done, several recommendations for the future can be made.

As mentioned during the report, during the extrusion of the multilayer films it was not possible to use the IR additive, therefore, it would be interesting to extrude several samples with this material to validate it in the model, since it has a strong influence on properties such as Haze or Thermal effect.

Another important consideration is the fact of being able to scale the predictive model realized on two lab-scale machines to the most similar to the industrial level available at Tarragona Pack Studios: *Macchi 5L*, *Windmöller & Hölscher Varex II 9L*, etc. This would allow estimating properties for direct application films in the greenhouse area.

Looking to the future, models using correlations can be replaced with alternatives such as AI or Artificial Neuronal Networks (ANN), capable of predicting linear and nonlinear responses. However, one of their main limitations is the number of samples needed to be able to predict the different properties of this type of film (estimated to range from hundreds to thousands of samples).

9. REFERENCES

1. *Film Extrusion Manual Third Edition.* Peachtree Corners : Tappi Press, 2020. pp. 3-340. ISBN: 978-1-59510-299-7.

2. *Agricultural Film.* AMI. World Trade Center, Barcelona : AMI, 2022.

3. STANDARDIZATION, EUROPEAN COMMITTEE FOR. *Plastics - Thermoplastic covering films for use in agriculture and horticulture* . Brussels : s.n., 2020. p. 51, EUROPEAN STANDARD. Ref. No. EN 13206:2017+A1:2020 E.

4. Badiee, Amir. *An examination of the response of ethylene-vinyl acetate film to changes in environmental conditions.* Nottingham : s.n., 2016. p. 159.

5. Monomerpolymer. [Online] [Cited: 10 31, 2022.] https://www.monomerpolymer.com/shop/monomers/2-ethylbutyl-acrylate/.

6. Plastika Kritis S.A. [Online] 2022. [Cited: 10 31, 2022.] https://www.plastikakritis.com/en/light-diffusion; https://www.plastikakritis.com/en/anti-drip-effect.

7. *Ethylene Vinyl Acetate (EVA): 2022 World Market Outlook and Forecast up to 2031.* s.l. : Merchant Research and Consulting ltd, 2022. p. 205.

8. 2025 sustainability goals. [Online] 2022. [Cited: 10 17, 2022.] https://corporate.dow.com/en-us/science-and-sustainability/2025-goals.html.

9. Dr. Collin Laboratory Blown Film Line. [Online] Aaron equipment company inc. [Cited: 11 4, 2022.] https://www.aaronequipment.com/usedequipment/plastics-equipment/blown-film-lines/dr-collin-20-x-25d-46952001.

10. LabTechEngineering. Co-Extrusion Blown Film 9 Layer Line. [Online] 2021. [Cited: 03 04, 2023.] https://labtechusa.net/product/co-extrusion-blown-film-9-layer-line/.

11. José Britti Bacalhau, Túlio Mumic Cunha, Conrado Ramos Moreira Afonso. Effect of Ni content on the Hardenability of a Bainitic Steel for Plastics Processing. *24th ABCM International Congress of Mechanical Engineering.* 2017.

12. Ana G. Azevedo, Carolina Barros, Sónia Miranda. Active Flexible Films for Food Packaging: A Review. *MDPI.* June 2022, p. 32.

13. ASTM D1003 Film Haze And Light Transmittance Measurement Haze Tester With Integrating Sphere. [Online] [Cited: 04 10, 2023.] https://www.color-spectrophotometer.com/sale-12068210-astm-d1003-film-haze-and-light-transmittance-measurement-haze-tester-with-integrating-sphere.html.

14. Portal Frutícola. [Online] 07 21, 2017. [Cited: 11 22, 2022.] https://www.portalfruticola.com/noticias/2017/07/21/paso-a-paso-para-el-diseno-y-construccion-de-distintos-tipos-de-invernaderos-incluye-manuales/.

All results are from own source. The document can contain internal company information such as data on the resins used, data on the European Norm or the standard used for testing. All this information has *been used without any risk of confidentiality*.

APPENDIX I: Samples description

Table AI.1. Monolayer samples of the last project with the old ID and the verification one.

Old Sample ID	Verification Sample ID	Formulation	Thickness
907248	-	LDPE-1	100
907249	1378338	LDPE-1	150
907250	-	LDPE-1	175
907251	1378044	LDPE-1	200
907252	1378045	LDPE-1 + LLDPE-1 80-20%	100
907253	-	LDPE-1 + LLDPE-1 80-20%	150
907254	1378339	LDPE-1 + LLDPE-1 80-20%	175
907255	-	LDPE-1 + LLDPE-1 80-20%	200
907256	-	LDPE-1 + LLDPE-1 60-40%	100
907257	-	LDPE-1 + LLDPE-1 60-40%	150
907258	-	LDPE-1 + LLDPE-1 60-40%	175
907259	-	LDPE-1 + LLDPE-1 60-40%	200
907260	-	LDPE-1 + LLDPE-1 40-60%	100
907261	-	LDPE-1 + LLDPE-1 40-60%	150
907262	-	LDPE-1 + LLDPE-1 40-60%	175
907263	-	LDPE-1 + LLDPE-1 40-60%	200
907264	1378046	LDPE-1 + LLDPE-1 20-80%	100
907265	-	LDPE-1 + LLDPE-1 20-80%	150
907266	1378340	LDPE-1 + LLDPE-1 20-80%	175
907267	-	LDPE-1 + LLDPE-1 20-80%	200
907268	-	LLDPE-1	100
907269	1378048	LLDPE-1	150
907270	-	LLDPE-1	175
907271	1378342	LLDPE-1	200
927940	-	LDPE-1 + 1.5% IR-Add	100
923460	-	LDPE-1 + 1.5% IR-Add	175
927941	-	LDPE-1 + 1.5% IR-Add	200
930119	-	LDPE-1 + 3% IR-Add	100
927938	-	LDPE-1 + 3% IR-Add	175
923458	1378047	LDPE-1 + 3% IR-Add	150
927939	1378341	LDPE-1 + 3% IR-Add	200
918552	-	LDPE-1 + 5% IR-Add	100
930851	-	LDPE-1 + 5% IR-Add	150
918553	-	LDPE-1 + 5% IR-Add	175
927936	-	LDPE-1 + 5% IR-Add	200
947272	-	LDPE-1 + 8% IR-Add	100
947273	-	LDPE-1 + 8% IR-Add	150
927274	-	LDPE-1 + 8% IR-Add	200
923461	-	LLDPE-1 + 1.5% IR-Add	150
927944	-	LLDPE-1 + 1.5% IR-Add	100
927945	-	LLDPE-1 + 1.5% IR-Add	200
923459	-	LLDPE-1 + 3% IR-Add	100
927942	-	LLDPE-1 + 3% IR-Add	150
927943	-	LLDPE-1 + 3% IR-Add	200
918554	1378343	LLDPE-1 + 5% IR-Add	150
927937	1378049	LLDPE-1 + 5% IR-Add	175
918555	-	LLDPE-1 + 5% IR-Add	200
947269	-	LLDPE-1 + 8% IR-Add	100
947270	-	LLDPE-1 + 8% IR-Add	150
947271	-	LLDPE-1 + 8% IR-Add	200

926967		EVA + LDPE-1 80-20%	100
926968		EVA + LDPE-1 80-20%	150
926969		EVA + LDPE-1 80-20%	175
926970		EVA + LDPE-1 80-20%	200
936589	-	EVA	100
936590	-	EVA	150
936591	-	EVA	175
936592	-	EVA	200
936593	1378344	EVA + LLDPE-1 80-20%	100
936594	1378050	EVA + LLDPE-1 80-20%	150
936595	-	EVA + LLDPE-1 80-20%	200
936596	-	EVA + LLDPE-1 20-80%	100
936597	-	EVA + LLDPE-1 20-80%	175
936598	-	EVA + LLDPE-1 20-80%	200

Table AI.2. Monolayer samples for the new materials of the model.

Sample ID	Formulation	Thickness
1384950	LDPE-2 + LLDPE-1 25-75%	100
1384951	LDPE-2 + LLDPE-1 25-75%	150
1384952	LDPE-2 + LLDPE-1 25-75%	200
1384953	LDPE-2 + LLDPE-1 75-25%	100
1384954	LDPE-2 + LLDPE-1 75-25%	150
1384955	LDPE-2 + LLDPE-1 75-25%	200
1384956	LDPE-2	100
1384957	LDPE-2	150
1384958	LDPE-2	200
1385103	LDPE-2 + LLDPE-1 25-75% + 4% IR-Add	100
1385812	LDPE-2 + LLDPE-1 75-25% + 4% IR-Add	150
1385105	LDPE-2 + 4% IR-Add	200
1385106	LDPE-2 + LLDPE-1 25-75% + 8% IR-Add	200
1385107	LDPE-2 + LLDPE-1 75-25% + 8% IR-Add	150
1385108	LDPE-2 + 8% IR-Add	100
1385109	LLDPE-2	100
1385110	LLDPE-2	150
1385111	LLDPE-2	200
1385112	LDPE-2 + LLDPE-2 25-75%	100
1385113	LDPE-2 + LLDPE-2 25-75%	150
1385114	LDPE-2 + LLDPE-2 25-75%	200
1385115	LDPE-2 + LLDPE-2 75-25%	100
1385116	LDPE-2 + LLDPE-2 75-25%	150
1385117	LDPE-2 + LLDPE-2 75-25%	200
1385118	LLDPE-2 + 4% IR-Add	100
1385119	LDPE-2 + LLDPE-2 25-75% + 4% IR-Add	150
1385120	LDPE-2 + LLDPE-2 75-25% + 4% IR-Add	200
1385121	LDPE-2 + LLDPE-2 25-75% + 8% IR-Add	200
1385122	LDPE-2 + LLDPE-2 75-25% + 8% IR-Add	150
1385123	EBA	75
1385124	EBA	100
1385125	EBA	150
1385126	EBA + 4% IR-Add	150
1385127	EBA + LLDPE-1 75-25%	75
1385128	EBA + LLDPE-1 75-25%	100
1385129	EBA + LLDPE-1 75-25%	150
1385130	EBA + LLDPE-1 25-75%	75

1385131	EBA + LLDPE-1 25-75%	100
1385132	EBA + LLDPE-1 25-75%	150
1385162	EBA + LLDPE-1 25-75% + 4% IR-Add	100
1385133	EBA + LLDPE-1 25-75% + 8% IR-Add	100
1385134	EBA + LDPE-2 75-25%	50
1385135	EBA + LDPE-2 75-25%	100
1385136	EBA + LDPE-2 75-25%	150
1385137	EBA + LDPE-2 75-25% + 4% IR-Add	100
1385138	EBA + LDPE-2 25-75%	50
1385139	EBA + LDPE-2 25-75%	100
1385140	EBA + LDPE-2 25-75%	150
1385141	EBA + LDPE-2 25-75% + 4% IR-Add	150
1385142	EBA + LDPE-2 25-75% + 8% IR-Add	50
1385143	EBA + LLDPE-2 75-25%	75
1385144	EBA + LLDPE-2 75-25%	100
1385145	EBA + LLDPE-2 75-25%	150
1385146	EBA + LLDPE-2 25-75%	75
1385147	EBA + LLDPE-2 25-75%	100
1385148	EBA + LLDPE-2 25-75%	150
1385149	EBA + LLDPE-2 25-75% + 4% IR-Add	150
1385150	LDPE-3	100
1385151	LDPE-3	150
1385152	LDPE-3	200
1385153	LDPE-3 + LLDPE-3 75-25%	100
1385154	LDPE-3 + LLDPE-3 75-25%	150
1385155	LDPE-3 + LLDPE-3 75-25%	200
1385156	LDPE-3 + LLDPE-3 25-75%	100
1385157	LDPE-3 + LLDPE-3 25-75%	150
1385158	LDPE-3 + LLDPE-3 25-75%	200
1385159	LLDPE-3	100
1385160	LLDPE-3	150
1385161	LLDPE-3	200

Table AI.3. 5 layer film structures samples for the validation of the model. The layers distribution % goes from the external part to the internal part of the bubble.

			MATERIALS %								
Sample ID	**Thickness (µm)**	**Distribution (%)**	**LDPE**			**LLDPE**			**HPC**		**Add**
			1	2	3*	1	2	3*	EVA	EBA	IR
1402156 1403216	200 175	10		80			20				
		20		25			75				
		40		100							
		20		50		50					
		10		80			20				
1403217 1403218	200 175	10		80		20					
		20		100							
		40				100					
		20				100					
		10		80		20					
1403219 1403220	200 175	10		80			20				
		20		25			75				
		40								100	
		20		25			75				
		10		80			20				

		10	80	20		
1403221	200	20	70	30		
		40		30	70	
1403222	175	20	70	30		
		10	80	20		
		10	80	20		
1403223	200	20	80	20		
		40			100	
1403224	175	20	80	20		
		10	80	20		
		10	25	75		
1403225	200	20	70	30		
		40			100	
1403226	175	20	70	30		
		10	25	75		
		10	80	20		
1403227	200	20	40	60		
		40			100	
1403228	175	20	40	60		
		10	80	20		
		10	50	50		
1403229	200	20		100		
		40		25	75	
1403230	150	20		100		
		10	50	50		
		15	80	20		
1403231	200	30	100			
		10		100		
1403232	175	30		50	50	
		15	50	50		
		15	75	25		
1403233	200	30	75	25		
		10		25	75	
1403234	175	30	75	25		
		15	75	25		

APPENDIX II: Characterization

This section provides a more comprehensive understanding of the techniques employed for the characterization of the films, always adhering to the requirements outlined in the *European Norm EN 13206* for thermal clear films.

II.1 Mechanical testing

All the mechanical methods used to test the films are selected in accordance with *EN 13206* and are following the necessary standard. However, some tests can be adapted to new conditions due to time issues, like in the case of the creep, giving the same results as the norm propose.

II.1.1 Tensile

To prevent plastics from breaking during installation or exposure to harsh weather conditions like strong winds, it is essential to conduct tensile testing. This involves applying a load to the sample to maintain a constant strain ratio until it fails. This process generates a stress/strain curve, which indicates how the material responds during the tensile test deformation. There are two types of tensile tests, both based on the ISO 527-3 standard, that evaluate different properties. The first test, known as Secant Modulus, assesses the material's behavior in the elastic region, with minimal elongation (7 mm) of the sample. The second test, the interesting one for this project, evaluates the plastic deformation and breakage of the sample, with varying levels of strain velocity until it fails.

In this case it is measured at 23ºC, but the method can evaluate the influence of temperature on the materials at different values like 40ºC.

II.1.2 Creep

The creep test mechanics are similar to the tensile test, but with the former, there is a gradual deformation under constant stress at high temperatures. The results are utilized to assess the behavior and elongation of the film under low stress, simulating weather conditions such as water accumulation on top of a greenhouse.

The test is based on EN ISO 899, and the European Norm requires to be applied at 23ºC during 100h with a weight of 1kg to the machine direction (MD) of the film. In Tarragona Pack Studios, this test is called *HighThroughput Creep* and uses an equivalent way to measure the elongation by doing the test at 50ºC during 5h with the same weight of 1kg.

II.1.3 Dart Drop Impact (DDI)

The most commonly used technique for assessing the impact strength of a plastic film is the dart drop impact test. This method is particularly valuable in evaluating the resistance of greenhouse films against natural impacts like hail. The procedure is according to EN ISO

7765-1, so called *Method A*, consisting of the fall of a certain weight on a certain height impacting directly to the film.

II.1.4 Elmendorf tear resistance

Greenhouse films can suffer certain cuts when installed or when some labors are done inside or outside the building, and for this reason is interesting to see how resistant it is in this scenario. The Elmendorf method is used to measure tear resistance or the force required to continue tearing an initially cut film. While the European Norm does not require this method, it provides valuable insight into a durability of a film when it is damaged due to handling. The test follows the procedure outlined in ASTM d1922-15.

Figure AII.1. Tensile, Dart Drop Impact and Elmendorf tear machines. (Own source)

II.2 Optical testing

For greenhouse films, optical properties cannot be neglected. Any film for agricultural application, expect opaque ones, must allow the highest global light transmission in the visible range as the norm says. Light diffusion, also called cloudiness, will be more or less important depending on the place where the film is used.

When it comes to greenhouse films, optical properties play a critical role. According to regulations, any agricultural film, except for opaque ones, must allow the maximum global light transmission in the visible range. Light diffusion, also known as cloudiness, varies depending on the usage location of the films and can significantly impact its effectiveness.

When an object is illuminated by light, it interacts with the light in various ways:

- The light can be absorbed within the object, which is mostly responsible for its color.
- The light can be transmitted through the object, depending on its surface transparency and opacity.

- The light can be scattered either within or on the surface of the object, resulting in diffuse reflection, haze, and transmission.
- The light can be specularly reflected from the object, which determines its gloss.

II.2.1 Light transmission

In essence, light transmission refers to the percentage ratio of the luminous flux that a body transmits compared to the incident flux it receives. While the experimental procedure for measuring haze and light transmission is the same, the calculations differ, which will be explained later. Light transmission is measured according to ASTM d1003-13.

II.2.2 Haze (total and internal)

In areas with high light intensity, such as tropical and equatorial regions, greenhouse films with high light diffusion are necessary to prevent plant burn. Conversely, in regions with lower sun radiation, like the Netherlands, where most of the light is directly transmitted to the crops or leaves, fully transparent films are more suitable. Therefore, greenhouse films in these regions typically have a lower level of diffusion.

Haze, in the context of light transmission, refers to the scattering of light by a specimen, which results in reduced contrast of objects viewed through it and a smoky effect. Haze is defined as the percentage of transmitted light that is scattered and deviates its direction by more than 2.5º from the incident beam., as it is explained in the next Figure II.1. Haze is measured according to ASTM d1003-13.

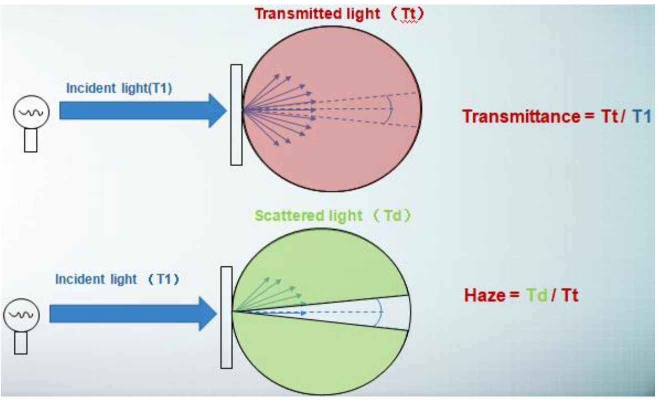


Figure AII.2. Transmittance and haze differentiation. (13)

Inside the term of haze there are two different branches of this property: the total and the internal one. The difference between these two values remains in the effect of the possible irregularities and the rugosity of the walls of the film studied in this case, and the total haze considers this effect, meanwhile internal haze only evaluates the light diffused by the internal composition of the film. The way to analyze the internal haze is by applying and special oil in the surfaces of the film to neglect the influence of the walls.

II.2.3 Clarity

The clarity of a film refers to the percentage of emitted light that deviates less than 2.5º from the incident beam as it passes through the sample. This parameter indicates the degree of distortion of an object when viewed through the film. Clarity is typically measured according to the guidelines provided by ASTM 1746.

II2.4 Gloss

Gloss is the visual perception of a surface's shiny appearance by an observer. This perception can change depending on variations in the relative position or spectral distribution of the source, the sample, or the observer. Gloss in plastics is typically measured at a 45º angle, as outlined in ASTM D2457.

II.3 Thermal effect

Eventually, thermicity, infrared effectiveness or thermal effect is evaluated as the ability to create the greenhouse effect. As it is known, this property is related with the capacity of some molecules and its links to vibrate or react at different frequencies. Applied in the greenhouse application, the idea is related with the transmission or not of the energetical waves generated by the Sun during the day and by the soil during the night. Basically, the Sun emits radiation of short waves that pass through the plastic film to increase the temperature inside the greenhouse structure during the day. Heated by these short waves, the ground radiates infrared rays that are not transmitted by the film, warming more the weather inside the greenhouse.

To conduct the thermal effect test, the amount of light absorbed by the film in the infrared wavelength range of 7-13µm (1429 and 769cm-1) is measured. The sample's absorbance is determined using an infrared spectrophotometer, an analytical device commonly employed to identify organic or inorganic substances that measures the absorption of radiation as a function of the wavelength of infrared radiation passing through the sample.

Once the measurement of the absorption is done, the software of the spectrophotometer generates a graph of the % of transmittance as a function of the wavelength of the range. The thermal effect then is calculated by the subtraction of the transmitted light to the total emitted. This transmitted light is basically the area under the curve of the graph generated and is measured using a planimeter as the norm stipulates. The value calculated is then the infrared radiation blocked by the sample.

APPENDIX III: Results

Table AIII.1. Results for each monolayer sample of the mechanical properties.

	TENSILE				DDI	CREEP	ELMENDORF TEAR	
Sample ID	**Stress at break MD**	**Strain at break MD**	**Stress at break CD**	**Strain at break CD**	**Impact (g)**	**Elongation (%)**	**Tear MD**	**Tear CD**
1384950	39,9	432,8	33,5	460,6	1897,4	96,1	1491,6	1561,5
1384951	38,2	543,0	34,5	547,7	2000,0	61,4	2447,5	2237,4
1384952	37,3	595,9	36,0	588,4	2000,0	27,6	2984,3	3052,8
1384953	25,2	267,7	25,9	397,3	583,8	72,1	393,1	599,9
1384954	26,2	423,0	28,0	522,0	765,5	38,0	752,7	853,1
1384955	27,0	498,6	28,8	542,3	971,3	17,4	1234,2	1206,9
1384956	12,1	210,8	11,5	251,0	402,2	63,2	228,3	238,3
1384957	14,6	348,1	19,4	414,9	496,7	26,7	402,6	321,4
1384958	17,1	433,9	21,1	449,4	618,5	15,4	669,8	489,7
1385103	30,9	528,8	35,9	554,7	1779,8	105,0	-	-
1385812	23,6	522,6	25,2	514,9	763,4	32,7	-	-
1385105	14,4	375,4	16,5	390,3	602,7	13,6	-	-
1385106	32,0	588,2	34,1	573,4	2000,0	32,0	-	-
1385107	23,2	520,6	23,6	500,4	750,8	38,3	-	-
1385108	15,2	311,8	16,5	372,8	370,7	64,1	-	-
1385109	38,0	566,2	40,0	600,2	455,7	105,0	1885,4	1777,0
1385110	41,6	626,8	41,1	624,3	675,2	28,5	2850,1	2735,1
1385111	42,5	655,1	42,5	647,1	924,0	17,4	3784,0	3616,2
1385112	34,4	511,8	34,4	566,3	446,3	105,0	1694,0	1582,2
1385113	35,6	614,4	37,6	603,0	612,2	32,5	2492,6	2433,6
1385114	39,8	624,0	38,0	620,4	891,5	12,9	3318,7	2932,2
1385115	24,2	382,6	20,6	418,2	421,1	43,6	345,3	483,6
1385116	25,6	561,6	26,2	531,5	564,9	31,2	752,3	905,9
1385117	29,4	566,1	29,0	562,3	765,5	12,9	1331,0	1053,0
1385118	36,7	581,4	33,6	566,0	448,4	97,0	-	-
1385119	32,9	606,4	29,1	562,5	681,5	34,3	-	-
1385120	20,7	504,3	22,3	490,9	681,5	14,7	-	-
1385121	31,6	602,5	30,2	580,6	867,3	15,6	-	-
1385122	20,8	481,9	23,0	486,6	596,4	28,9	-	-
1385123	16,2	505,6	15,3	530,7	770,7	105,0	239,6	268,2
1385124	16,2	543,9	15,5	544,9	975,5	105,0	440,4	386,6
1385125	15,4	570,6	17,1	563,8	1225,4	105,0	734,2	626,2
1385126	15,9	598,6	15,5	570,2	1121,4	105,0	-	-
1385127	21,9	552,5	19,8	558,3	1229,6	105,0	479,6	545,7
1385128	22,3	573,7	22,9	588,9	1584,5	105,0	743,9	726,8
1385129	20,0	581,0	25,5	612,6	2000,0	105,0	1360,7	1225,8
1385130	32,3	524,4	26,4	491,0	1960,4	105,0	975,7	1072,8
1385131	30,1	545,4	28,1	520,1	2000,0	105,0	1383,8	1279,3
1385132	29,9	552,0	30,4	532,7	2000,0	105,0	2207,7	2255,4
1385162	36,0	563,1	29,3	524,6	2000,0	105,0	-	-
1385133	40,1	0,0	28,3	510,4	2000,0	105,0	-	-
1385138	13,9	0,0	12,4	301,0	199,5	105,0	170,5	106,3
1385139	14,2	307,2	14,6	405,6	351,8	83,2	313,6	207,1
1385140	15,0	377,9	21,3	467,0	508,2	37,8	485,8	402,1
1385141	14,5	366,4	14,7	345,1	527,1	47,6	-	-
1385142	21,1	138,3	14,9	325,7	212,1	105,0	-	-
1385143	21,3	534,0	19,8	536,1	824,3	105,0	366,6	571,4
1385144	26,5	567,3	23,2	554,2	965,0	105,0	662,0	674,7
1385145	25,7	620,0	24,7	575,8	1420,7	105,0	1379,4	1198,8
1385146	29,0	527,8	24,2	540,4	684,6	105,0	1197,9	1480,5
1385147	32,2	526,6	27,3	558,5	894,6	105,0	1579,6	1791,0

1385148	32,7	585,7	29,7	578,4	1453,2	46,3	2532,2	2974,5
1385149	27,2	560,0	31,1	585,6	1415,4	56,1	-	-
1385150	15,7	342,0	12,0	299,9	293,0	90,8	346,8	313,4
1385151	16,3	435,3	16,1	423,1	395,9	32,0	467,9	520,7
1385152	16,9	469,6	17,2	464,6	487,2	7,1	738,5	628,5
1385153	17,3	401,6	15,8	398,7	320,3	69,0	733,7	613,5
1385154	18,3	465,9	20,2	486,5	515,6	28,0	964,9	944,9
1385155	19,0	475,5	22,4	539,2	631,1	11,1	1434,4	1033,2
1385156	30,7	462,9	30,9	526,6	436,8	68,5	1166,0	1310,4
1385157	34,4	491,7	36,8	563,9	750,8	20,0	1549,9	1863,9
1385158	27,0	419,2	27,9	480,2	377,0	105,0	1030,6	882,9
1385159	35,4	513,6	38,3	525,1	603,8	68,1	1563,1	1393,2
1385160	39,6	559,0	45,1	582,0	1076,3	20,0	1853,5	2042,0
1385161	28,6	506,0	33,5	495,9	476,7	105,0	1224,0	972,0

Table AIII.2. Results for each monolayer sample of the optical and thermal effect properties.

	OPTICS			THERMAL EFFECT
Sample ID	**Transmittance**	**Total Haze**	**Internal Haze**	**IR Absorption (%)**
1384950	91,4	14,0	1,5	26,5
1384951	90,7	17,5	2,4	33,2
1384952	90,1	20,8	3,7	39,9
1384953	91,1	23,2	1,9	26,7
1384954	90,5	23,5	2,7	33,0
1384955	90,1	31,2	4,5	39,3
1384956	90,9	21,8	2,2	26,9
1384957	90,6	27,1	4,0	32,9
1384958	89,9	29,6	5,2	39,0
1385103	91,1	26,6	7,3	50,5
1385812	90,0	36,6	8,6	59,8
1385105	89,3	35,4	11,5	70,4
1385106	89,3	43,1	21,2	78,7
1385107	89,6	45,2	14,0	75,1
1385108	89,8	49,9	14,1	64,5
1385109	91,3	14,7	9,0	24,4
1385110	90,8	20,9	15,8	31,3
1385111	90,4	25,7	19,5	38,2
1385112	91,2	18,6	4,1	25,0
1385113	90,6	21,1	6,4	31,7
1385114	90,2	19,6	9,1	38,4
1385115	90,7	29,5	2,9	26,3
1385116	90,3	33,6	4,9	32,5
1385117	89,7	34,6	6,4	38,8
1385118	90,7	25,4	11,0	48,2
1385119	90,2	31,0	12,0	61,1
1385120	89,2	41,5	14,2	71,5
1385121	89,5	38,1	18,0	80,6
1385122	89,8	45,6	11,3	75,8
1385123	92,1	7,9	0,8	58,0
1385124	92,0	9,3	1,2	63,1
1385125	91,7	9,5	1,9	73,1
1385126	91,1	29,6	14,9	81,2
1385127	92,0	10,7	0,9	52,6
1385128	91,8	10,1	1,3	60,2
1385129	91,3	10,6	2,1	68,6

1385130	92,1	3,3	1,2	38,4
1385131	91,8	3,4	2,0	42,8
1385132	91,4	4,8	3,1	53,6
1385162	91,5	18,2	7,2	57,1
1385133	90,9	32,2	11,7	64,9
1385138	91,1	37,3	1,5	33,6
1385139	90,5	42,1	3,7	44,0
1385140	89,6	44,6	6,1	52,6
1385141	89,4	44,0	11,1	74,2
1385142	90,5	56,3	7,0	51,8
1385143	91,7	14,8	1,3	52,3
1385144	91,4	15,0	2,1	58,2
1385145	91,0	15,2	4,8	70,7
1385146	91,2	12,1	6,6	36,6
1385147	91,1	12,8	7,3	40,3
1385148	90,2	18,7	13,9	52,2
1385149	89,7	30,5	19,1	65,4
1385150	90,9	11,5	5,3	24,5
1385151	90,3	12,9	11,5	31,4
1385152	89,7	16,5	15,2	38,2
1385153	91,0	10,7	4,0	24,7
1385154	90,2	12,3	8,1	31,4
1385155	90,0	14,4	9,5	38,2
1385156	91,4	7,9	2,8	25,0
1385157	90,8	9,1	4,5	31,6
1385158	91,6	6,8	2,4	21,6
1385159	90,9	16,8	14,6	25,1
1385160	90,0	24,5	24,0	31,7
1385161	91,3	13,3	10,4	21,8

Table AIII.3. Results for each multilayer sample of the mechanical properties.

	TENSILE				**DDI**	**CREEP**	**ELMENDORF TEAR**	
Sample ID	**Stress at break MD**	**Strain at break MD**	**Stress at break CD**	**Strain at break CD**	**Impact (g)**	**Elongation (%)**	**Tear MD**	**Tear CD**
1402156	27,0	575,3	27,9	588,3	880,4	14,2	1609,3	1488,6
1403216	27,8	561,1	29,2	579,0	767,0	22,3	1204,5	1359,9
1403217	36,5	569,6	37,9	574,1	2100,0	20,0	3021,7	2842,2
1403218	37,0	569,6	38,8	581,0	2100,0	36,9	2548,7	2349,9
1403219	26,8	617,3	28,3	642,9	1782,5	24,0	3545,3	3066,3
1403220	25,3	591,2	27,3	630,2	1515,9	41,8	2762,1	3026,7
1403221	31,6	602,0	33,1	614,9	1940,4	27,6	1855,7	1731,6
1403222	31,4	585,4	34,7	606,8	1616,6	38,3	1332,1	1535,4
1403223	27,5	595,5	30,4	627,8	1352,2	32,5	1775,4	1753,2
1403224	28,8	589,2	28,4	586,3	1229,4	41,8	1414,6	1528,2
1403225	26,6	630,9	26,9	637,3	1656,9	28,9	2468,4	2364,3
1403226	28,9	644,5	28,0	642,1	1313,6	39,6	2271,5	2029,5
1403227	26,9	640,9	26,2	631,4	1439,9	20,9	2959,0	2538,0
1403228	27,5	636,0	25,8	634,4	1235,9	39,6	2360,6	2417,4
1403229	33,8	630,1	34,1	638,8	2100,0	24,9	4118,4	3990,6
1403230	34,3	600,3	36,1	624,2	2100,0	49,4	3116,3	3786,3
1403231	30,5	599,3	32,8	622,7	2100,0	28,9	2358,4	2234,4
1403232	29,3	583,8	29,4	591,8	2100,0	39,2	1832,6	1985,4
1403233	28,5	584,5	30,2	587,6	1376,9	14,7	1801,8	1739,7
1403234	28,8	564,7	30,3	569,3	1339,3	22,7	1388,2	1339,2

Table AIII.4. Results for each multilayer sample of the optical and thermal properties.

	OPTICS		THERMAL EFFECT
Sample ID	**Transmittance**	**Total Haze**	**IR Absorption (%)**
1402156	89,7	33,9	38,4
1403216	90,2	34,9	36,0
1403217	90,3	20,6	39,9
1403218	90,6	22,6	35,4
1403219	90,1	34,0	66,0
1403220	90,3	36,0	62,1
1403221	90,0	8,1	63,8
1403222	90,4	7,1	58,7
1403223	90,3	22,5	68,4
1403224	90,5	24,5	65,3
1403225	90,5	8,8	64,1
1403226	90,8	7,2	61,2
1403227	90,3	10,6	65,3
1403228	90,4	10,1	61,8
1403229	89,3	16,3	59,9
1403230	90,1	13,7	50,1
1403231	89,8	9,5	55,3
1403232	90,1	8,9	52,3
1403233	89,8	10,0	49,4
1403234	90,2	8,7	46,3

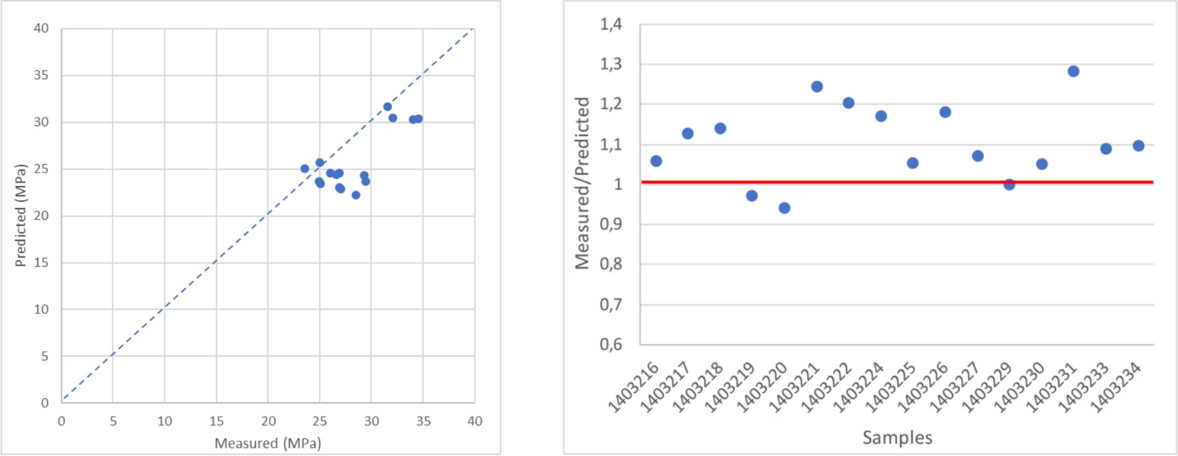


Figure AIII.1. Stress at break MD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

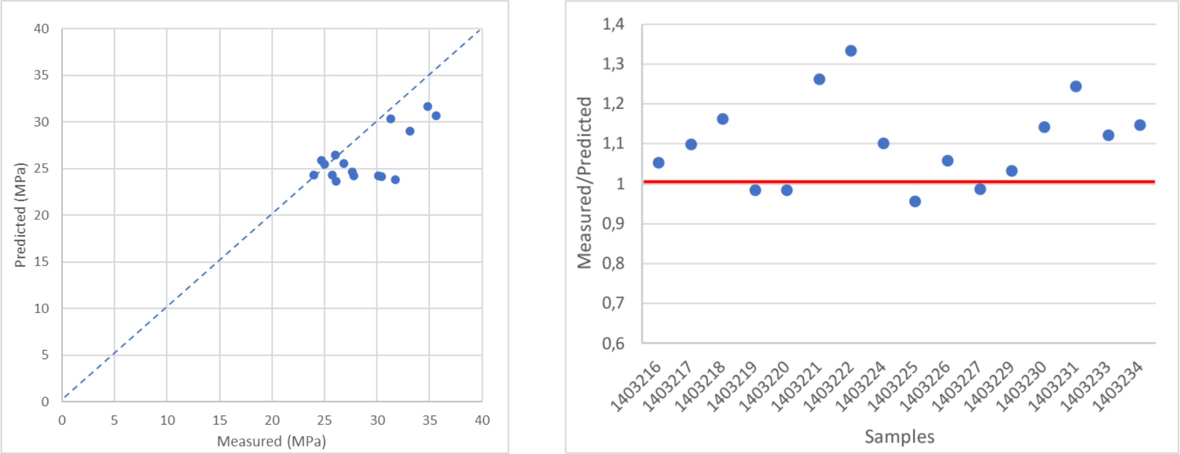


Figure AIII.2. Stress at break CD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

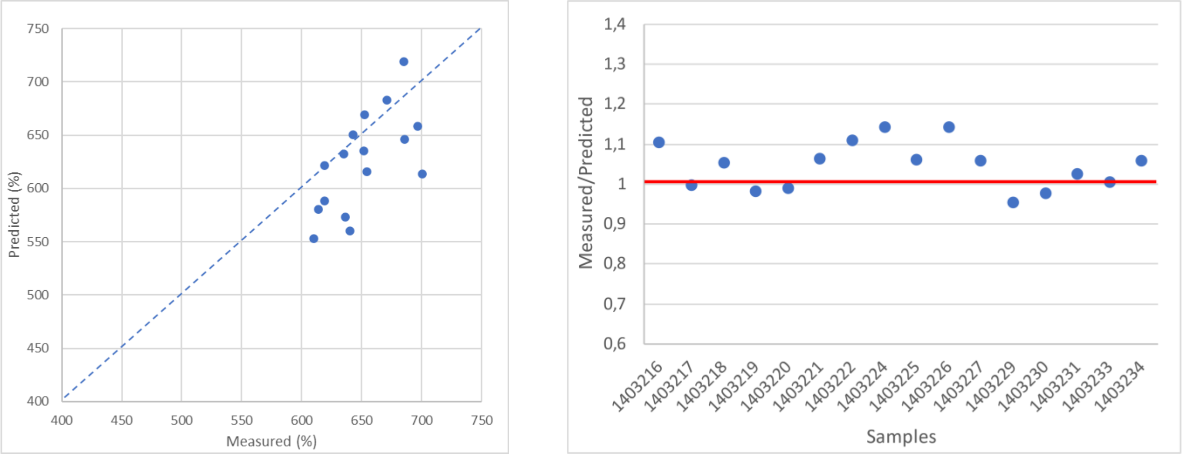


Figure AIII.3. Strain at break MD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

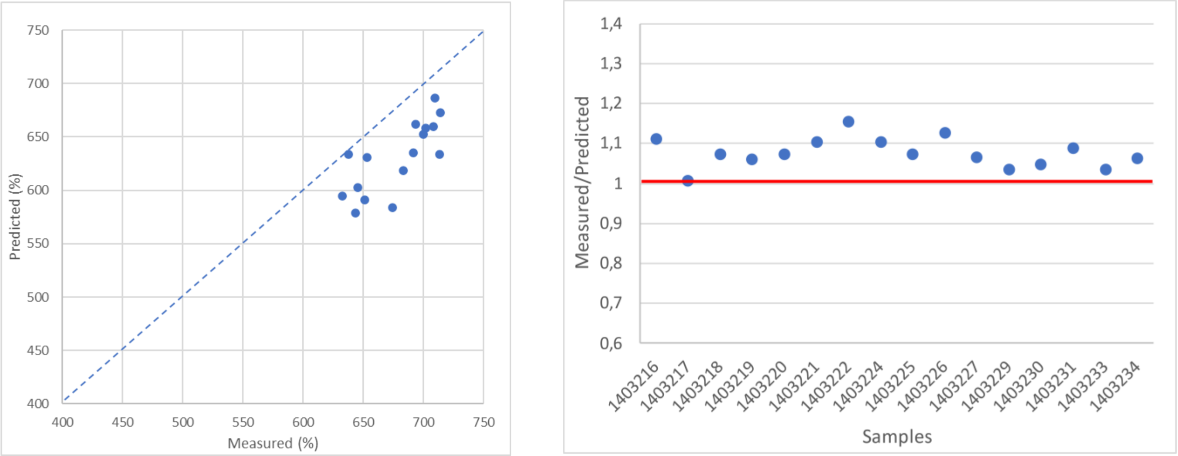


Figure AIII.4. Strain at break CD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

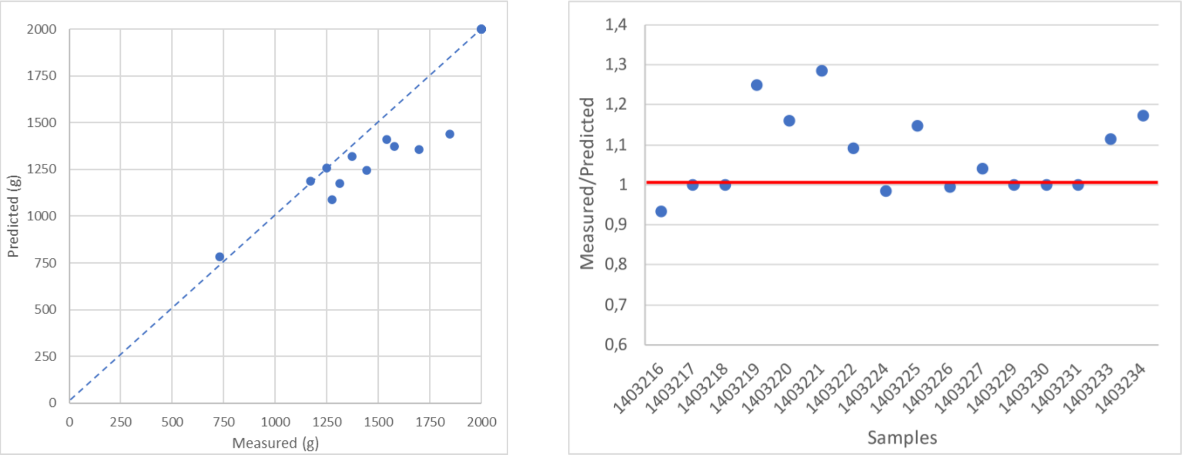


Figure AIII.5. Dart drop impact results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

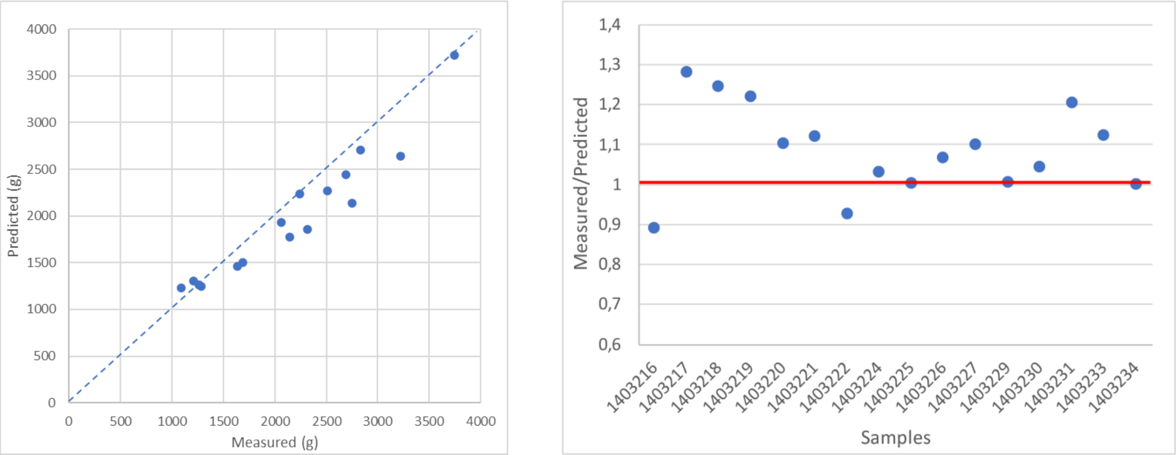


Figure AIII.6. Elmendorf tear MD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

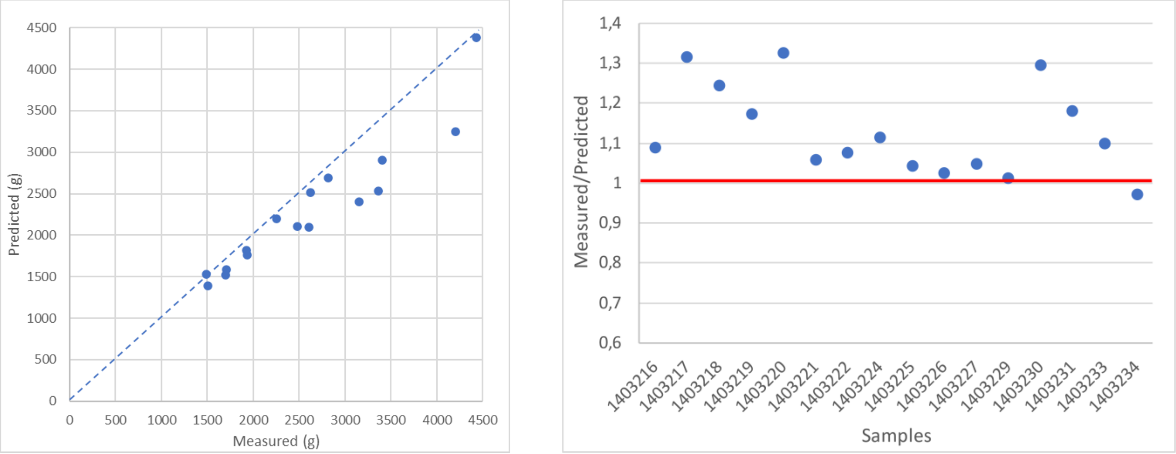


Figure AIII.7. Elmendorf tear CD results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

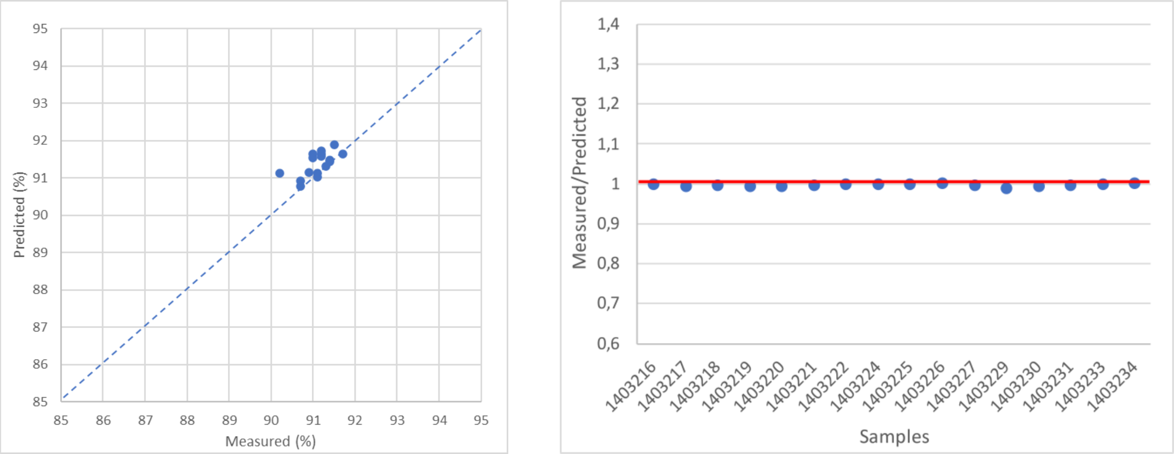


Figure AIII.8. Light transmission results comparison for the prediction and the measured values. In the left, the values directly compared in both axes, in the right, the values of the measured/predicted for each sample.

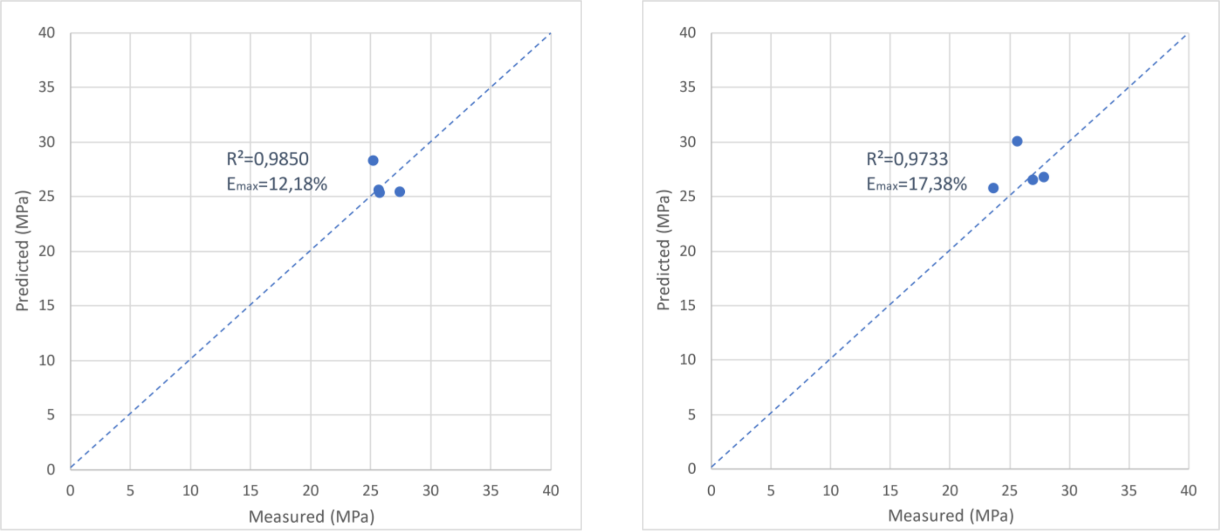


Figure AIII.9. Test results for the Stress at break in MD and CD respectively property showing the coefficient of determination and the maximum error achieved.

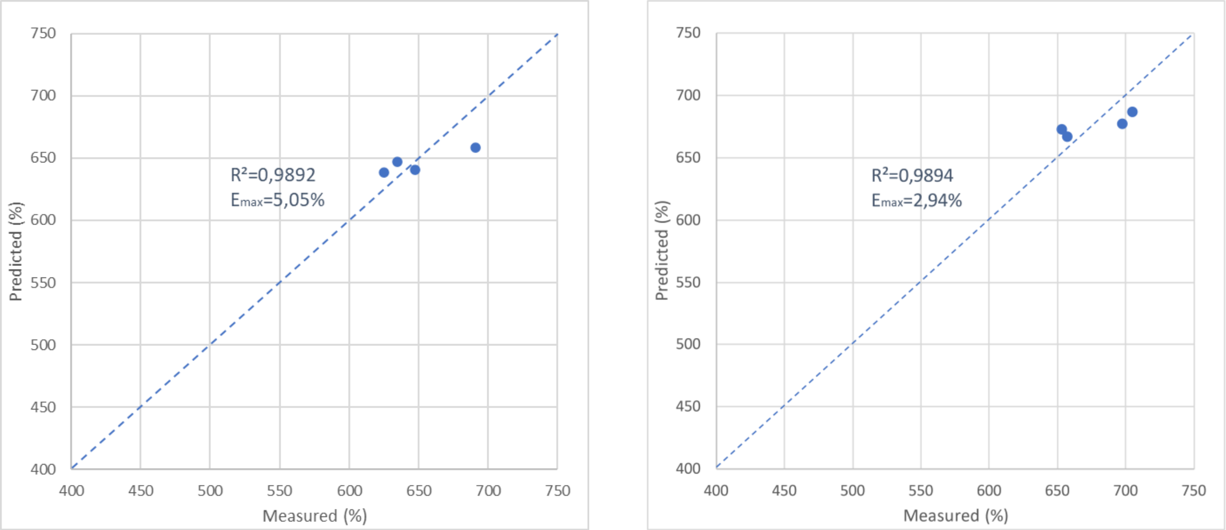


Figure AIII.10. Test results for the Strain at break in MD and CD respectively property showing the coefficient of determination and the maximum error achieved.

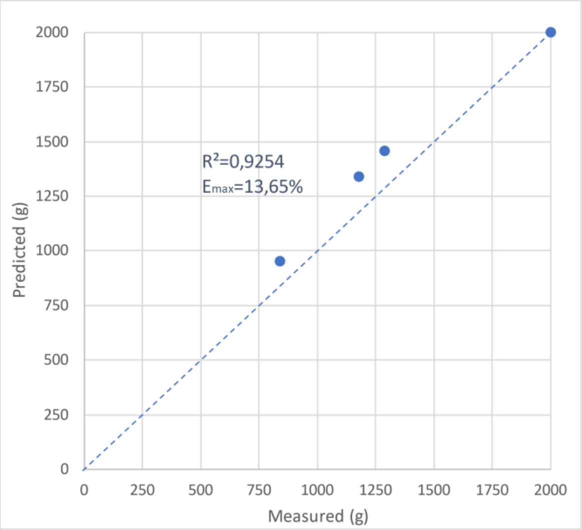


Figure AIII.11. Test results for the Dart drop impact property showing the coefficient of determination and the maximum error achieved.

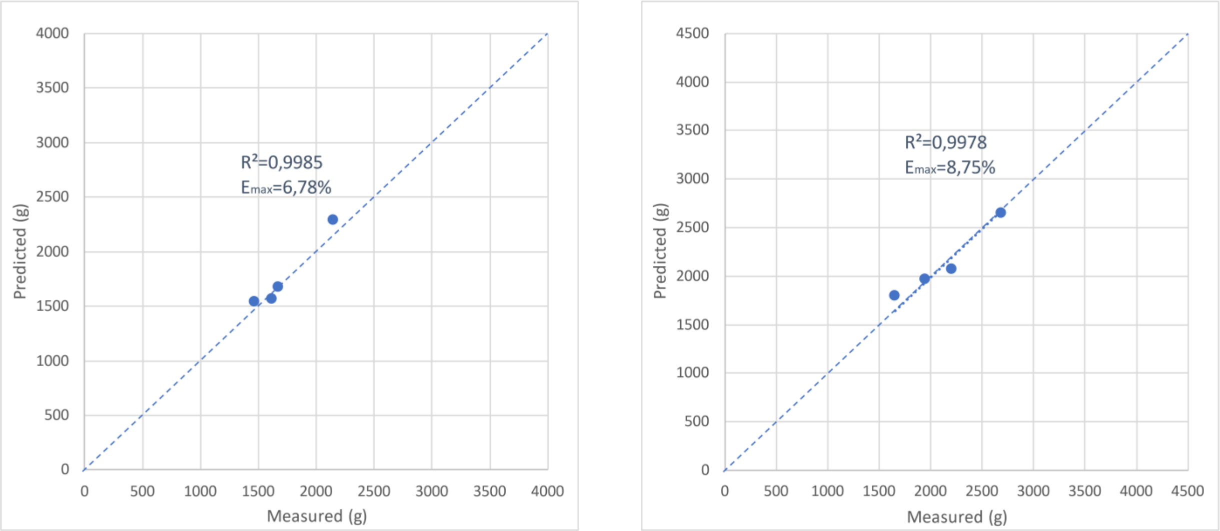


Figure AIII.12. Test results for the Elmendorf tear in MD and CD respectively property showing the coefficient of determination and the maximum error achieved.

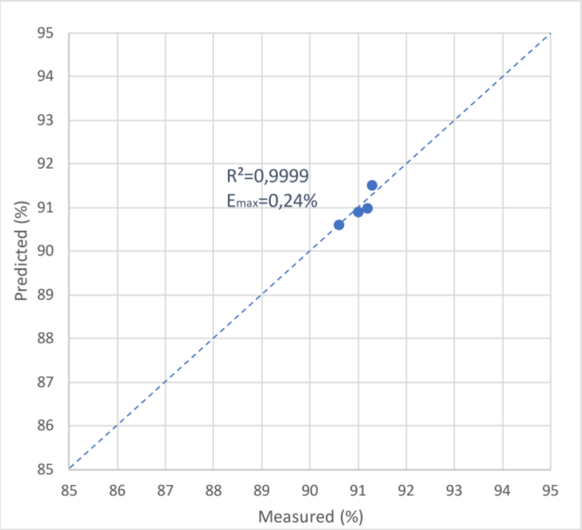


Figure AIII.13. Test results for the Light transmission property showing the coefficient of determination and the maximum error achieved.

APPENDIX IV: Self-evaluation Questionnaire

a) Evaluate the acquired **competences** according to the **tasks** you have carried out.

Degree Competences		**Task in which you have observed the competence**	**Self-evaluation [Rank 1 to 10]**	**Aspects to be improved**
SPECIFIC COMPETENCES				
A1.1	Effectively apply knowledge of basic, scientific and technological materials pertaining to engineering.	Design of experiments and experimental plan	9	-
A1.2	Design, execute and analyze experiments related to engineering	Experimental plan	9	Consider other methodologies
A1.3	Be able to analyze and synthesize the continuous progress of products, processes, systems and services, whilst applying criteria of safety, economic viability, quality and environmental management. (G6)	Extrusion and characterization	9	Take into account a hypothetical environmental impact section generated by the project.
A1.4	Know how to establish and develop mathematical models by using the appropriate software in order to provide the scientific and technological basis for the design of new products, processes, systems and services and for the optimization of existing ones. (G5)	Model generation	10	-
A2.1	Be able to apply the scientific method and the principles of engineering and economics to formulate and solve complex problems that arise in processes, equipment, installations and services, in which the material undergoes changes to its composition, state or energy content, these changes being characteristic of industrial chemistry and other related sectors such as pharmacology, biotechnology, materials sciences, energy, food and the environment. (G1)	Extrusion	10	-
A2.2	Conceive, project, calculate and design processes, equipment, industrial installations and services in the field of chemical engineering and related industrial sectors in terms of quality, safety, economics, the rational and efficient use of natural resources and the conservation of the environment. (G2)	Entire project	9	-
A2.3	Lead and technically and economically manage projects, installations, plants, companies and technological centres in the ambit of chemical engineering and related industrial sectors. (G3)	Extrusion of multilayers and other projects	10	-
A3.1	Apply knowledge of mathematics, physics, chemistry, biology and other natural sciences by means of study, experience, practice and	Model generation and design of experiments	9	Economic analysis of the viability of the films generated with the different alternatives proposed.

	critical reasoning in order to establish economically viable solutions for technical problems (I1).			
A3.2	Design and optimize products, processes, systems and services for the chemical industry on the basis of various areas of chemical engineering, including processes, transport, separation operations, and chemical, nuclear, elctrochemical and biochemical reactions engineering (I2).	Extrusion	10	-
A3.3	Conceptualize engineering models and apply innovative problems solving methods and appropriate IT applications to the design, simulation, optimization and control of processes and systems (I3).	Entire project	10	ANN model designed (not included for confidentiality reasons)
A3.4	Be able to solve unfamiliar and ill-defined problems by taking into account all possible solutions and selecting the most innovative. (I4)	Model generation	10	-
A3.5	Lead and supervise all types of installation, process, system and service in the different industrial areas related to chemical engineering (I5).	Extrusion and characterization	10	-
A3.6	Design, construct and implement methods, processes and installations for the integrated management of waste, solids, liquids and gases, whilst also taking into account the impacts and risks of these products (I6).	Extrusion and characterization	8	Take into account a hypothetical environmental impact section generated by the project.
A4.1	Lead and organize companies and production and service systems by applying knowledge and abilities regarding industrial organization, commercial strategy, planning and logistics, mercantile and labour legislation, and financial and costs accounting (P1).	Other projects	7	Contact with customers from this agricultural sector to learn and apply ideas for the project.
A4.2	Lead and manage the organization of work and human resources by applying criteria regarding industrial safety, quality management, occupation risk prevention, sustainability and environmental management (P2).	Entire project	10	-
A4.3	Manage research, development and technological innovation whilst ensuring the transfer of technology and taking into account property and patent rights (P3).	Innovating tool for blown extrusion project	10	-
A4.4	Adapt to structural changes in society caused by economic, energy or natural factors so as to be able to solve any resulting problems and to contribute technological solutions with a high commitment to sustainability (P4).	Entire project	10	-
A4.5	Lead and monitor the control of installations, processes, products, certification, auditing, verification, testing and reports (P5).	Entire project	10	-
A5.1	Carry out, present and defend (once all the curriculum credits have been obtained) an original	Project developed	10	-

	individually produced piece of work before a university panel. The work will consist of a professional integrated Chemical Engineering project that synthesizes (TFM1)			
TRANSVERSAL COMPETENCES				
B1.1	Communicate and discuss proposals and conclusions in a clear and unambiguous manner in specialized and non-specialized multilingual forums (G9).	Design of the model and predictions	8	To have more opinions about the task performed (internally).
B1.2	Adapt to changes and be able to apply new and advanced technologies and other important developments with initiative and entrepreneurial spirit. (G10)	Entire project	10	-
B2.1	Lead and define multidisciplinary teams that are able to make technical changes and address management needs in national and international contexts. (G8)	Other projects done	10	-
B3.1	Work in a team with responsibilities shared among multidisciplinary, multilingual and multicultural teams	Other projects done	10	-
B4.1	Be able to learn autonomously in order to maintain and improve the competences pertaining to chemical engineering that enable continuous professional development. (G11)	Entire project	10	-
B5.1	Carry out and lead the appropriate research, design and development of engineering solutions in new or little understood areas, whilst applying criteria of creativity, originality, innovation and technology transfer. (G4)	Entire project	9	To have more time to make another model and compare it with the current one.
B5.2	Bring together knowledge, make judgements and take decisions on the basis of incomplete or limited knowledge whilst taking into account the social and ethical responsibilities of professional practice. (G7)	Entire project, other projects and conversation with the students program	10	-
NUCLEAR COMPETENCES				
C1.1	Have an intermediate mastery of a foreign language, preferably English	All the internship	10	-
C1.2	Be advanced users of the information and communication technologies	Entire project	10	-
C1.3	Be able to manage information and knowledge	Entire project	10	-
C1.4	Be able to express themselves correctly both orally and in writing in one of the two official languages of the URV	During all the master's degree	10	-
C2.1	Be committed to ethics and social responsibility as citizens and professionals	During all the master's degree	10	-
C2.2	Be able to define and develop their academic and professional project	Entire project	10	-

b) Evaluate the final master project and suggest improvements.

Key steps	**Evaluation [Mark 1 to 10]**	**Improvement proposed**
Selection/assignment of the project (dissemination, communication, assignment requirements...)	10	No improvements, I would just like to highlight the ease of the whole process as well as the communication. In our case, two different projects were given to two students as the tutors considered with our profiles.
Stay (welcome, length, relationship, follow-up made by the company...)	10	Again no improvements. I would like to highlight the good treatment received during the nine months, the knowledge acquired, the help, the personal opinion. Without a doubt I think that the agreement between URV and Dow is fantastic.
Follow-up made by URV tutor	10	The relationship with Antoni Cabello has been great, direct and very professional. Perhaps I would highlight my own opinion of having more meetings, although I have not missed any comments of improvement with the project carried out.
Other aspects to be considered (which ones...)	-	-