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**Escola Tècnica Superior
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DOW

Development of a MDO Polyethylene film for convenient packaging

**Master thesis presented by Francesc
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to obtain the Master's degree in chemical engineering
from the Universitat Rovira i Virgili

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NOMENCLATURE

PE: Polyethylene

LDPE: Low Density Polyethylene

LLDPE: Linear Low-Density Polyethylene

MDPE: Medium Density Polyethylene

HDPE: High Density Polyethylene

MDO: Machine Direction Orientation

BUR: Blow-Up Ratio

MD: Machine Direction

CD: Cross Direction

SR: Stretching ratio

MI: Melt Index

TS&D: Technical Service and Development

CRI: Central Report Index

BOPP: Biaxially oriented polypropylene

BOPET: Biaxially oriented polyethylene terephthalate

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SUMMARY

A comprehensive study has been conducted to evaluate the feasibility of replacing multimaterial structures containing Biaxially Oriented Polypropylene (BOPP) or Biaxially Oriented Polyethylene Terephthalate (BOPET) with monomaterial structures of Polyethylene (PE) using Machine Direction Orientation (MDO) post-extrusion technology.

This report presents the design of a MDO PE film that exhibits heat resistance, high stiffness, good optical properties, and near-easy tearing in both machine and cross directions. The study meticulously examined all process parameters of the MDO, gaining a thorough understanding of their impact on the desired properties.

The findings of this study demonstrate the viability of substituting BOPP and BOPET films with MDO PE films, offering significant advancements in film performance and sustainability.

1. INTRODUCTION

In the modern food industry, the demand for convenient packaging solutions has become increasingly prominent. Convenient packaging not only ensures the safety and freshness of food products but also enhances the consumer experience through ease of use, portability, and extended shelf life.

One of the key technologies driving advancements in this area is the Machine Direction Orientation (MDO) machine, which significantly can enhance the mechanical properties and performance of extruded films by stretching them in the machine direction (MD).

Film extrusion, the process of melting plastic polymers and forming them into continuous films, serves as the foundation for the MDO process. These films, produced through either cast or blown film extrusion methods, are integral to the creation of various types of packaging, such as shrink wraps, barrier films, resealable bags... These packaging solutions offer practical benefits like moisture resistance, durability, and flexibility. Additionally, the ability to produce multi-layer films through co-extrusion further enhances the functionality of packaging by combining different materials to achieve desired properties.

This thesis will explore the intersection of convenient packaging, film extrusion and a particular focus on the use of the MDO machine.

By examining how innovations in post-extrusion technology, specifically the MDO process, contribute to the development of packaging solutions that cater to consumer demands for convenience and sustainability, this research aims to provide a comprehensive understanding of the role of MDO in shaping the future of food packaging.

1.1. Plastic blown film coextrusion

Coextrusion blown film is a sophisticated manufacturing process used to produce multi-layer plastic films with enhanced properties by combining different polymers. The process begins with the selection of appropriate polymers. Additives also play an important role to enhance the film's properties and processing performance.

Multiple extruders are employed, each dedicated to melting and conveying a specific polymer. The extruders consist of a hopper, a heated barrel, and a screw. The polymer resin is fed into the hopper, transported through the barrel by the rotating screw, and melted by the applied heat. Precise temperature control is essential to ensure the polymers reach the correct viscosity for extrusion without degrading [1]. In Figure 1.1. can be seen the Extruder system.

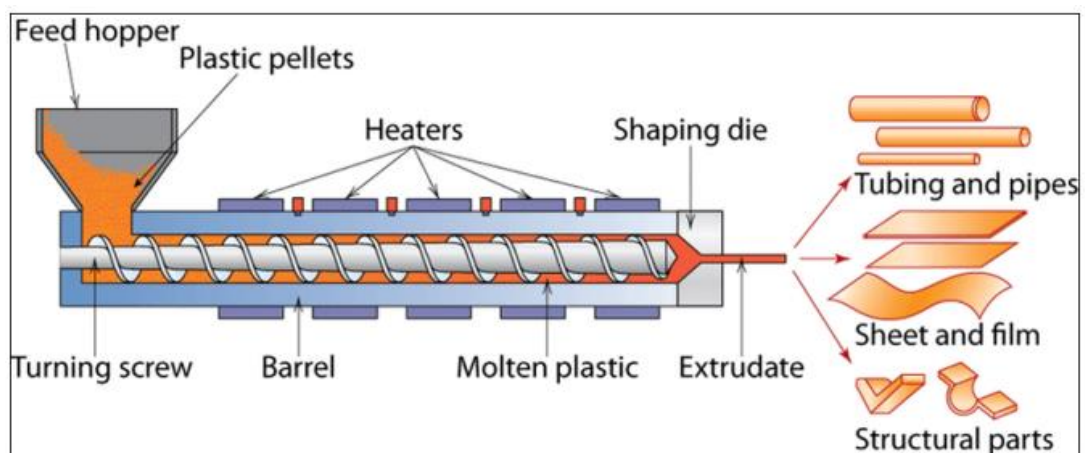


Figure 1.1. Extruder system

The molten polymers from each extruder are fed into a single annular die. The die combines the different polymer melts into a multi-layered tubular film, ensuring uniform layer distribution and adhesion. The configuration of the layers (e.g., A/B/C, where A, B, and C can represent different polymers) is determined based on the desired properties of the final film.

Air is introduced into the center of the die through an air ring, inflating the extruded tube into a bubble. The air ring also provides cooling to the outer surface of the bubble. Maintaining bubble stability is crucial, and parameters such as blow-up ratio (BUR) are carefully controlled. BUR is the ratio of the final bubble diameter to the die diameter.

The bubble is cooled using a combination of external air rings and internal bubble cooling systems. The cooling rate affects the film's crystallinity and mechanical properties.

The cooled bubble is collapsed by nip rollers into a flat tube, also known as lay-flat tubing. The lay-flat tubing is then wound onto rolls for further processing, with winding tension controlled to prevent film deformation [2]. In Figure 1.2. can be seen a blown film line overview.

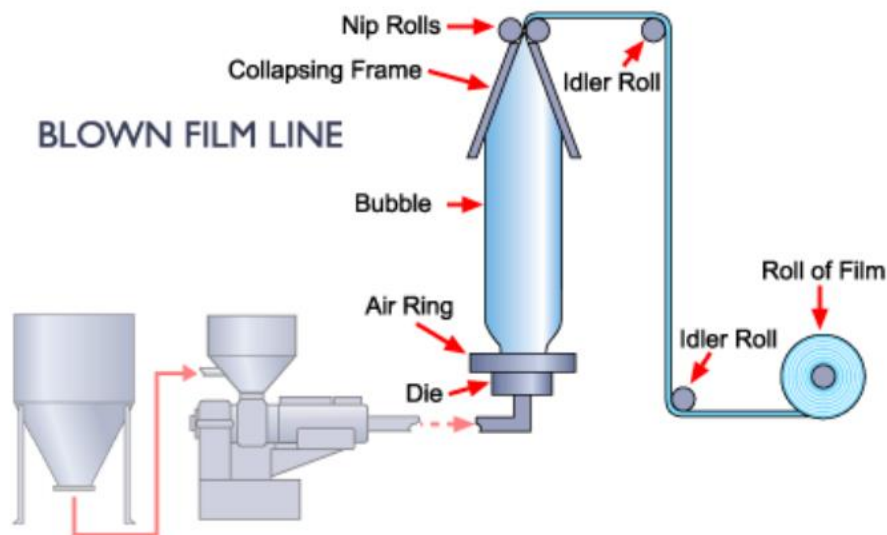


Figure 1.2. Blown Film Line Overview

1.2. MDO Process fundamentals

Machine Direction Orientation (MDO) is a post-extrusion process used to enhance the properties of plastic films. This process involves stretching the film in the machine direction (MD), which aligns the polymer chains and tries to improve various film characteristics such as barrier properties, stiffness, clarity, tensile strength...

A general MDO process begins with the heating phase, where the film is conveyed over a set of heated rollers to reach the required temperature for stretching. This heated film is fed into a slow stretching roll with nip roller, which has the same or all most same rolling speed as the heated roller.

The film then enters a fast stretching roll, running at a speed faster than the slow stretching roll, resulting in a stretch ratio of more than 1, and effectively orients the film on continuous basis in the MD. The ratio of the speed of these two rollers regulates the stretching ratio. Stretching ratio will be explained in next section.

The next phase is annealing, where the film passes over a set of rollers that help to relieve internal stresses induced during stretching. Finally, the film is cooled down in the cooling phase, stabilizing its new dimensions and properties. In Figure 1.3. below can be seen an overview of a MDO.

MDO is typically carried out after the blown film extrusion process. Once the blown film is produced and wound into rolls, it can be fed into the MDO unit for further processing. This sequential approach allows manufacturers to produce films with tailored properties, combining the benefits of both blown film extrusion and machine direction orientation. The result is a high-performance film suitable for demanding applications in packaging and other industries [3] [4].

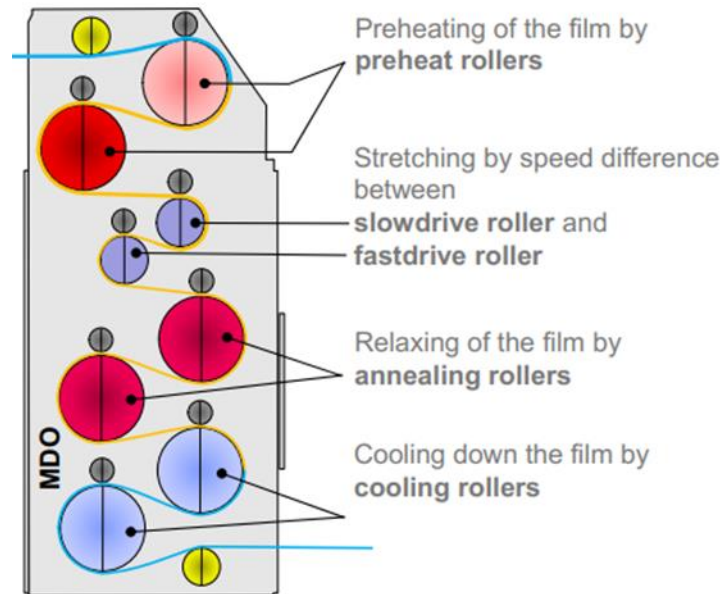


Figure 1.3. MDO Process fundamentals

The team has identified several critical parameters to study the Machine Direction Orientation (MDO) process: the stretching ratio, the temperature of the rolls, the stretching gap between the rolls, the velocity of the rolls, and the method of stretching. By carefully studying these parameters, the MDO process can significantly enhance the properties of the blown film, making it suitable for high-performance applications.

1.2.1. Stretching Ratio

This parameter refers to the ratio of the final thickness of the film to its original thickness before stretching. Additionally, the stretching ratio can be calculated as the division of the speed of the fast stretching roll by the speed of the slow stretching roll. This ratio is crucial for determining the degree of orientation and the resulting mechanical properties of the film.

$$\text{Stretching Ratio (SR)} = \frac{\text{Thickness of the unstretched film}}{\text{Thickness of the stretched film}} \quad (1)$$

$$\text{Stretching Ratio (SR)} \approx \frac{\text{Speed of the fast stretching roll}}{\text{Speed of the slow stretching roll}} \quad (2)$$

1.2.2. Temperature of the Rolls

The temperature at which the rolls operate is vital for achieving the desired film properties. Proper temperature control ensures that the film is sufficiently pliable for stretching without causing thermal degradation. The temperature must be optimized to balance between ease of stretching and maintaining film integrity.

1.2.3. Stretching Gap Between the Rolls

This is the distance between the rollers where the film is stretched. The gap must be precisely controlled to ensure uniform stretching and to avoid issues such as high neck-in or uneven thickness. Neck-in refers to the reduction in the width of a film as it undergoes stretching in the MDO process. This phenomenon occurs due to the Poisson effect, where the material contracts laterally (in width) as it is stretched longitudinally (in length).

1.2.4. Speed of the Rolls

The speed of the fast and slow rolls is synchronized with the stretching ratio. The speed of the other rolls also plays a crucial role. For example, a slower velocity in the heating rolls increases the contact time between the film and the roll, resulting in improved heat transfer. Proper control of roll velocity is essential for achieving the desired orientation and mechanical properties of the film.

1.2.5. Stretching method

This parameter pertains to the selection of rolls used for film stretching in the MDO process. Specifically, it involves determining which roll will serve as the slow stretching roll and which will serve as the fast stretching roll. The choice of rolls is critical for the final output. Stretching between the first two rolls of the MDO differs significantly from stretching between the last two rolls. In the former scenario, heat transfer between the rolls and the film may be insufficient if high-temperature stretching is desired. Conversely, in the latter scenario, there is more time for heat transfer between the roll and the film, but there is also a risk of the film melting before reaching the stretching rolls if a high temperature is applied.

1.3. Description of the problem

Machine Direction Oriented (MDO) films are a key pillar for designing recyclable and sustainable packaging. At present, a significant portion of Dow's polyethylene (PE) volume is used in multi-material structures, mixed with dissimilar materials, making it non-recyclable and often leading to landfill or incineration due to varying melting temperatures and material incompatibility.

Recyclability and sustainability are increasingly important in packaging due to growing environmental concerns and regulatory pressures. Sustainable packaging not only reduces waste and conserves resources but also meets consumer demand for eco-friendly products. By focusing on recyclable materials, companies can minimize their environmental footprint and contribute to a circular economy.

The project focuses on design for recycling by re-engineering packaging to replace biaxially oriented polypropylene (BOPP) and biaxially oriented polyethylene terephthalate (BOPET) print webs with oriented PE print webs, resulting in mono-material packaging that can be recycled.

Orientation technologies, such as MDO, are known to enhance the properties of PE films, making them suitable for replacing BOPP/BOPET print webs.

Some properties— good optics, good stiffness, good heat resistance, and easy tearing in both directions — are essential for maintaining the quality and functionality of food packaging. Good optical properties enhance product visibility and appeal, stiffness provides structural integrity, heat resistance ensures the packaging can withstand various temperatures, and easy tearing improves user convenience.

If these properties can be achieved through MDO PE films, they can effectively replace traditional multi-material films, offering a sustainable and high-performance solution for food packaging. In the following study, the team has been focused on achieving easy tear in both directions, with a particular emphasis on improving the ease of tearing in the cross direction (CD), while maintaining the other desired properties.

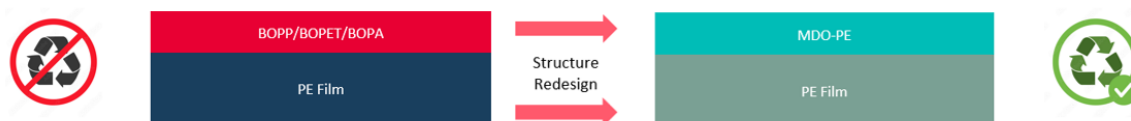


Figure 1.4. Problem statement

In Figure 1.5 can be seen some examples of final products in convenient food packaging.



Figure 1.5. Examples of convenient food packaging

2. SCOPE OF THE PROJECT

The scope of the project includes understanding of the problem and initial research, the selection of materials for coextrusion, the selection of process parameters for the blown extrusion method, and the selection of parameters for the Machine Direction Orientation (MDO). Additionally, the project involves conducting mechanical property testing of the film in the laboratory.

2.1. Objective

The objective of this project is to develop a Machine Direction Oriented (MDO) polyethylene (PE) film that possess:

- good optical properties
- good stiffness
- good heat resistance
- easy tearing in both directions (machine and mostly cross)

2.2. Strategic Plan

Optimizing the process parameters of the Machine Direction Orientation (MDO) will yield a film that meets all the desired properties.

By understanding the impact of each process parameter on these properties—such as optical properties, stiffness, heat resistance, and tearability—the MDO process can be fine-tuned to achieve optimal results. This optimization not only ensures the production of high-quality films but also presents an opportunity to develop a cost-effective solution.

3. STUDENT'S ROLE IN THE COMPANY

Developing a master thesis in a company is crucial for the student as it provides invaluable practical experience and industry insights that enhance his academic research. It allows the student to apply theoretical knowledge to real-world problems, gain access to advanced technologies and resources, and benefit from the mentorship of experienced professionals. Additionally, working within a company fosters networking opportunities, which can be instrumental for future career prospects.

3.1. Description of the company

DOW is a leading materials science company headquartered in Midland, Michigan, with operations in approximately 160 countries. The company specializes in creating innovative solutions through its deep expertise in materials science, offering a diverse product portfolio that includes chemicals, plastics, performance chemicals, catalysts, and coatings. DOW is committed to sustainability and innovation, striving to deliver best-in-class performance while addressing some of the world's most pressing challenges.

The company's goal is to be the most innovative, customer-centric, inclusive, and sustainable materials science company in the world [5]. This ambition drives DOW's efforts to continuously seek materials science breakthroughs, enhance customer interactions, champion inclusivity, and promote sustainability. DOW's 2025 Sustainability Goals reflect this commitment, focusing on advancing a circular economy, reducing greenhouse gas emissions, supporting healthy ecosystems, and eliminating plastic waste [6] [7].

DOW's products are designed to meet the needs of various industries, including packaging, infrastructure, consumer care, electronics, and transportation. By leveraging its materials science expertise, DOW aims to create solutions that improve the quality of life for people around the world while ensuring a positive impact on society and the planet [5].

DOW's 2025 Sustainability Goals include several key initiatives. The company aims to develop societal blueprints that integrate public policy solutions, science and technology, and value chain innovation to facilitate the transition to a sustainable planet and society. DOW has already published blueprints on topics such as carbon reductions, sustainable watershed management, product safety, and valuing nature [6]. Additionally, DOW collaborates with partners to implement major projects that advance the circular economy, such as chemical recycling and the development of recycled plastic resins [6].

In terms of innovation, DOW is committed to delivering breakthrough sustainable chemistry innovations that have a net-positive impact on global sustainable development. The company has set ambitious targets to increase the net-positive impact of its products across all markets and to align its innovation portfolio with sustainability outcomes [6]. DOW's businesses also set their own sustainability goals and track progress using the Dow Innovation Portfolio Sustainability Assessment, a science-based, future-oriented tool that helps embed sustainability in key business decisions [6].

Overall, DOW's dedication to innovation, customer-centricity, inclusivity, and sustainability positions it as a leader in the materials science industry, driving positive change and creating value for its customers, employees, and society as a whole.

3.2. Specific tasks of the student

The development of the project can be divided in the following steps.

3.2.1. Understanding of the project

It may seem obvious, but this step is absolutely fundamental. The student must have a clear understanding of what is required and the scope of the project. This involves comprehensively reviewing the project guidelines, objectives, and deliverables. By doing so, the student can ensure they are aligned with the expectations and can effectively plan their approach.

Understanding the scope of the project means recognizing the boundaries and limitations, as well as identifying the key tasks and milestones. This clarity helps in setting realistic goals and timelines, which are crucial for successful project management. Additionally, it allows the student to anticipate potential challenges and devise strategies to address them proactively.

Moreover, having a thorough grasp of the project's requirements enables the student to communicate effectively with supervisors, mentors, and team members. It fosters a collaborative environment where everyone is on the same page, contributing to a more cohesive and productive workflow.

3.2.2. Internal and External Research

Once the previous step is completed, the research phase can start. This involves a thorough search for data and information from both external and internal sources. External sources may include patents, academic journals, industry publications, and other publicly available resources. These sources provide a wealth of information on existing technologies, methodologies, and innovations that can inform and guide the research process.

Internal sources are equally important and include Central Report Indexs (CRIs). CRIs are key research projects within the organization that are prioritized due to their potential impact on innovation, sustainability, and business growth. These initiatives are often at the forefront of the company's research and development efforts, addressing critical challenges and exploring new opportunities.

At the beginning of the research phase, the student had access to a limited number of CRIs, specifically five. However, as the research progressed, there was an opportunity to expand this access, allowing the student to explore an unlimited number of CRIs. This expanded access provided a broader perspective on the company's research landscape and enabled the student to leverage a more extensive range of internal data and insights.

3.2.3. Fabrication

Once the information-gathering phase is completed, the student transitions to the fabrication phase. During this phase, the student is responsible for creating a comprehensive "fabrication report" for the fabrication team. This report details the materials to be extruded, the structure of these materials within the film, the film's thickness, film length, film width, the processing conditions for the blown extrusion line...

Upon completion of the fabrication report, the extrusion process is carried out by the fabrication team. The student is encouraged to attend this process to gain a deeper understanding of the operational aspects. With the extrusion process completed and the samples extruded, the next step is the stretching process in the Machine Direction Orientation (MDO) unit.

For the MDO stretching process, another fabrication report is generated in the system. This report specifies the conditions under which the stretching should be conducted, including the temperature of the rolls, the speed of the rolls the spacing between the rolls...

This entire stretching phase has been conducted in Singapore, as the MDO machine in Tarragona has been out of service since the student arrived at DOW. Utilizing the Singapore facility has presented several challenges for both the team and the student. These challenges include familiarizing themselves with the Singapore team, adapting to the operational differences of the Singapore machine compared to the one in Tarragona (needed changes to the manufacturing study), negotiating the deadlines for the stretching phase and managing the time zone differences.

Despite these challenges, the experience has been invaluable. It has provided the student with a unique opportunity to learn and adapt to different operational environments, enhancing their problem-solving skills and flexibility. The collaboration with the Singapore team has also fostered a deeper understanding of global manufacturing practices and has underscored the importance of effective communication and coordination across different geographical locations.

3.2.4. Testing

The testing for this project has also been carried out in Singapore and samples were sent to Tarragona for visual inspection.

3.2.5. Side Projects

The student has also been actively involved in various side projects, contributing to a broader range of research and development activities. One such project includes studying the replacement of old polystyrene applications with MDO polyethylene. This project aims to explore the feasibility and benefits of using MDO polyethylene as a more sustainable and efficient alternative to traditional polystyrene applications.

Another significant side project involves evaluating the performance of different grades of a DOW product across various substrates, including PET, PP, and glass. This study is crucial for understanding how the product interacts with different materials and identifying the optimal grades for specific applications. The insights gained from this research can lead to improved product formulations and enhanced performance in diverse industrial applications.

The development of these side projects follows the same rigorous steps as the main project, including thorough research, data analysis, and detailed reporting. However, it is important to note that for the project on replacing polystyrene with MDO polyethylene, no fabrication has been conducted. This project is currently in the research and feasibility assessment phase, focusing on theoretical analysis and preliminary evaluations.

By engaging in these side projects, the student has gained valuable experience in handling multiple research initiatives simultaneously. This involvement has not only broadened their technical knowledge but also enhanced their project management and problem-solving skills. The exposure to different materials and applications has provided a well-rounded understanding of the complexities and challenges in the field of materials science.

3.3. Alignment with the company goals

The work done aligns with DOW's values and future goals in several significant ways. By focusing on the development of recyclable mono-material packaging, it directly supports DOW's commitment to sustainability and advancing a circular economy. This approach reduces waste and minimizes environmental impact by replacing non-recyclable multi-material structures with recyclable polyethylene (PE) films. The innovative use of Machine Direction Oriented (MDO) technology to enhance the properties of PE films demonstrates DOW's dedication to being a leader in materials science innovation. These MDO PE films can offer essential qualities making them a high-performance alternative to traditional packaging materials like biaxially oriented polypropylene (BOPP) and biaxially oriented polyethylene terephthalate (BOPET).

Furthermore, the project addresses the growing consumer demand for eco-friendly packaging solutions, aligning with DOW's customer-centric approach. By providing sustainable packaging options, DOW can meet market needs while contributing to environmental protection. The project also likely involved collaboration with various stakeholders, reflecting DOW's emphasis on partnerships and collective efforts to achieve sustainability goals. Overall, the project not only supports DOW's current values but also positions the company to meet future challenges and opportunities in the realm of sustainable packaging. This comprehensive approach ensures that DOW remains at the forefront of innovation while making a positive impact on the environment and society.

4. METHODOLOGY AND DESIGN OF EXPERIMENTS

To achieve the project's objective of developing a Machine Direction Oriented (MDO) polyethylene (PE) film with good optical properties, high stiffness, robust heat resistance, and ease of tearing in both machine and cross direction, a comprehensive and methodical approach was implemented.

4.1. Selection of Materials

The selection of materials is critical in a project involving a blown extrusion line combined with Machine Direction Orientation (MDO) due to its direct impact on the film's performance. Choosing the appropriate polyethylene (PE) grades ensures that the film exhibits the desired properties such as stiffness, heat resistance, optical clarity, and easy tear in both directions, while also being easy to process during the extrusion and orientation stages. Easier processing minimizes defects and enhances production efficiency. Additionally, the chosen materials must be cost-effective to ensure commercial viability, balancing performance with economic considerations.

4.1.1. Multilayer film structure

The team opted for a multilayer film, which consists of multiple layers of different materials, each selected for its specific properties. These films are commonly used in packaging to provide enhanced performance compared to mono-layer films. In this case, the film has five layers:



Figure 4.1. Layer distribution of a 5 layer film

The structure extruded in the blown extrusion line is as follows in Figure 4.2.

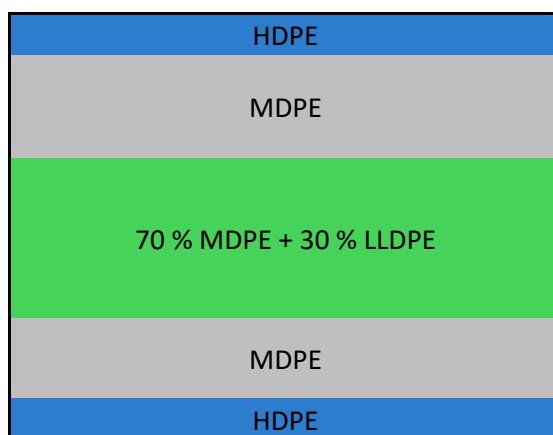


Figure 4.2. Materials used in each layer

The two skin layers represented 20% of the total film, the two sub-skin layers represented 40%, and the core layer constituted the remaining 40%.

The choice of materials was driven by several factors. Incorporating HDPE in the skin layers grants the heat resistance characteristic of this type of polyethylene. HDPE also contributes to the high stiffness required. Moreover, internal documents (CRIs) indicate that multilayer films with a density gradient—where density increases from the core to the outer layers—exhibit higher stiffness. The core layer, a blend of medium-density polyethylene (MDPE) and linear low-density polyethylene (LLDPE), combines the mechanical toughness of LLDPE with the improved processability and melt strength of MDPE. Melt strength, a measure of a polymer melt's resistance to stretching or deformation under tension, is crucial for film blowing.

This configuration aimed to achieve high stiffness and heat resistance, while addressing the need for good optics and easy tear in both directions. Good optics will be achieved through the MDO stretching process, which aligns the polymer chains, develop small crystals, reducing light scattering and haze, resulting in clearer and more transparent films. Additionally, MDO smooths the film's surface, enhancing its gloss and providing a polished appearance. The discussion on achieving easy tear in both directions is addressed in the chapter of MDO, where is explored the significant impact of each process parameter on the film properties.

4.2. Blown Extrusion Line

The blown extrusion line was set up with the Blow-Up Ratio (BUR) at the minimum to ensure optimal orientation of the polymer chains in the machine direction (MD). The BUR, defined as the ratio of the diameter of the blown film bubble to the diameter of the die from which the film is extruded, was kept low. This minimized expansion helps align the polymer chains more effectively in the MD. This alignment is beneficial because research has shown that MD orientation significantly decreases CD tear strength, making it a critical parameter in the process. This observation will be further clarified in the following chapter, 'MDO', which demonstrates how a higher stretching ratio in MD (higher MD orientation) enhances the ease of tearing in the CD.

The extruded film length was 300 meters, which was initially deemed sufficient for conducting all the planned tests at the Machine Direction Orientation facility in Tarragona. However, due to ongoing technical issues at the Tarragona MDO facility, the film roll had to be redirected to the operational MDO facility in Singapore.

Upon review, the technical team in Singapore indicated that a 300-meter length would be inadequate to perform the full suite of desired experiments. Consequently, the team had to revise and prioritize the experimental procedures to fit within the available film length. This adjustment ensured that the most critical tests could still be conducted, but with some limitations on the scope of the experiments.

4.3. MDO

The primary objective of the Machine Direction Orientation study was to comprehensively understand the impact of various process parameters on the mechanical properties of the film, with a particular focus on cross-direction tear strength, which was the project's key challenge. Section 1.2.1 detailed all the identified MDO unit process parameters:

- Stretching Ratio
- Temperature of the Rolls
- Stretching Gap Between the Rolls
- Velocity of the Rolls
- Stretching Method

Among these parameters, two were not investigated in this project: the velocity of the rolls and the temperature of stretching. This decision was driven by the constraint of limited sample length. The rationale for excluding these two parameters was as follows:

- Temperature of Stretching: Based on previous studies, it was well understood that the highest temperature at which the film could be heated without melting and adhering to the MDO rolls resulted in the most favorable CD tear properties. Given this established knowledge, the team decided to conserve sample length by not further investigating the temperature parameter.
- Velocity of the Rolls: The velocity parameter was not studied and was kept at low speeds because the available sample quantity was limited. It is easier to collect samples at lower speeds than at higher speeds.

By focusing on the remaining parameters, the team aimed to optimize the MDO process to enhance the film's mechanical properties, particularly the ease of tear in the cross direction.

4.3.1. Singapore's MDO

Section 1.2 outlines the fundamental principles of MDO. However, it is important to note that not all MDO systems are identical. This section delves into the specifics of the MDO system utilized at DOW Singapore.

The Figure 4.3 below illustrates the arrangement of the rolls and the temperature control strategy employed. The system comprises a total of 16 rolls, which are divided into 7 distinct heating groups. Each roll within a heating group is maintained at the same temperature, ensuring uniform thermal conditions across the group. Additionally, the system features two stretching groups, allowing for flexibility in the stretching process. This means that the film can be stretched in the first group, the second group, or both.

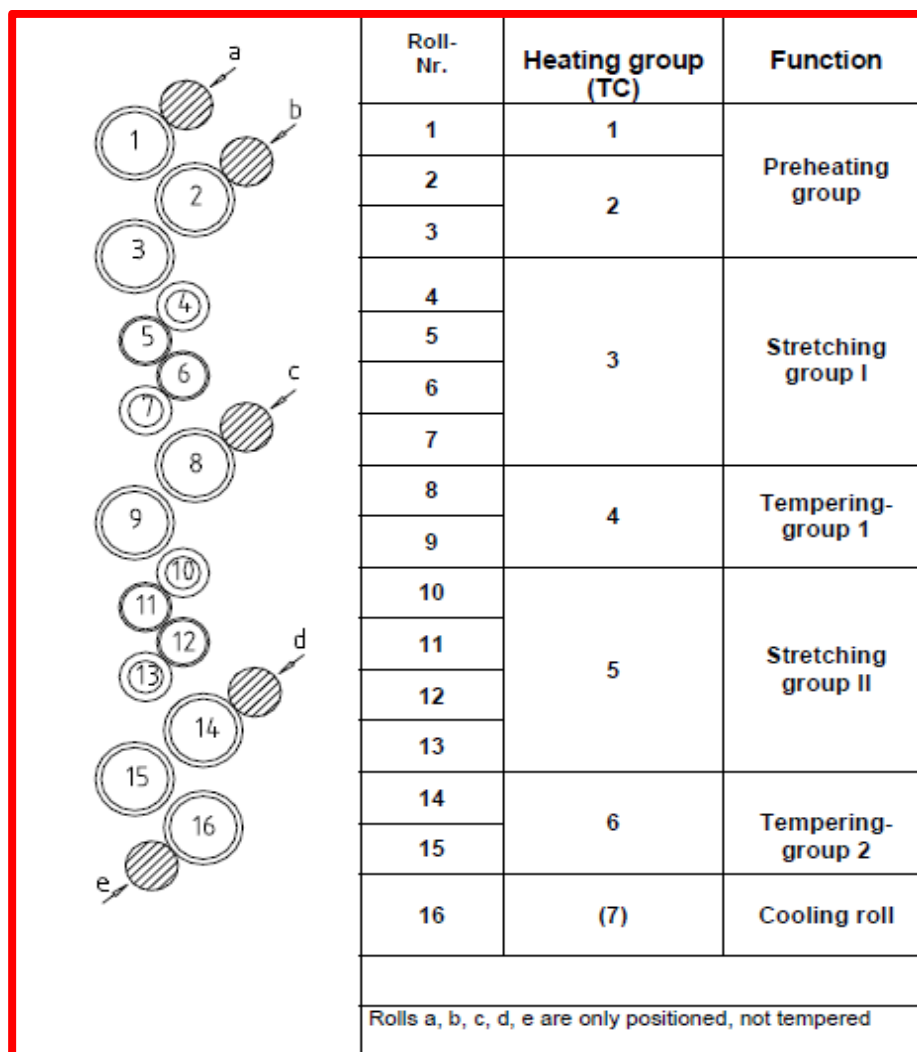


Figure 4.3. Singapore MDO

4.3.2. MDO's Experiments

Considering the length of the film to be stretched in the MDO and the process variables that were desired to study, the team designed 3 groups of experiments. Every group tries to study one variable.

4.3.2.1. Changing Stretching ratio

Achieving easy tearability in both the machine direction and cross direction is a crucial objective in the final film. The process of obtaining easy tear in the MD should be easy during the MDO process. This is because the film is stretched in the MD, causing the polymer chains to align predominantly along this direction. This alignment results in a film that is more susceptible to tearing along the MD, where the polymer chains are less entangled and more aligned. However, the challenge arises when trying to achieve easy tear in the CD.

Interestingly, the research uncovered a counterintuitive phenomenon with high-density polyethylene resins. After stretching in the machine direction (MD), the ease of tearing decreased in the MD but improved in the cross direction (CD). Figures 4.4 and 4.5 illustrate this unique behavior.

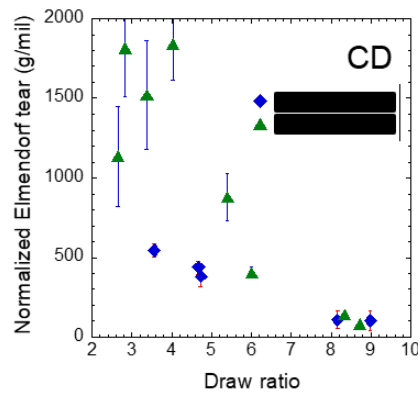


Figure 4.4. HDPE Resins CD tear strength as function of stretching ratio

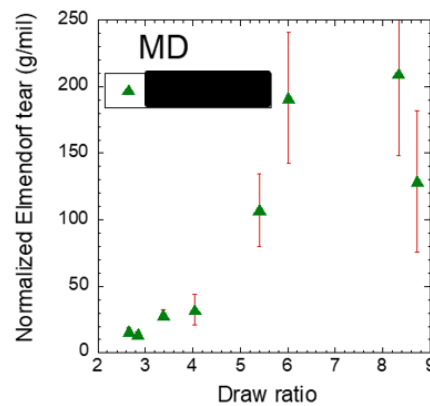


Figure 4.5. HDPE Resins MD tear strength as function of stretching ratio

Tie chains connect crystals, tie chains are important for the mechanical properties such as tear strength [2]. When these chains are lacking, like in HDPE resins, the film has lower mechanical properties and tears more easily, especially when the polymer chains of the film are aligned in the direction of stretch. Normally, stretching HDPE films makes them more stiff with many small crystals and reduces their tear strength in the direction of the stretch. However, in this case, the tear strength in the machine direction (MD) actually increases with levels of stretching, which is unexpected and suggests a complex interaction of factors that need further study.

On the other hand, the tear strength in the cross direction (CD) decreases as the stretching ratio increases. This is supposed to happen because stretching aligns the polymer chains, making the film more crystalline and less flexible, which makes it more brittle. This alignment also creates stress points, especially in the CD, where there are fewer tie chains to reinforce the material, making it more prone to tearing.

Figure 4.6. showcase similar patterns of increasing MD tear strength and decreasing CD tear strength with higher stretching ratios that were observed in another CRI. It was used a film formulation similar to the one proposed by the team.

Table 4.1. Stretching Ratio of each sample, every sample having the same formulation.

Sample	Stretching Ratio
M2	5.0
M3	5.5
M4	6.0
M5	6.5
M6	7.0

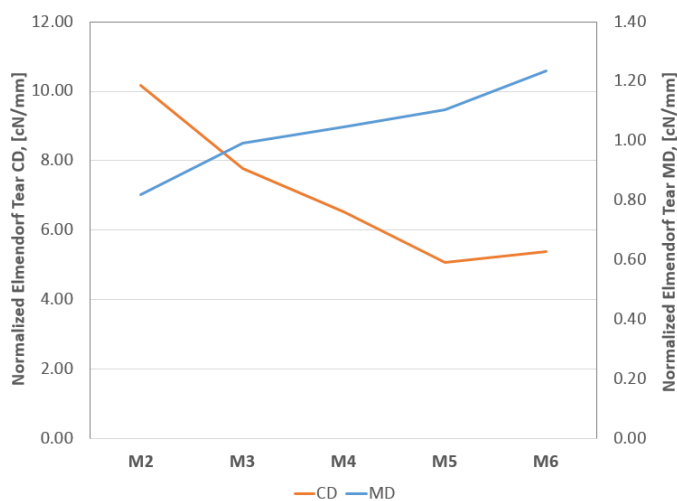


Figure 4.6. Tear strength as function of the stretching ratio

The team aimed to replicate this tendency to achieve the easiest possible Cross Direction (CD) tear. In the subsequent experiments, all process parameters were kept constant except for the stretching ratio, which was varied to study its effect.

The stretching temperature, as previously mentioned, was intended to be as high as possible. Initially, the team attempted to work with a temperature of 130°C; however, the film melted at this temperature. Subsequently, the temperature was reduced to 125°C, but the film still melted. It is important to note that when a film melts during the MDO stretching process, it adheres to the rolls in its molten state, rendering the production of the film impossible. The melting behavior of a multilayer film is governed by the distinct thermal properties of each polymer layer. The team hypothesized that incorporating HDPE in the skin layers would enable the film to withstand high temperatures. However, the experimental results indicated that was not enough. When the multilayer film was subjected to heat, the core layer, composed of LLDPE and MDPE, began to melt due to its lower melting point, making the operability not sustainable.

Below can be seen the process parameters of the first sample:

1				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	5,5	8,25	
7	120	1	8,25	
8	120	1	8,25	
9	120	1	8,25	
10	105	1	8,25	
11	105	1	8,25	
12	105	1	8,25	
13	105	1	8,25	
14	75	1	8,25	
15	75	1	8,25	
16	-	1	8,25	

Figure 4.7. Sample 1: 120°C, 5.5 SR, 5mm gap

The first sample was supposed to be conducted at a 5 SR, but the phenomenon called tiger striping occurred. Tiger striping is characterized by visual stripes appearing in cross direction of the film, where the film thickness in the stripe area can be significantly lower than the rest of the film, potentially leading to uneven film thickness and some time holes. To overcome this issue, the stretching ratio was adjusted to 5.5 SR instead of 5.

Below can be seen the process parameters of the second sample

2				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	6	9	
7	120	1	9	
8	120	1	9	
9	120	1	9	
10	105	1	9	
11	105	1	9	
12	105	1	9	
13	105	1	9	
14	75	1	9	
15	75	1	9	
16	-	1	9	

Figure 4.8. Sample 2: 120°C, 6 SR, 5mm gap

The film for the second sample was collected without any fabrication problem.

Below can be seen the process parameters of the third sample:

3				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	7	10,5	
7	120	1	10,5	
8	120	1	10,5	
9	120	1	10,5	
10	105	1	10,5	
11	105	1	10,5	
12	105	1	10,5	
13	105	1	10,5	
14	75	1	10,5	
15	75	1	10,5	
16	-	1	10,5	

Figure 4.9. Sample 3: 120°C, 7 SR, 5mm gap

The film for the third sample was collected without any fabrication problem.

Below can be seen the process parameters of the fourth sample:

4				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	8	12	
7	120	1	12	
8	120	1	12	
9	120	1	12	
10	105	1	12	
11	105	1	12	
12	105	1	12	
13	105	1	12	
14	75	1	12	
15	75	1	12	
16	-	1	12	

Figure 4.10. Sample 4: 120°C, 8 SR, 5mm gap

The film for the fourth sample was collected without any fabrication problem. With these four samples, the MDO stretching for the first group was successfully completed, achieving sample collection at four different stretching ratios while keeping all other process parameters constant.

4.3.2.2. Changing Stretching gap

The methodology for this set of experiments was the same like the previous one. All process parameters were meticulously maintained at constant levels, with the sole exception of the stretching gap, which was systematically varied to investigate its impact on the film's properties.

According to the research conducted, the team observed that a tighter stretching gap results in the application of a greater compressive force in the film. This increased compressive force imparts a degree of cross-directional (CD) orientation to the film.

Below can be seen the process parameters of the fifth sample:

5				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	2
6	120	6	9	
7	120	1	9	
8	120	1	9	
9	120	1	9	
10	105	1	9	
11	105	1	9	
12	105	1	9	
13	105	1	9	
14	75	1	9	
15	75	1	9	
16	-	1	9	

Figure 4.11. Sample 5: 120°C, 6 SR, 2mm gap

The film for the fifth sample was collected without any fabrication problem.

Below can be seen the process parameters of the sixth sample:

6				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	90	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	8
6	120	6	9	
7	120	1	9	
8	120	1	9	
9	120	1	9	
10	105	1	9	
11	105	1	9	
12	105	1	9	
13	105	1	9	
14	75	1	9	
15	75	1	9	
16	-	1	9	

Figure 4.12. Sample 6: 120°C, 6 SR, 8mm gap

The film for the sixth sample was collected without any fabrication problem. With the successful collection of these two samples, the MDO stretching for the second group was completed, achieving sample collection at two different stretching gaps while maintaining all other process parameters constant. It is important to note that Sample 2 is identical to Samples 5 and 6, except for a gap of 5mm. Therefore, the team effectively obtained three comparable samples with varying gaps to study the effect of the stretching gap on the film's properties.

4.3.2.3. Changing Stretching methodology

Up to this point, the stretching process was conducted exclusively within the first stretching gap, specifically between rolls 5 and 6. However, there are two additional possibilities for the stretching process: performing the stretching in the second gap, located between rolls 11 and 12, or utilizing both gaps sequentially. In this group of experiments, these two alternative stretching configurations were systematically tested to evaluate their effects on the film's properties.

Below can be seen the process parameters of the seventh sample:

7				
Roll Nr.	T(°C)	SR	Velocity (m/min)	Gap (mm)
1	85	1	1,5	
2	100	1	1,5	
3	100	1	1,5	
4	110	1	1,5	
5	110	1	1,5	
6	110	1	1,5	
7	110	1	1,5	
8	120	1	1,5	
9	120	1	1,5	
10	120	1	1,5	
11	120	1	1,5	5
12	120	6	9	
13	120	1	9	
14	100	1	9	
15	100	1	9	
16	-	1	9	

Figure 4.13. Sample 7: 120°C, 6 SR (2nd gap), 5mm gap

The film for the seventh sample was collected without any fabrication problem.

Below can be seen the process parameters of the eighth sample. The idea was to stretch a film with a 2.45 SR in both gaps. However, the MDO had a limitation in the first decimal place, so the technical team in Singapore decided to stretch two samples: one with a 2.4 SR in both gaps and another with a 2.5 SR in both gaps.

8				
Roll Nr.	T(°C)	Stretching	Velocity (m/min)	Gap (mm)
1	95	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	2,4	3,6	
7	120	1	3,6	
8	120	1	3,6	
9	120	1	3,6	
10	120	1	3,6	
11	120	1	3,6	5
12	120	2,4	8,64	
13	120	1	8,64	
14	100	1	8,64	
15	100	1	8,64	
16	-	1	8,64	

Figure 4.14. Sample 8: 120°C, 2.4 x 2.4 SR (both gaps), 5mm gap

Below can be seen the process parameters of the ninth sample.

9				
Roll Nr.	T(°C)	Stretching	Velocity (m/min)	Gap (mm)
1	95	1	1,5	
2	110	1	1,5	
3	110	1	1,5	
4	120	1	1,5	
5	120	1	1,5	5
6	120	2,5	3,75	
7	120	1	3,75	
8	120	1	3,75	
9	120	1	3,75	
10	120	1	3,75	
11	120	1	3,75	5
12	120	2,5	9,375	
13	120	1	9,375	
14	100	1	9,375	
15	100	1	9,375	
16	-	1	9,375	

Figure 4.15. Sample 9: 120°C, 2.5 x 2.5 SR (both gaps), 5mm gap

The film collected for samples 8 and 9 was not ideal, as shown in the picture below sent by the Singapore technical team. However, it was still collected due to the remaining sample length.



Figure 4.16. Film Condition for Samples 8 and 9

Upon completing this series of stretching experiments, the team obtained several samples, each with the same stretching ratio, identical gap, and consistent stretching temperature. The primary variable was the specific gap where the film was stretched.

Finished this group, the team had 9 samples ready to test, to analyze the results obtained during the test and to validate the hypotheses made during the project.

5. RESULTS AND DISCUSSION

This section presents the results obtained from testing the various samples produced in the previous process. As mentioned at the beginning of this report, the testing was conducted in Singapore.

5.1. Elmendorf Tear

The focus of the results and discussion is on the Elmendorf tear strength of the films in both the machine and cross directions. The Elmendorf tear strength was measured using the ASTM D-1922 – 23 standard [8]. This test determines the force, in grams, required to propagate a tear across a film or sheeting specimen using a precisely calibrated pendulum device. The pendulum, acting by gravity, swings through an arc, tearing the specimen from a precut slit. The specimen is held on one side by the pendulum and on the other side by a stationary member. The loss of energy by the pendulum is indicated by a pointer, with the scale reading reflecting the force required to tear the specimen.

The results of the Elmendorf testing in both directions for all stretched samples are shown below in Figure 5.1.

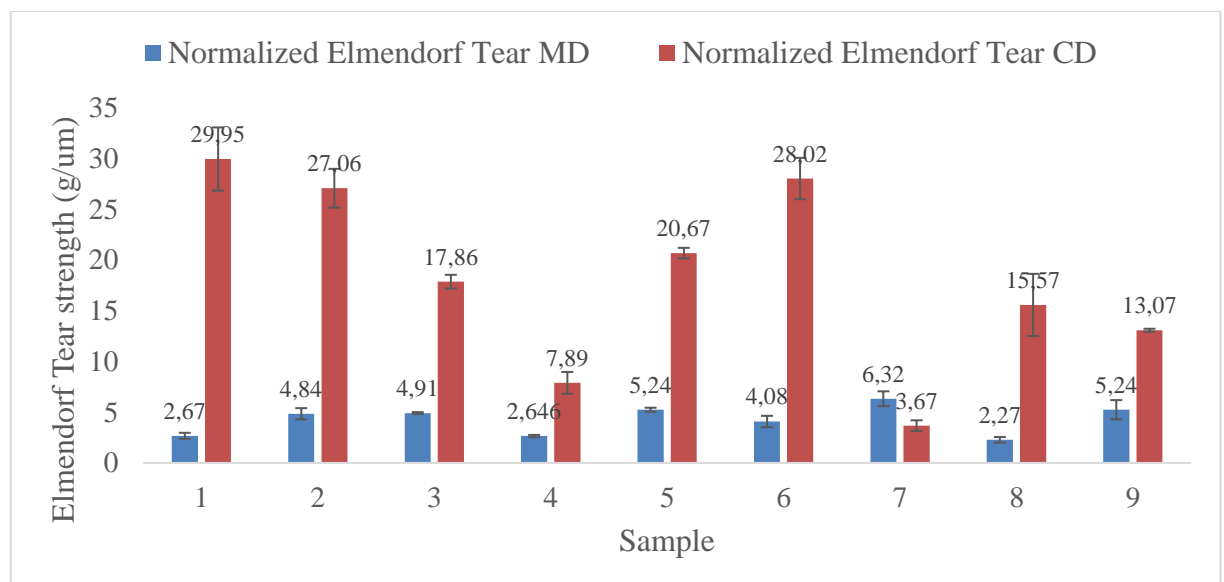


Figure 5.1. Elmendorf testing results

The figure above reveals several trends in the results. Notably, one sample stands out with a cross-direction (CD) tear strength that is lower than its machine-direction (MD) tear strength. To gain a comprehensive understanding of the impact of each process variable, the results will be analyzed group by group.

5.1.1. Stretching ratio effect on tear

This group embraces the first 4th samples. The results can be seen in the figure 5.2. below.

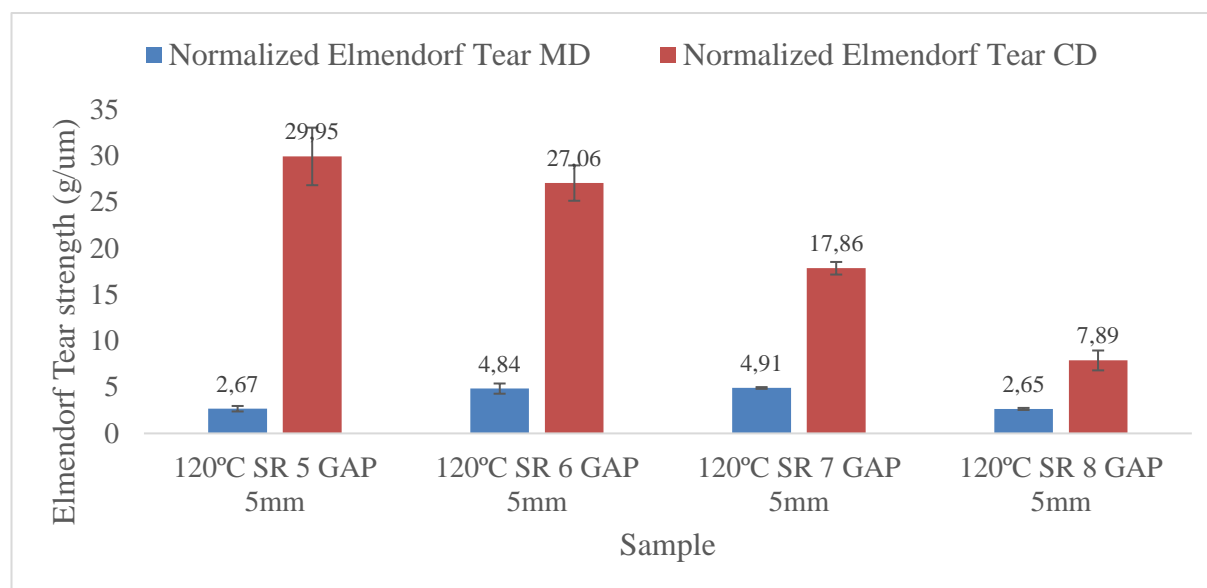


Figure 5.2. Elmendorf testing results of samples with different stretching ratio

The data clearly indicate that a higher stretch ratio, which corresponds to greater machine-direction orientation, facilitates easier tearing in the cross-direction. For MD tear strength, the value initially increases but subsequently decreases to the same level observed at 5 SR when it reaches 8 SR. However, all the values remain low, which is good.

These results are consistent with the trends observed in previous discussions. It is evident that a high stretch ratio is desirable to achieve easier tearing in the cross direction. However, it is important to note that as the stretch ratio increases, the likelihood of film breakage also increases. While there were no issues collecting samples in this case, it is crucial to consider the implications in an industrial setting where a MDO operates continuously. A film breakage in such an environment would necessitate interrupting the production line, resulting in downtime and financial losses for the company. Operating at these high stretch ratios is approaching the limits of industrial process feasibility. This will be further discussed in chapter 5.5.

Temperature plays a crucial role in the stretching phase of the MDO. If no issues were observed during the stretching, it indicates that the heating of the film was well executed. When the film is stretched close to its melting point, as in this case, the polymer chains become more flexible. This increased mobility allows the material to stretch more uniformly and reduces the internal film stress, resulting in less defect probability.

5.1.2. Stretching gap effect on tear

This group includes the second, fifth, and sixth samples. The only difference in these experiments is the gap. The results can be seen in the figure 5.3. below.

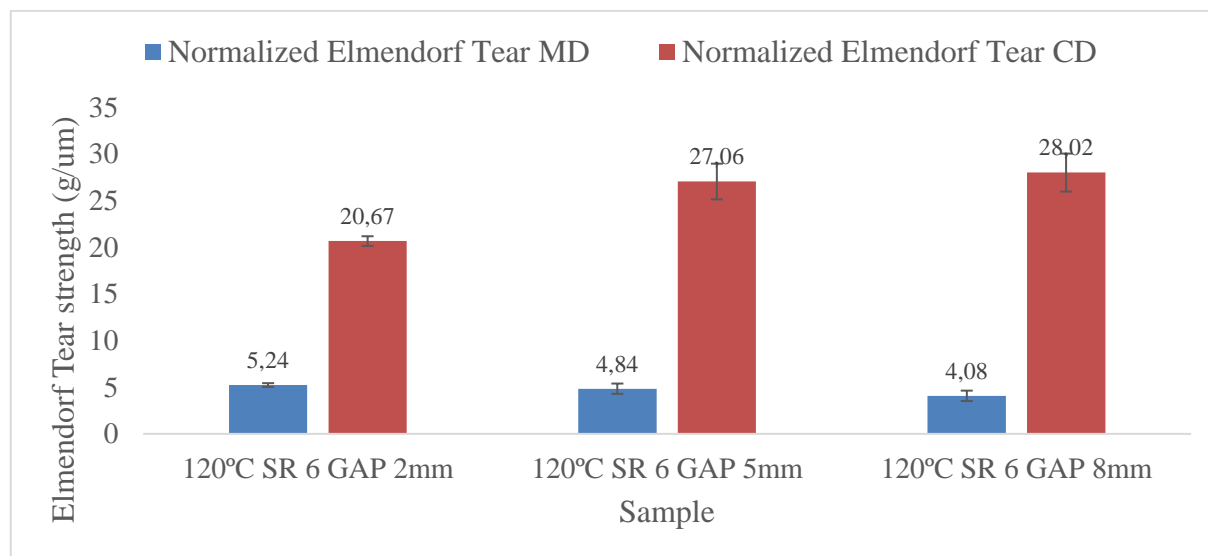


Figure 5.3. Elmendorf testing results of samples with different stretching gap

In accordance with the findings presented in the previous chapter, it has been established that a lower stretching gap during MDO stretching results in less orientation in the machine direction, which in turn leads to higher orientation in the cross direction for the film. This is due to the material's tendency to compensate for the reduced MD orientation by aligning more in the CD. The experimental results indicate that a tighter gap facilitates easier tearing in the cross-direction and increases the difficulty of tearing in the machine direction.

This phenomenon suggests that applying compression force to impart a minor orientation in the cross-direction enhances the ease of tearing in the cross-direction while simultaneously making it more challenging to tear in the machine direction. However, the results from the previous set of experiments conflict with this explanation, as the results of varying the stretching ratio showed that higher MD orientation (due to increased stretching) results in lower CD tear strength and higher MD tear strength. These results indicate a complex interplay of factors that require further investigation to fully understand.

5.1.3. Stretching methodology effect on tear

This group includes the second, seventh, eighth and ninth samples. The difference in these experiments is the stretching methodology. The results can be seen in the figure 5.4. below.

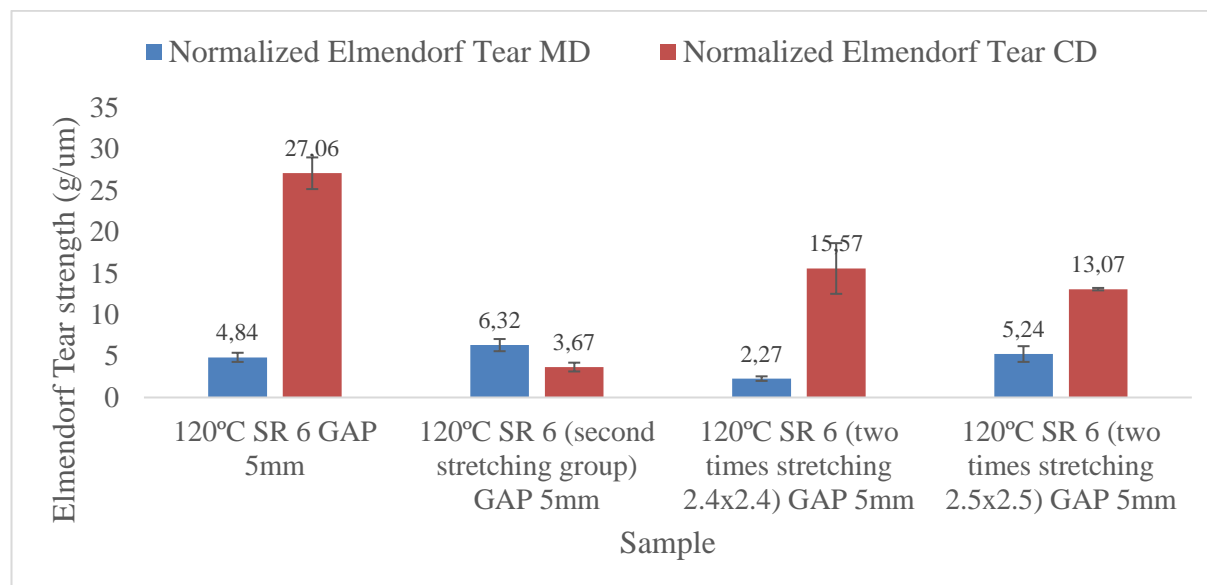


Figure 5.4. Elmendorf testing results of samples with different stretching methodology

It is worth mentioning that the results of the two-time stretching samples are not entirely reliable. As explained in the previous chapter, the collection of these two samples was not ideal. The process involved: heating, stretching, relaxing the film after the first stretch, and then performing a second stretch. This sequence did not result in uniform stretching of the film.

After the first stretch, the film was allowed to relax. This relaxation phase could have caused the film to revert partially to its original state, leading to uneven stress distribution when the second stretch was applied.

The best results obtained during this study were observed when stretching in the second group. This may be attributed to the heating process applied to this sample. In this case, better heat transfer was achieved. After roll 7 of the MDO process, the temperature of the rolls was maintained at 120°C. Since the stretching was conducted between rolls 11 and 12, the temperature of the film during stretching was close or equal to 120°C.

In contrast, the samples being stretched in the first stretching gap may not have reached the desired temperature of 120°C. Stretching occurred between rolls 5 and 6 for these samples, and until the fourth roll, the rolls did not reach 120°C. This means that the film only had the surface of the rolls 4 and 5 to reach the desired stretching temperature, which is more difficult than in the case of the samples being stretched in the second gap. These results highlight that achieving the desired temperature of stretching before doing it is crucial.

The sample stretched in the second gap reached a temperature of 120°C, whereas the samples in the first gap did not. This indicates that higher temperatures facilitate easier tearing in the cross direction. Another notable difference lies in the annealing process. The sample stretched between rolls 5 and 6 was subsequently heated, allowing the polymer chains to relax. In contrast, the sample stretched between rolls 11 and 12 was cooled after stretching, resulting in stress being induced in the polymer chains within the film. This difference in annealing could be another reason for the observed results.

5.2. Stress

Polariscope is the method for evaluating the stress produced in film samples stretched in a machine like the MDO. This stress is reflected in the polariscope in the form of different colors.

Both monolayer and multilayer films are translucent and optically isotropic. This means that the light rays passing through them are refracted in the same direction, which is why nothing is seen through the polariscope.

When these films are subjected to mechanical load or tension, they transform into anisotropic materials, which causes them to exhibit birefringence. This phenomenon is an optical characteristic that involves the separation of a light ray into two, allowing us to see different colors in the sample depending on the degree of stress it has undergone.

The colors vary according to how stressed the samples are. Slightly stressed samples show reddish tones, while higher stress levels result in pink, blue, and green colors.

All the samples stretched in the MDO were evaluated using a polariscope.

5.2.1. Stretching ratio effect on stress

Figure 5.5. illustrates the stress induced in the first group of experiments, where the stretching ratio varied.

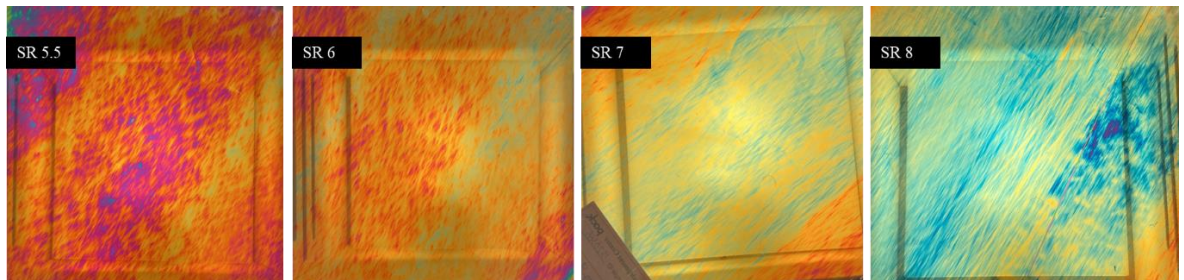


Figure 5.5. Stress results of samples with different stretching ratio

It is evident that as the stretching ratio increases, greater stress is observed in the film. As seen in Chapter 5.1.1, the CD tear strength decreased as the stretching ratio increased. Therefore, one could formulate the following hypothesis: as the stretching ratio increases, the stress in the film increases, causing the CD tear strength to be lower.

5.2.2. Stretching gap effect on stress

Figure 5.6. illustrates the stress induced in the second group of experiments, where the stretching gap varied.

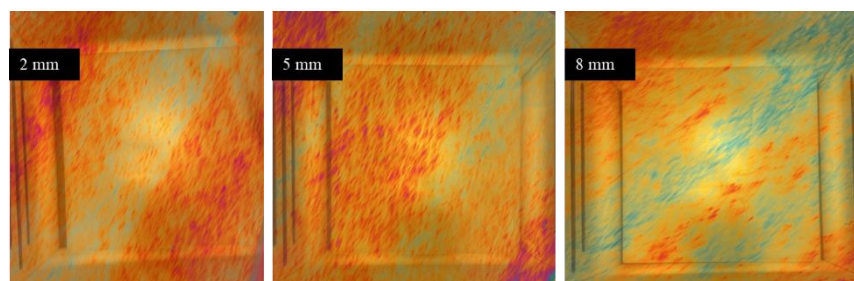


Figure 5.6. Stress results of samples with different stretching gap

For samples with gaps of 2 and 5 mm is difficult to observe any difference. However, in the sample with the gap of 8 mm it can be seen that a higher stress is induced in the film.

When there is a bigger gap between the stretching rolls, the film experiences increased tension force. This phenomenon could explain the observed results. Figure 5.6 below provides a graphical representation of the formulated hypothesis.

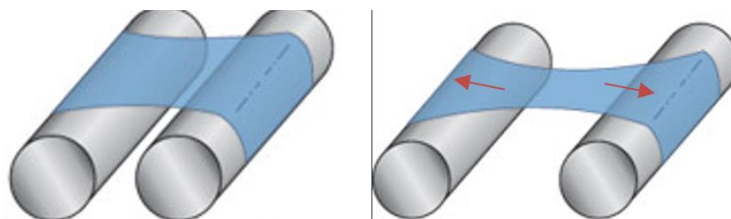


Figure 5.7. More tension applied with bigger gap

Another reason why a wider gap results in more stress on the film could be the increased time the film is not in contact with the roll. When the film is in contact with the roll at high temperatures, heat transfer occurs between the film and the roll, causing the polymer chains to relax. With a wider gap, the film is exposed to ambient temperature for a longer period compared to a tighter gap. This extended exposure allows the film temperature to decrease slightly before it increases again upon contact with the roll, resulting in a less relaxed film and more stress.

5.2.3. Stretching methodology effect on stress

Figure 5.8. illustrates the stress results of samples in the third group of experiments, where the stretching methodology varied.

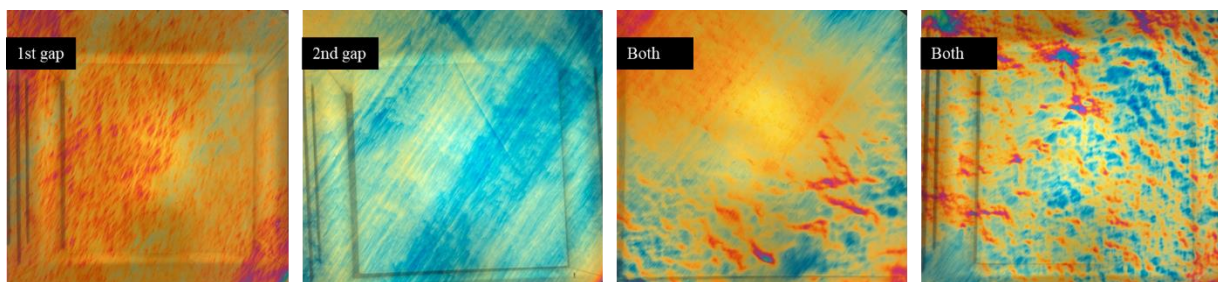


Figure 5.8. Stress results of samples with different stretching methodology

By examining the samples stretched in both gaps, it is clear that the stretching was not uniform. This is also evident in Figure 4.16, which shows a picture taken of these samples.

The sample stretched in the second gap exhibits the highest stress values in the entire study and, notably, it also has the lowest CD tear strength. This observation supports the hypothesis that higher stress results in easier tearing in the cross-direction.

It is important to note the significant difference between stretching in the first gap and the second gap. The sample from the first gap shows practically no induced stress, whereas the sample from the second gap exhibits a high level of stress. As mentioned in the previous chapter, this difference is due to the annealing process that occurred after stretching in the first gap. After stretching, the temperature of the rolls was maintained constant (which, in fact, increased the film temperature if it did not reach 120°C), allowing the polymer chains to relax. This relaxation helped to reduce the internal stresses previously introduced during the stretching process. The heat allowed the polymer chains to move more freely, relieving tension and aligning the chains in a more stable configuration. In contrast, the sample stretched in the second gap did not undergo annealing. The film was stretched, then the temperature was reduced, and the film was collected without the benefit of stress relaxation, which appears to be beneficial for achieving easy tear in the cross direction.

5.3. Stiffness

After thoroughly examining the tear properties of the various samples and analyzing the stress of each sample to establish the stress-tear correlation, the stiffness of the samples was studied.

Young's modulus, also known as the elastic modulus, is a measure of a material's stiffness. It quantifies the amount of stress (force per unit area) required to achieve a given amount of strain (deformation) in the linear elastic region of the stress-strain curve. Essentially, it indicates how much a material will stretch or compress under a given load, and is calculated from the initial, linear portion of the stress-strain curve. The ASTM standard used to measure Young's modulus is ASTM E111 [9].

The secant modulus at 2% strain, on the other hand, is a measure of the material's stiffness at a specific point on the stress-strain curve. It is calculated by taking the ratio of stress to strain at 2% strain, providing an average measure of stiffness over that range. This is particularly useful for materials that do not exhibit perfectly linear behavior when stretched. The ASTM standard used to measure the secant modulus at 2% strain is ASTM D5323 [10].

In the current report, the secant modulus at 2% strain was used to measure the film's stiffness instead of Young's modulus. This preference arises because MDO PE films typically exhibit non-linear behavior beyond the initial elastic region, making Young's modulus less representative of the material's overall stiffness. Additionally, using the secant modulus at a specific strain level ensures consistency in measurement across different samples. In figure 5.9, can be observed the secant modulus at 2% strain of the different samples.

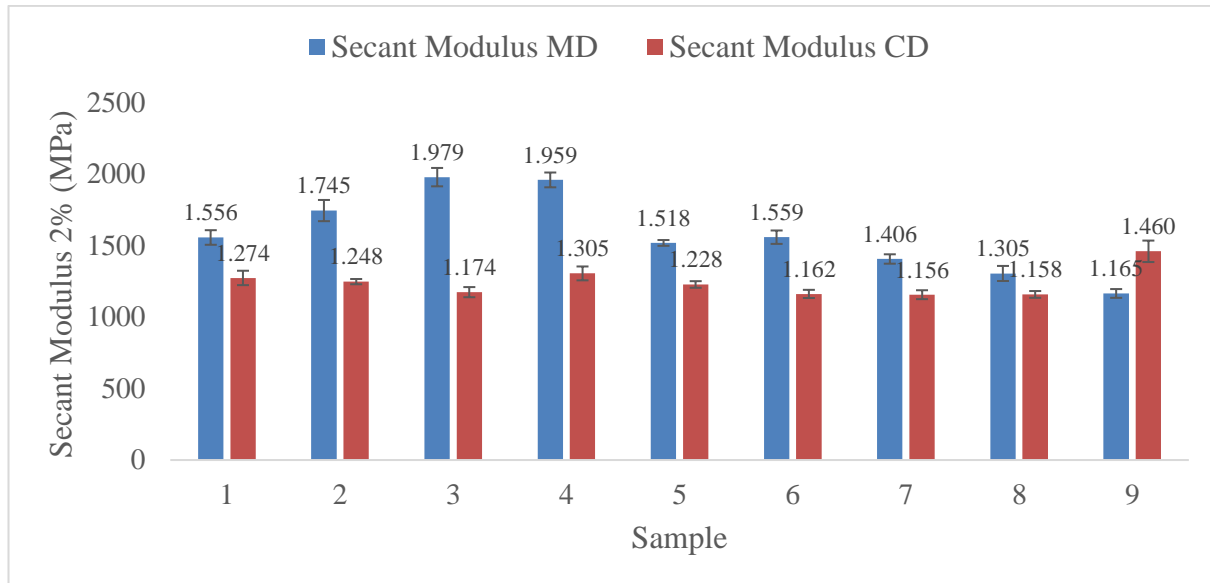


Figure 5.9. Stiffness results

From the previous graph, many samples have shown great results in secant modulus.

5.3.1. Stretching ratio effect on stiffness

In figure 5.10. is observed the stiffness values of samples with different stretching ratio.

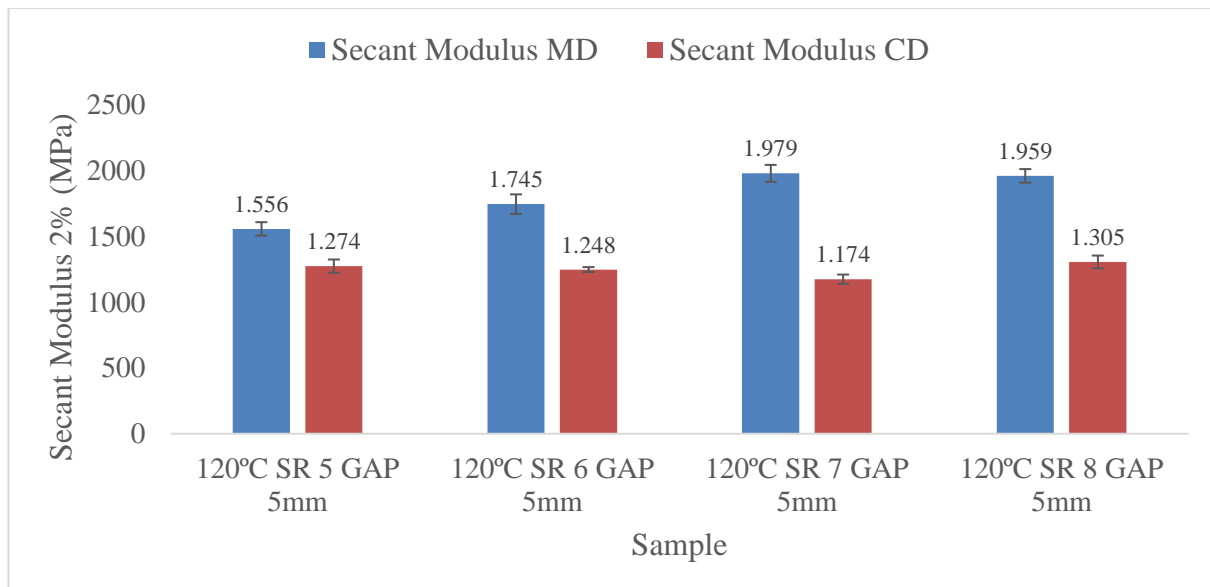


Figure 5.10. Stiffness results of samples with different stretching ratio

It can be observed that the secant modulus in the MD tends to increase with the stretching ratio, which can be attributed to the increase in orientation. CD modulus is first decreased to then increase to the starting point.

5.3.2. Stretching gap effect on stiffness

In figure 5.11. is observed the stiffness values of samples with different stretching gap.

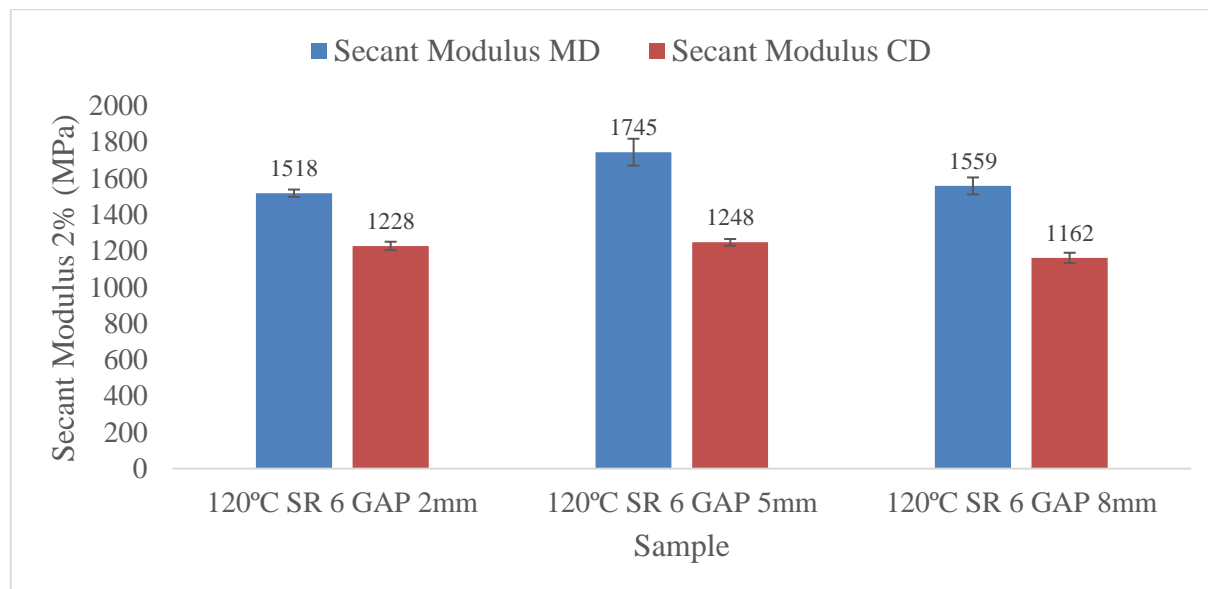


Figure 5.11. Stiffness results of samples with different stretching gap

When comparing the samples with varying stretching gaps (5mm, 2mm, and 6mm, from smaller to larger gaps), it is observed that the stiffness initially increases but then decreases again. This behavior can be explained as follows: the lower stiffness values observed with a tighter gap (2mm) can be attributed to the compression force exerted on the film when the rolls are closer together. This compression force enhances the alignment of the polymer chains in the cross direction, as discussed in the tear chapter.

The decrease in stiffness from the sample with a 5mm gap to the sample with an 8mm gap was not expected since a wider gap allows the film to deform in response to the force applied and arrange in the stretching direction while a tight gap forces the structure to stay in place. An explanation to these results could be related with the induced stress. As shown in the polariscope figures, the sample with an 8mm gap exhibits the highest level of stress of these samples. This increased stress could negatively impact the stiffness property, resulting in a weaker sample.

5.3.3. Stretching methodology effect on stiffness

In figure 5.12. is observed the stiffness values of samples with different stretching methodology.

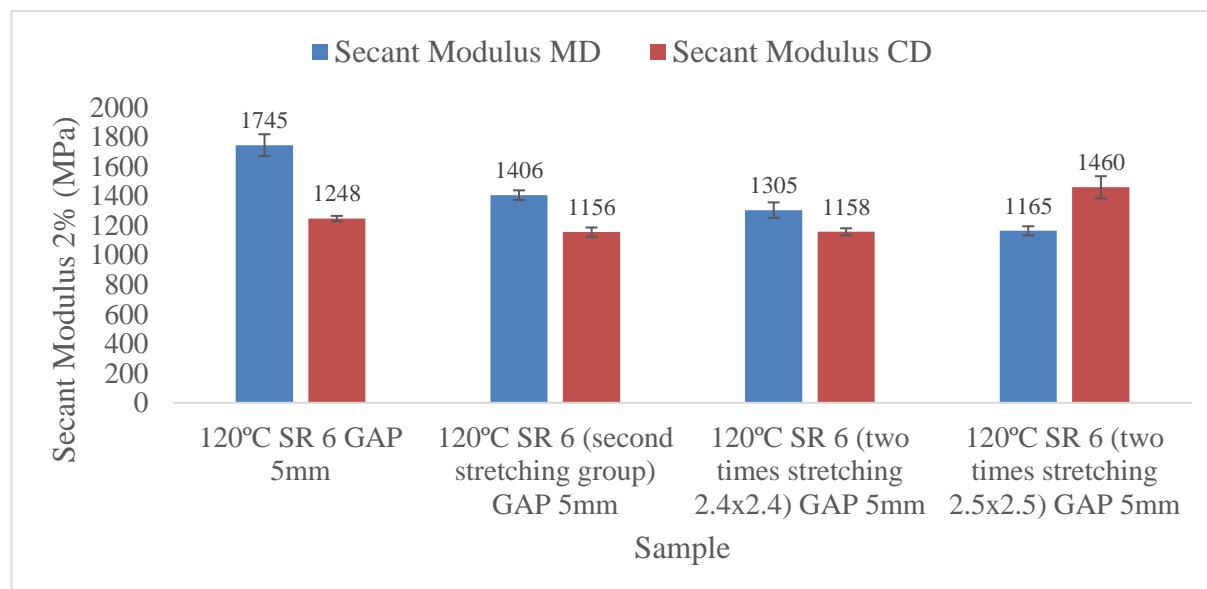


Figure 5.12. Stiffness results of samples with different stretching methodology

A noteworthy observation is the comparison between the first two samples, where the difference lies in the temperature profile applied to the film. The variation in these values relies again on the stress differences between these samples. Heating after stretching (like in first sample) can help alleviate stresses introduced during stretching. These residual stresses can weaken the material and reduce its secant modulus. By applying heat, the polymer chains are allowed to relax and reorganize, resulting in a more stable and rigid structure. Conversely, cooling the sample immediately after stretching (like in second sample) can lock in the residual stresses within the material's structure. These stresses can prevent the polymer chains from organizing optimally, resulting in a sample with a lower secant modulus compared to a sample that has been heated after stretching.

5.4. Optical properties

Haze and gloss properties were analyzed. The results are presented in Figure 5.13. below, providing a comprehensive overview of the optical performance of the samples.

ASTM D1003 [11] is the standard test method for measuring haze and luminous transmittance of transparent plastics. Haze refers to the amount of light that is scattered as it passes through a material. It is measured as the percentage of light that, when passing through a sheet, deviates from the incident beam at an angle greater than 2.5 degrees. A higher haze value indicates greater light scattering.

ASTM D2457 [12] is the standard test method for measuring the gloss of plastic films and solid plastics. Gloss is the measure of the amount of light reflected from the surface of a material. This test helps in determining the surface finish and appearance of the material.

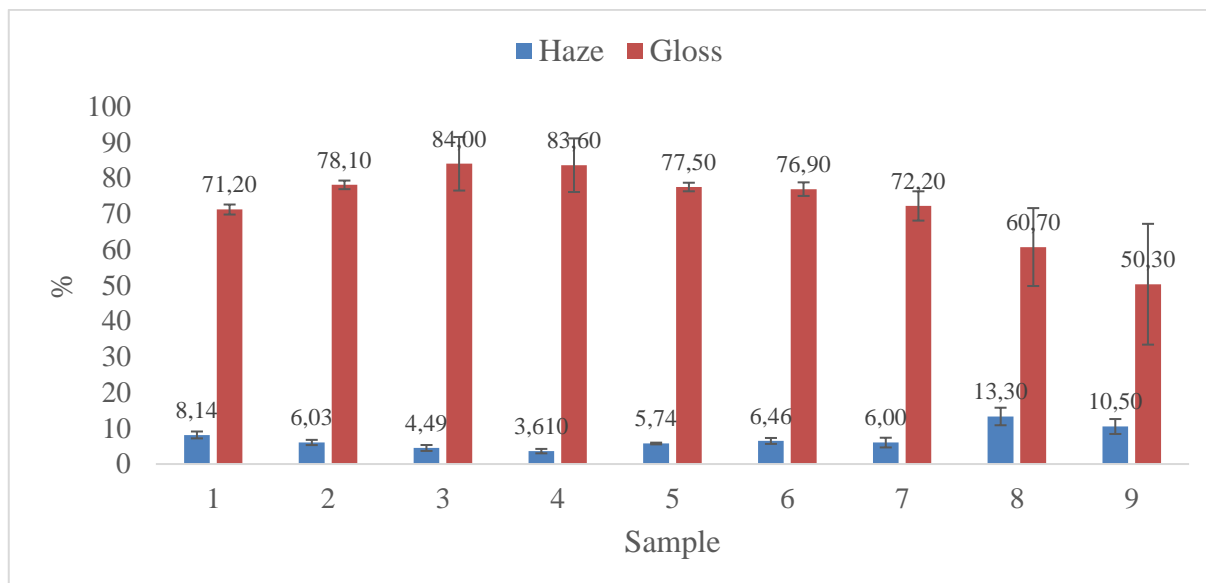


Figure 5.13. Optical properties results

All samples demonstrated high gloss and low haze. These properties make the films ideal for packaging applications that require a clear view of the product inside while maintaining an attractive, glossy appearance.

5.4.1. Stretching ratio effect on optics

In figure 5.14. is observed the optical values of samples with different stretching ratios.

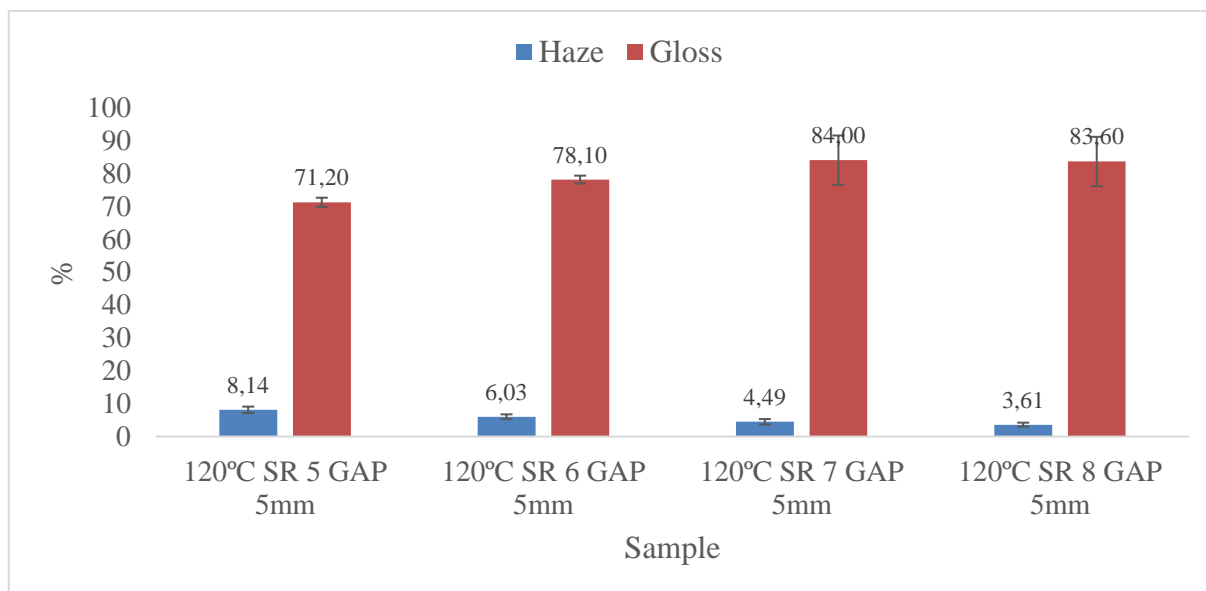


Figure 5.14. Optical results of samples with different stretching ratio

An enhancement in gloss and a reduction in haze as the stretching ratio increases can be observed in the first four samples, where the stretching ratio was increased with each sample.

5.4.2. Stretching gap effect on optics

In figure 5.15. is observed the optical values of samples with different stretching gap.

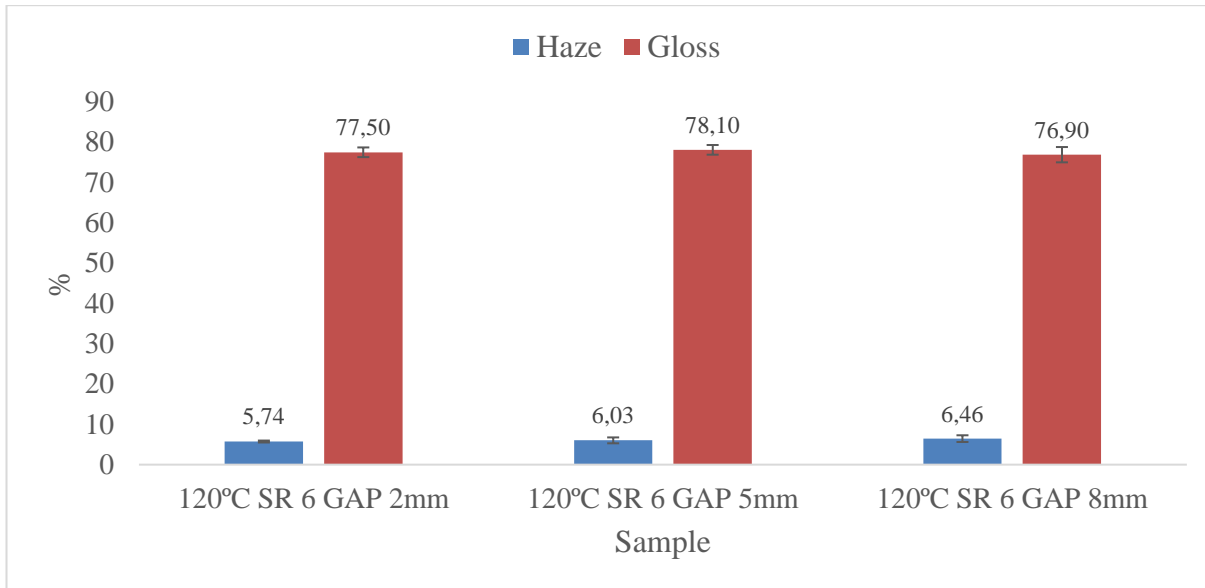


Figure 5.15. Optical results of samples with different stretching gap

Upon examining samples with varying distances in the stretching gap, a slight increase in haze was observed as the gap size increased. Gloss increased when the gap was adjusted from 2mm to 5mm, but subsequently decreased when the gap was further extended from 5mm to 8mm. However, it is important to note that these differences are minimal.

5.4.3. Stretching methodology effect on optics

In figure 5.16. is observed the optical values of samples with different stretching methodology.

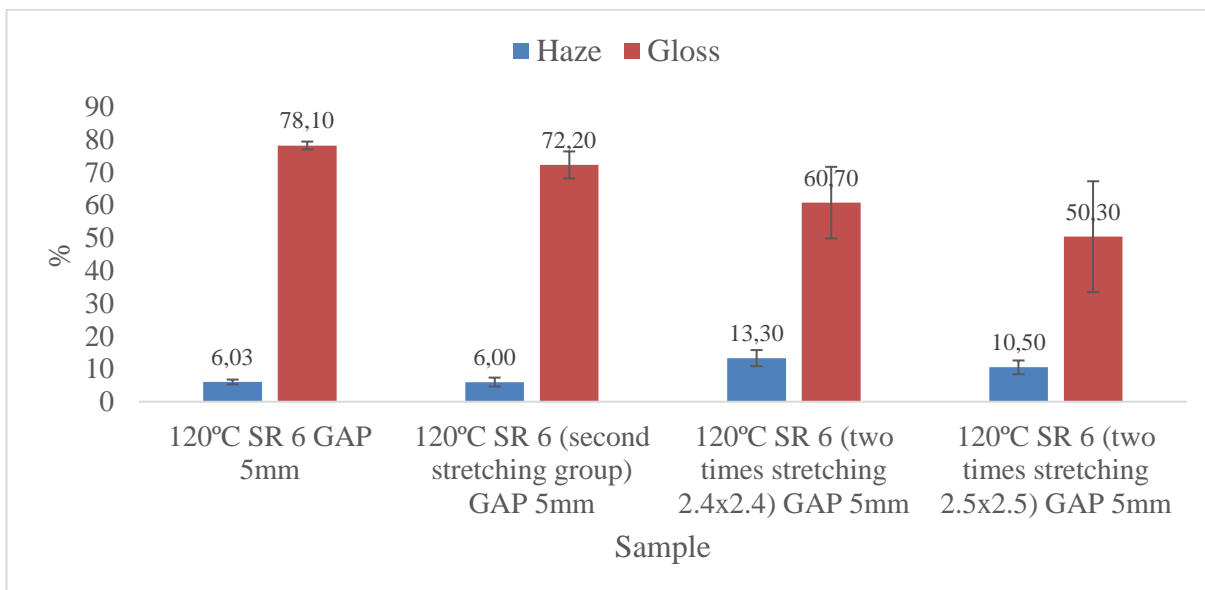


Figure 5.16. Optical results of samples with different stretching methodology

Comparing the first two samples, where the stretching rolls were different, a decrease in gloss was noted in second sample, which had a more accurate thermal profile during preheating before stretching and no annealing after stretching.

The last two samples showed high standard deviation due to difficulties encountered during the stretching process.

5.5. Ultimate Stress and Elongation

Having studied the effect of MDO process parameters on the film properties, the team also conducted tensile strength tests to obtain results for ultimate elongation. Ultimate elongation provides valuable insights into the material's performance.

Ultimate elongation measures the extent to which a material can stretch before breaking, offering insights into its ductility and flexibility. It is particularly instructive to follow ultimate strain as an indicator of how much potential for further stretching remains in the film because this parameter provides valuable insights into the material's mechanical performance and its ability to undergo additional deformation. By monitoring ultimate strain, you can determine how much further the material can be stretched before it reaches its breaking point.

A higher ultimate strain means that the sample can withstand higher levels of stretching ratio without breaking. This is crucial in the context of MDO films, where the stretching ratio directly impacts the film's properties. For example, a higher ultimate strain indicates that the film can be stretched more in the machine direction, allowing for a greater stretching ratio while maintaining its mechanical integrity. This helps achieve the desired improvements in optical and mechanical properties without risking film failure during the MDO process.

The tests for ultimate elongation were conducted according to ASTM standards, specifically ASTM D882 [13] and can be seen in figure 5.17 below.

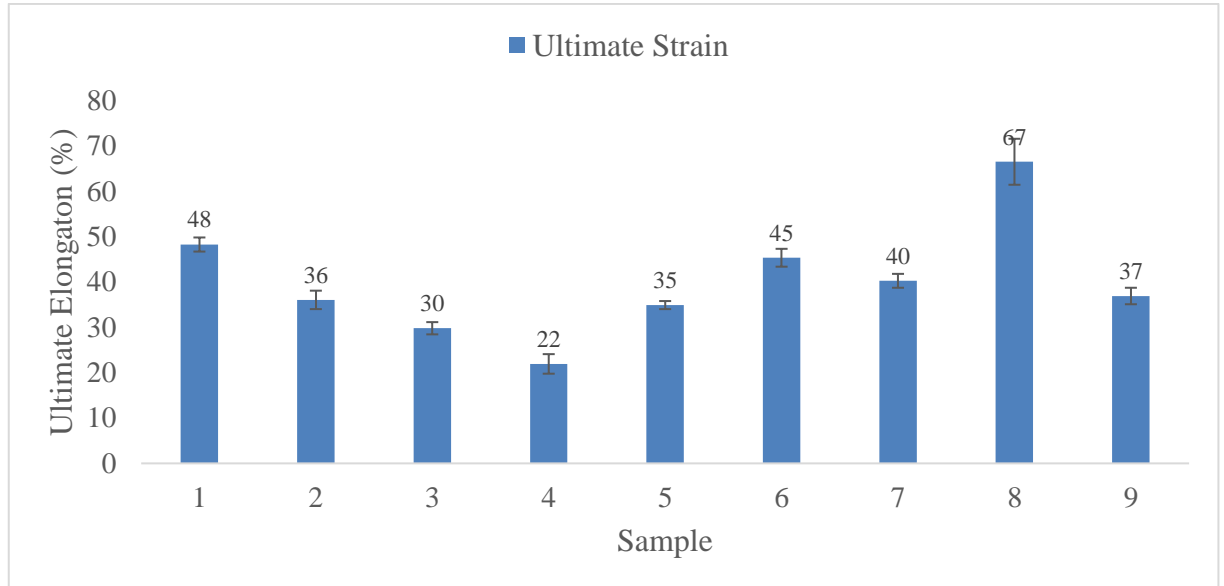


Figure 5.17. Ultimate strain results of samples

The stretchability limits of an MDO sample can be defined by an ultimate stress elongation below 20%. Below this threshold, there is a risk of film breakage. As observed in the results, the sample closest to these stretchability limits is the one with the highest stretching ratio (8 SR). This sample exhibits excellent stiffness and optical properties and is nearing the point of achieving easy tear in both directions. It has been noted that with an increase in the stretching ratio, even better results can be anticipated. However, this sample is near its breaking limit, raising concerns about the industrial viability of further stretching.

Focusing on sample 7, as discussed in previous chapters, this sample demonstrates easier tear in the CD, which is the primary issue in the project. An elongation value of 40% indicates that the sample can be further stretched. It is recommended to study additional stretching ratios with this configuration to observe their effect on properties. A higher stretching ratio could potentially lead to easier tear, as previously observed, resulting in even better outcomes. However, in terms of stiffness, this sample does not exhibit excellent stiffness. The question arises: What would happen when increasing the stretching ratio? Would it increase as observed in the trend, or would it induce more residual stress in the film (considering no annealing in this sample), thereby worsening its stiffness?

6. CONCLUSIONS

The critical process parameters of the Machine Direction Orientation (MDO) post-extrusion process have been meticulously identified. These parameters include the stretching ratio, stretching gap, temperature of the rolls, speed of the rolls, and the methodology of stretching.

An in-depth study was conducted to understand the effect of these process parameters on tear strength, stiffness, and optical properties. Based on the results obtained, several key conclusions can be drawn:

- **Stretching Ratio:** A higher stretching ratio facilitates easier tearing in the cross direction (CD) while slightly increasing tear strength in the machine direction (MD). Higher stretching ratios also result in greater stiffness and improved optical properties.
- **Stretching Gap:** A tighter stretching gap is beneficial for achieving easier tearing in the cross direction. Conversely, tear strength in the machine direction suffers a little increase when there is minimal space between the stretching rolls. Identifying the optimal stretching gap is crucial for stiffness, as both small and large gaps result in less stiffness compared to an optimal gap. A smaller gap leads to marginally lower haze, while changes in gloss are even less noticeable.
- **Temperature of the Rolls:** Higher stretching temperatures make it easier for the material to tear in the cross direction while simultaneously making it a bit more difficult to tear in the machine direction. Annealing plays a crucial role in stiffness and tear properties.

It is essential to consider the selection of materials, as different materials may respond differently to each process parameter.

The sample stretched at an 8 SR gave outstanding results in stiffness and optical properties. It was also close to reach easy tear in both directions. Higher stretching ratios could provide the sample with all the desired properties in an excellent manner but also cast doubt on the industrial viability of the project. An alternative could be stretching at high values while reducing the gap, potentially achieving easy tear in both directions renouncing from excellent to good stiffness.

The sample with high stretching temperature and no annealing gave the best results in cross-direction tear, which is the primary focus of the project. It is highly recommended to study the effects of higher stretching ratios with the same temperature profile as this sample. Even easier tear in the CD could be achieved, and it is worth examining the effect of higher stretching ratios on other desired properties.

Further studies, such as examining the crystal morphology and conducting cross-sectional microscopy of the MD-ND and CD-ND planes, may provide valuable insights into the tie chain organization, thereby improving the understanding of the results obtained in this report.

In conclusion, the substitution of BOPP and BOPET films with MDO PE blown films is on the horizon, promising significant advancements in film performance and sustainability.

7. REFERENCES

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The document may contain proprietary company information, including data from testing in previous studies and the standards used for testing.

APPENDIX: SELF-EVALUATION QUESTIONNAIRE

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	
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)	During all project	8	I missed a bit the economic part
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)		1	No models were used
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)	During all project	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)	During all project	10	
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)	During all project	10	
A3.1	Apply knowledge of mathematics, physics, chemistry, biology and other natural sciences by means of	Design of Experiments and	10	

	study, experience, practice and critical reasoning in order to establish economically viable solutions for technical problems (I1).	understanding of the results		
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, electrochemical and biochemical reactions engineering (I2).	Experimental plan	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).	During all project	10	
A3.4	Be able to solve unfamiliar and ill-defined problems by taking into account all possible solutions and selecting the most innovative. (I4)	During all project, when MDO not worked in Tarragona	10	
A3.5	Lead and supervise all types of installation, process, system and service in the different industrial areas related to chemical engineering (I5).	During all project	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).		0	Not needed in 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).	During all project	8	I missed to see all the costs associated in 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).	During all project	7	
A4.3	Manage research, development and technological innovation whilst ensuring the transfer of technology and taking into account property and patent rights (P3).	During all 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).	During all project	10	
A4.5	Lead and monitor the control of installations, processes, products, certification, auditing, verification, testing and reports (P5).	During all project	9	

A5.1	Carry out, present and defend (once all the curriculum credits have been obtained) an original individually produced piece of work before a university panel. The work will consist of a professional integrated Chemical Engineering project that synthesizes (TFM1)	Project	10	
TRANSVERSAL COMPETENCES				
B1.1	Communicate and discuss proposals and conclusions in a clear and unambiguous manner in specialized and non-specialized multilingual forums (G9).	During all project	8	
B1.2	Adapt to changes and be able to apply new and advanced technologies and other important developments with initiative and entrepreneurial spirit. (G10)	During all 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)	During all project	10	
B3.1	Work in a team with responsibilities shared among multidisciplinary, multilingual and multicultural teams	During all project	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)	During all project	9	
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)	During all project	10	
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)	During all project	10	
NUCLEAR COMPETENCES				
C1.1	Have an intermediate mastery of a foreign language, preferably English	During all project	10	
C1.2	Be advanced users of the information and communication technologies	During all project	9	
C1.3	Be able to manage information and knowledge	During all 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 project	10	
C2.1	Be committed to ethics and social responsibility as citizens and professionals	During all project	10	
C2.2	Be able to define and develop their academic and professional project	During all 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...)	7	The MDO in Tarragona was not operational upon my arrival and remained non-functional throughout the entire project. While overcoming this challenge was a valuable learning experience, I believe it would be more effective to assign students to projects that do not rely on non-operational equipment, especially when there are other available projects. The treatment and guidance from the company supervisor were exceptional, and I gained a great deal from their mentorship, both personally and professionally.
Stay (welcome, length, relationship, follow-up made by the company...)	10	No improvements. The treatment received by the company was excellent.
Follow-up made by URV tutor	10	No improvements. Toni Cabello gave advice when needed.
Other aspects to be considered (which ones...)		