Master in Chemical Engineering

Development of biobased composites for the production of more sustainable packaging components

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Abstract

Plastics comprise a family of extremely useful materials for mankind but, in the past years, their negative impact on the environment has been growing exponentially. Efforts all around the world to mitigate climate changes have been made, diverting plastics from landfills and trying to eradicate single-use packaging, hence, promoting a circular economy. Moreover, some movements were created in order to eradicate single-use packaging. Regarding all these concerns, bioplastics emerged as a viable solution to replace conventional fossil fuels.

In this dissertation, two different cork-polymer composites (CPC) were developed by blending polylactic acid (PLA) and a biobased high-density polyethylene (HDPE) with different cork loads from 5 up to 15 wt. %. The main purpose was to develop sustainable alternatives for polystyrene (PS), the current standard plastic used by *Amorim Top Series* (*ATS*). The developed materials were studied under different scenarios in order to mimic their transport conditions, storage and handling, and to evaluate and compare their production parameters with the actual used fossil-based material. In order to validate those materials, their behaviour was tested under different weathering scenarios, as well as their absorption levels and chemical stability when exposed to water and alcohol solutions. The composites' resistance under compression and abrasion conditions was also analysed to evaluate their mechanical properties. In the end, a cost analysis of the final products was made, along with a brief discussion of their end-of-life alternatives.

The PLA composites exhibited better mechanical properties and were easier to produce than the HDPE and cork blends. On the other hand, HDPE composites demonstrated high chemical stability in all the studied scenarios. In general, HDPE biocomposites exhibited identical performances when compared to PS, aside from the mechanical properties. In conclusion, gathering all the work developed during this dissertation, HDPE materials proved to be the most attractive solution for PS replacement.

Keywords: bioplastics, sustainable, cork-polymer composites.

Resumo

Os plásticos constituem uma família de materiais extremamente úteis para a humidade, contudo, nos últimos anos, o seu impacto negativo no ambiente tem vindo a crescer exponencialmente. Com o objetivo de atenuar o impacto das alterações climáticas, têm sido feitos esforços por todo o mundo, desviando plásticos dos aterros e reencaminhando-os para unidades de recuperação apropriadas, promovendo assim uma economia circular. Para além disso, alguns movimentos têm vindo a surgir, tendo em vista a eliminação dos plásticos de utilização única. Tendo em conta todas estas preocupações, os bioplásticos emergem como uma solução viável para a substituição dos plásticos convencionais provenientes de combustíveis fósseis.

Nesta dissertação, foram desenvolvidos dois compósitos de plástico e cortiça a partir da mistura de ácido polilático (PLA) e polietileno de alta densidade (PEAD) de origem natural com diferentes cargas de cortiça com um teor mássico de 5 a 15 %. O principal objetivo foi o desenvolvimento de alternativas sustentáveis para a substituição do poliestireno (PS), o plástico utilizado atualmente pela *Amorim Top Series* (*ATS*). Os materiais desenvolvidos foram estudados em diferentes cenários a fim de serem simuladas as condições de transporte, armazenamento e utilização, e para avaliar e comparar os seus parâmetros de produção com os utilizados atualmente para o material de origem fóssil. Para validar estes materiais, o seu comportamento foi testado com a aplicação de testes climáticos bem como os seus níveis de absorção e estabilidade química uma vez expostos à água e soluções alcoólicas. Para avaliar as propriedades mecânicas dos compósitos, a sua resistência à compressão e abrasão também foi analisada. No final, foi feita uma análise do custo final de cada produto, juntamente com uma breve discussão das suas alternativas de fim-de-vida.

Os compósitos de PLA exibiram melhores propriedades mecânicas e foram mais fáceis de produzir do que as misturas de PEAD com cortiça. Por outro lado, os compósitos de PEAD demonstraram uma estabilidade química elevada em todos os cenários de estudo. No geral, os compósitos de PEAD exibiram performances idênticas às do PS, exceto em relação às propriedades mecânicas. Concluindo, reunindo todo trabalho desenvolvido ao longo da dissertação, os matérias de PEAD mostraram ser a solução mais atrativa para a substituição do PS.

Palavras-chave: bioplásticos, sustentável, compósitos de plástico e cortiça.

Declaration

I hereby declare, on my word of honour, that this work is original and that all non-original contributions were properly referenced with source identification.



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Abbreviations

List of variables

$P_{inj.}$	Injection pressure	bar	
P_{back}	Back pressure	bar	
$Ø_e$	External diameter	mm	
$Ø_i$	Internal diameter	mm	
H	Total height	mm	
$H_{ins.}$	Insertion height	mm	
P_i	Initial pressure	bar	
P_j	Second pressure	bar	
P_f	Final pressure	bar	
V_S	Sample volume	cm^3	
V_C	Sample chamber volume	cm^3	
V_E	Expansion chamber volume	cm^3	
$t_{cut\text{-}off}$	Time interval of a cut-off filament	s	
$m_{av.}$	Mass average	g	
T_{room}	Room temperature	^oC	
X_{H2O}	Water absorption	%	
X_{EtOH}	Alcohol absorption	%	
m_t	Mass of the sample at a specific time t	g	
m_i	Initial mass of the sample	g	
t_{cycle}	Cycle time	s	
$t_{cooling}$	Cooling time	s	
$V_{inj.}$	Injection velocity	mm/s	
T_{max}	Maximum temperature	^oC	
T_{mould}	Mould temperature	^oC	
F	Load applied	kN	kN
A_0	Initial cross-sectional area	m^2	m^2
L_0	Initial height	mm	mm
L	Height at a specific deformation	mm	mm
T_g	Glass transition temperature	^oC	

Greek letters

σ	Stress	MPa
ε	Strain	%
σ_y*	Offset yield stress	MPa
ε_y*	Offset yield strain	%

List of acronyms

ASTM	American Society for Testing and Materials
ATS	*Amorim Top Series*
BCC	Biobased Carbon Content
BPI	Biodegradable Products Institute
CC	Climatic Chamber
CISL	Cambridge Institute for Sustainability Leadership
CO_2	Carbon Dioxide
CPC	Cork-polymer Composite
EUBP	European Bioplastics
EVA	Ethylene-vinyl Acetate
FDA	Food and Drug Administration

GHGs	Greenhouse Gases
GPPS	General Purpose Polystyrene
GWP	Global Warming Potential
HDPE	High-density Polyethylene
He	Helium
Hg	Mercury
HIPS	High Impact Polystyrene
LCA	Life Cycle Assessment
MFR	Mass Flow Rate
NIR	Near-infrared
PBAT	Polybutylene Adipate Terephthalate
PCL	Polycaprolactone
PE	Polyethylene
PEAD	Polietileno de alta densidade
PHB	Polyhydroxybutyrate
PLA	Polylactic Acid
PP	Polypropylene
PS	Polystyrene
RH	Relative Humidity
SEM	Scanning Electron Microscopy
TPS	Thermoplastic Starch
UK	United Kingdom
US	United States
USDA	United States Department of Agriculture
WF	Wood Fibres
WPC	Wood-polymer Composite

1 Introduction

1.1 Framing and Presentation of the Work

Plastics have been a big contribution to human life but, since the last decade, they are raising huge concerns around the globe. The plastic market has been in constant change and in continuous growth, despite all the challenges associated with plastic waste and its management. In order to mitigate these problems, countries are putting a lot of effort to eliminate single-use packaging materials, which are made from fossil fuels. Bioplastics arise as a good solution, because they comprehend two different characteristics: in one hand, they can be made partially or entirely from renewable sources, thus being capable of replacing fossil-based materials and, on the other hand, apart from being able to enter on the existing recycling systems, they also offer other end-of-life alternatives. Considering this, bioplastics play a key role in the transition to a circular economy by increasing recycling targets and waste management efficiency [1].

This project aims to develop sustainable plastic solutions for the spirit drinks market, where the main objective is to replace polystyrene (PS), the currently material used for the production of the bartops, by other renewable and greener plastics or cork-polymer composite (CPC) options. This replacement will allow an increase in the number of end-of-life solutions of the final product, making it way far more worldwide interesting. Given this, two different raw materials, polylactic acid (PLA) and high-density polyethylene (HDPE), and their blends with different cork loads were chosen and studied under selected conditions, based on some market studies and their properties and advantages regarding the company's applications. The used cork granulates are mainly prevenient from industrial cork wastes and, by reintroducing them into other products, the company is also contributing and thinking of circular economy. Moreover, having different materials allows the company to have a broader range of products with different prices to offer to its clients.

1.2 Presentation of the Company

Amorim Group is a multinational company of Portuguese origin which is currently leading the cork business. It is divided into four business units: cork stoppers, cork composites, floor and wall coverings and insulations [2, 3]. The company is divided into five units, each one of them with its respective subunits. A simple chart of the cork stoppers' business segment can be seen in Figure A. 1 (Appendix A), where only *Amorim Top Series* (*ATS*) unit is presented in detail since it was the place where the present project was developed.

ATS produces packaging components for the spirit drinks market, mainly bartops, consisting of a single product combining a capsule with a stopper. Plastic capsules are produced in *ATS* plants

by injection moulding and, at *BioCap* and *Elfverson*, the capsules are wooden made. Glass and ceramic tops are bought from external providers. At *ATS Portugal* plant there are two process flows, converging nearly the end. The following Figure 1 briefly represents *ATS*' process flow diagram.

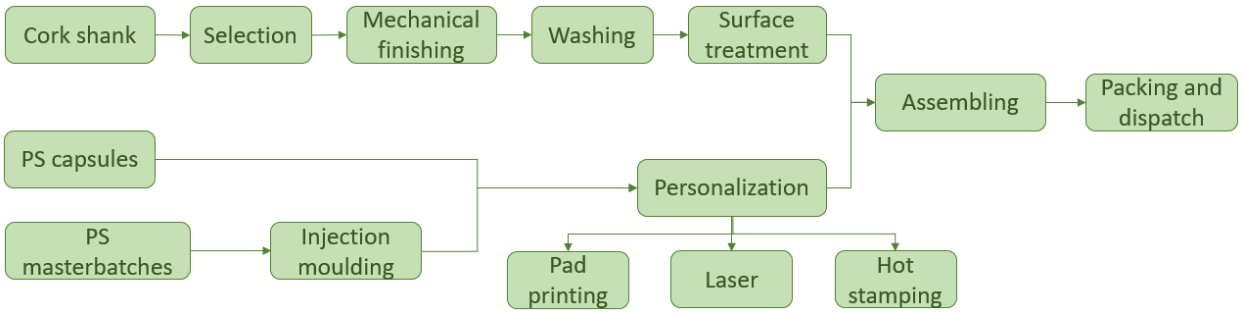


Figure 1 – ATS' process flow diagram.

ATS' brochure is divided into four distinct market segments: *Prestige*, *Elegance*, *Premium* and *Classic Value*. Some examples of each one can be seen in Figure 2.



Figure 2 – Examples of each ATS market segments.

Prestige segment comprises capsules made of luxurious materials, such as crystals and precious metals. Clients receive individual support from the company and have the opportunity to create a whole new product. *Elegance* segment follows market trends, and its capsule tops can be made of a wide range of materials such as ceramic, wood, metal or metallised plastic. *Premium* segment offers good liberty for the client to choose between some different colours, shapes and materials and combining low and high relief profiles. *Classic Value* segment makes its point by offering competitive prices and allowing a colour and shape customization [4].

In this project, the developed solutions are inserted in the *Classic Value* segment. If low and high reliefs are applied, the product can also be part of the *Premium* segment.

1.3 Contributions of the Work

In an initial phase of this work, it was required from me to start searching for the best raw material alternatives to test. Moreover, I had also to interact with the manufacturers, in order to have detailed information, which was not mentioned on the available products' specification sheets.

Moving on to the tests phase, I had to look for suitable places to conduct specific tests, such as the mechanical and morphological analysis. Finally, some clients conduct specific tests after the products' acquisition, following standardized procedures where specific machinery is required, which the company does not own. The abrasion resistance test presented in this dissertation is a simulation of these post-purchasing tests, where I had to build an improvised system for its implementation.

1.4 Organization of the Thesis

The present project is divided into six main chapters, as described below:

- Chapter 1 [Introduction] introduces the problem and presents the company and its market segments.
- Chapter 2 [Context and State of the Art] provides essential information to understand the problem, the situation of the market, the materials selected for this dissertation and the production method.
- Chapter 3 [Materials and Methods] presents and describes in detail all the materials used and tests performed to characterize them.
- Chapter 4 [Results and Discussion] comprises an in-depth discussion of all the achieved results, a cost analysis of the final developed solutions, as well as their end-of-life alternatives.
- Chapter 5 [Conclusion] states briefly the main conclusions observed in the project as a whole.
- Chapter 6 [Assessment of the Work Done] presents all the objectives achieved, parallel work that was also taken but was not mentioned in this dissertation, some suggestions to implement in the future and a final assessment of the work carried out.

2 Context and State of the Art

2.1 Bioplastics: What are they, their evolution and new sustainable strategies

According to *European Bioplastics* (EUBP), bioplastics are defined as a broad range of materials and products that are either biobased, biodegradable, or present both properties [5]. A biobased plastic is a material made partially or entirely from biomass, such as corn, sugarcane or cellulose [6] and, according to its biobased carbon content (BCC), the product can receive a label ranging from one to four-star-biobased [7, 8] – Figure B. 1 (Appendix B). Contrary of what society thinks, a biobased material is not inherently biodegradable, because biodegradability strongly depends on the chemical structure of the polymer and its degradation characteristics instead of its origin, so it can be either fossil or natural based. Bioplastic's range and some examples that comprehend each category can be seen in Figure 3 [6].

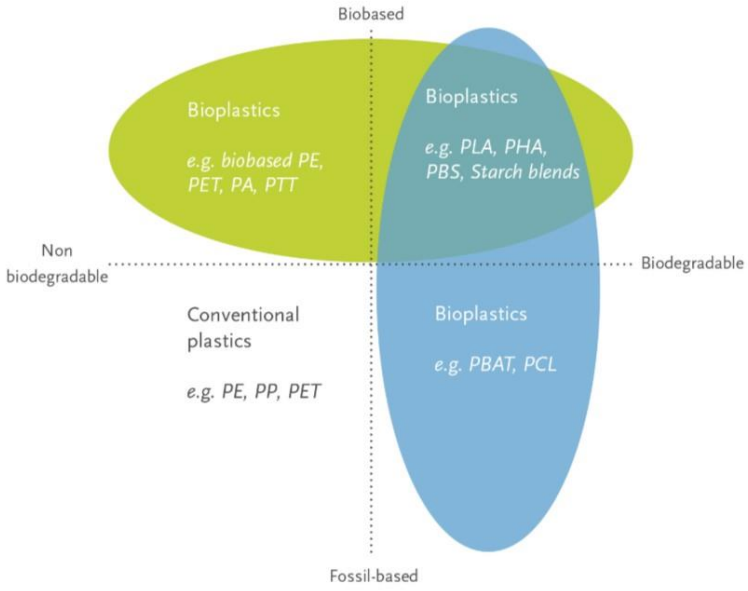


Figure 3 – Division of the bioplastic's family.

A material is considered biodegradable if it is decomposed through the action of micro-organisms, within no specific time frame, and resulting in the formation of water, carbon dioxide (CO_2), methane or both and, usually, a residue which is non-harmful to the environment [9, 10]. Moreover, according to the European Standard EN 13432, a biodegradable plastic can also be considered as compostable if it disintegrates after 12 weeks and completely biodegrades after 6 months on a monitored industrial environment. If a given material complies with the information stated on this standard, it can be awarded an OK Compost Certificate, either for home or industrial composting depending on the degradation times and conditions (temperature, oxygen

concentration, moisture content) [11, 12]. For home composting, there are no current standards which specify the conditions it should undergo, however, some countries have developed national standards for this effect, all based on the reference standard EN 13432 [12]. Respecting labels can be seen in Figure B. 2 (Appendix B) [13]. All of these labels and certifications make it possible to safeguard the future of bioplastics mainly by:

- Giving clear and transparent information of the product to the end user;
- Making possible proper sorting in waste collection and recovery systems [14].

Bioplastics started to appear many years ago. In fact, the first man-made plastic known as Parkesine, made from cellulose, was created by Alexander Parkes on 1862 [15, 16]. A few years later, in 1897, a biodegradable and biobased plastic based on milk called Galalith was invented by German chemists. Moving forward to the 20th century, polyhydroxybutyrate (PHB) was developed by Maurice Lemoigne, the first bioplastic made from bacteria [16]. The list goes on and, today, there are bioplastic alternatives for almost conventional (fossil-based) plastic materials and their corresponding applications [6].

Furthermore, society is increasingly becoming more concerned about the environment, promoting initiatives and new strategies to implement a circular economy of plastics, as a matter of mitigating environmental impacts caused by greenhouse gases (GHGs, mainly CO_2 emissions) and plastic litter. Some good examples of these new efforts can be taken from United Kingdom (UK), where it was established a roadmap to 2025 having four main targets [17], each one with its corresponding challenge and potential solution:

- Invest in a product's redesign in order to eliminate single-use packaging;
- Aim for the entire package to be reusable, recyclable or compostable;
- Reaching effective recycling or composting efficiency of 70 %;
- Aim for an average recycled content of 30 % across all domains of plastic packaging.

The *University of Cambridge Institute for Sustainability Leadership* (CISL) also started a plan to eliminate plastic packaging waste from UK bottled water and soft drinks called *Towards sustainable packaging* [18]. Their milestones comply with UK's roadmap targets, thus trying to introduce the concept of a circular economy. Also, in 2018, the European Commission embraced the European Strategy for Plastics, where Portugal has put a relevant contribution, which will mark Europe's transition to a circular economy, aiming for, once again, the elimination of single-use packaging and for its total or at least partially recyclability [19, 20]. Therefore, bioplastics appear as an attractive solution because the biobased ones use renewable feedstocks instead of fossil resources, contributing for product's carbon footprint reduction, and the biodegradable ones offer better end-of-life alternatives, such as mechanical or organic recycling and energy recovery, depending on the base of the plastic [9]. Moreover, biobased plastics have, generally, the same characteristics of their conventional alternatives, so they can be separated together in the

recycling streams and, nowadays, apart from PS and styrene-based polymers, there is the possibility to produce all existent polymers at least partially from biosources [6, 21, 22]. Moreover, at the end of 2018, it was estimated that the land used for the growing of the renewable feedstock accounted only for less than 0.02 % of the global agriculture area (5 billion hectares), which is insignificant, as Francois de Bie, the Chairman of *European Bioplastics,* said [23]. On the other hand, there are both new biodegradable and biobased polymers which have different properties, requiring more research both for the consumer and the waste management systems, hence, higher investments.

2.2 Bioplastics: Market options and *ATS*' past and present work

Currently, and considering the drinking market, there is a lot of research and development on the bioplastics' field. Since 2011, *Fabri-Kal* sells cold cups and lids made from PLA with 100 % BCC (United States Department of Agriculture (USDA) certified and having *BioMass Packaging* following the same trend, both having a Biodegradable Products Institute (BPI) certification, which states that the product is suitable for industrial composting [24–26]. On 2016, *Tetra Pak* launches the first Tetra Top carton bottle with biobased plastic for *JUST water*'s company, where more than 80 % of the total package (cap and top included) is made of HDPE derived from sugarcane [27, 28]. In the same line, *UNITED CAPS* in collaboration with *Braskem* have developed in 2018 two types of bioplastic bottle screw caps made of HDPE, also derived from sugarcane, for dairy products and still drinks, both pressurized or non-pressurized [29, 30]. All these companies state their will to pursue more sustainable operations and that their products should increasingly bring less impact to the environment, offering competitive advantages to their customers.

Apart from a study for the development of biocomposites made of different PLAs and polycaprolactone (PCL) with cork loads, in order to study the mechanical, structural and thermal properties of these blends [31], where capsules for wine bottles were produced as specimens, the author did not find any information regarding capsule tops made from bioplastic materials for the spirit drinks market, specifically (minimum alcohol content of 18 % V/V). *ATS* tried to develop new sustainable solutions in the past, using PLA, polybutylene adipate terephthalate (PBAT) and a blend of PLA and PBAT, both biodegradable polymers, and also their blends with cork loads of 10 and 25 wt. %. However, since it was the first time that such materials were tested, there were a lot of problems regarding the optimization of the injection moulding parameters, leading to low-quality samples. The best results were achieved with the PLA-cork blends, where cork turned out to be a crucial component for the quality of the products and allowed to achieve lower cooling times when compared to other tested new materials. However, natural PLA was not tested to prove the advantages of adding cork loads.

At the moment, European Bioplastics' annual market data shows that there is a predicted growth for the bioplastics' industry by roughly 25 % over the next 5 years, as shown in Figure 4 [23], due

to the increasing demand for sustainable products and the supportive policies and incentives to implement a bioeconomy. *ATS* wants to create new solutions to replace PS mainly because of clients requests due to nowadays' increasing environmental awareness. In addition, it is non-biodegradable and has a low resistance to organic solvents. Moreover, it is made from the polymerization of styrene monomer, which is considered to be linked to cancer, and breaks down easily once exposed to sunlight, affecting the food chain. Since it is mainly used for disposable goods, it will contribute to worsening the plastic litter problematic. Furthermore, many businesses and countries are banning or trying to ban PS, but it will not be an easy task because no other material can compete with its low price and well-known processing parameters [32]. Thus, for its replacement, *ATS* has chosen to keep testing PLA *INGEO™* from *NatureWorks*, as a biobased and biodegradable option, since market data shows its production capacities to double by 2023 – Figure 5 [23, 33] – and considering composting or chemical recycling as a possible end-of-life solution. Considering biobased and non-biodegradable plastics, a biobased HDPE from *Braskem*'s *I'm green™* PE line was chosen due to its mechanical properties, easier recycling process and also considering market data reports – Figure 5 [34]. These two materials are also advantageous because they are non-dependent on fossil resources and their price fluctuations.

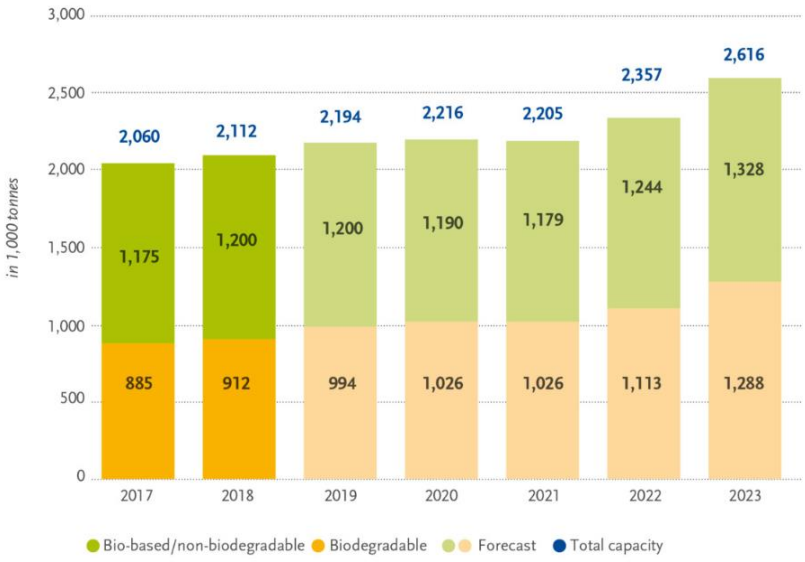


Figure 4 - Bioplastics' global production capacities [23].

For aesthetical purposes, different cork loads were added to the previously mentioned plastics, and some mechanical properties of interest were measured, in order to conclude if cork does or does not improve the overall performance of the capsule tops. A prepared blend of polypropylene (PP) with wood fibres (WF) from *Stora Enso* was also considered to compare some of the differences between cork and WF loads since wood is one of the main cork's competitors

in the market. The PP content in the blend was from fossil origin because its biobased formulation is only predicted to be available at high scales in 2023.

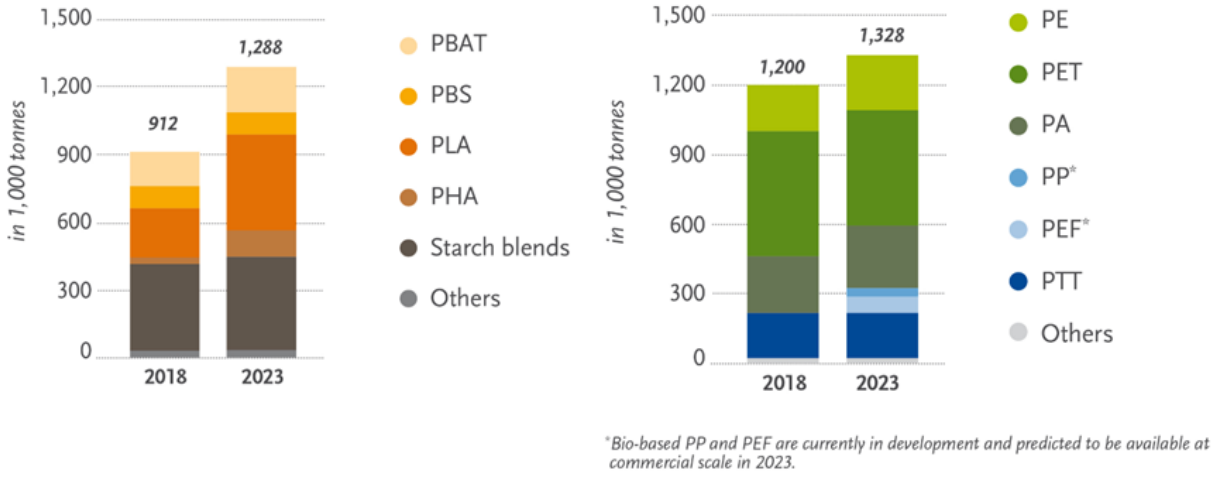


Figure 5 - Expected evolution of biodegradable and biobased bioplastics, respectively [33, 34].

2.3 Raw materials: Properties, applications and end-of-life solutions

This section focusses on end-of-life alternatives for PLA and biobased HDPE, based on scientific studies and waste management reports. A more in-depth study was considered because, before substituting one plastic for another, it is highly necessary to think about its impacts on the environment during its life cycle to not turn a solution into a problem.

The two raw materials studied are thermoplastics with high molecular weights. Their intermolecular forces are weakened once submitted to certain high temperatures, leading to the formation of a viscous fluid, without losing their properties. Then, they can be reshaped and cooled down by different processes, such as injection moulding, which is the one used in this project. Thermoplastics can undergo this reheat, reshape and refreeze cycle almost indefinitely, making them attractive for mechanical recycling [35].

PLA integrates the aliphatic polyester's family, which is known for its biodegradable properties, and is derived from renewable sources, mainly sugarcane and corn. The principle is to use these plants to capture and sequester CO_2, producing long-chain sugar molecules, as known as plant starches. Starch is extracted from the feedstocks and converted to dextrose by a process called enzymatic hydrolysis. Then, by the action of microorganisms (generally fermentation), lactic acid, the monomer of PLA, is produced. Finally, PLA is industrially produced by two main processes: direct condensation polymerization of lactic acid or ring-opening polymerization of lactide, an intermediate obtained by lactic acid's condensation [36, 37]. In the beginning, PLA was only used in medical applications due to its low production, being too much expensive in consequence. Now, it can be processed by different well-known techniques already applied for other polymers and is used to produce a wide range of materials, like food trays, tableware and cups for beverage

drinks, being certified by the Food and Drug Administration (FDA) as suitable for food contact. Moreover, when compared to other plastics, such as PS and PP, it exhibits similar optical, mechanical, thermal and barrier properties, does not emit harmful gases once incinerated and offers composting as a different end-of-life alternative [37]. Moreover, its production requires less energy consumption when compared to the majority of the fossil-based plastics. Even though it reveals a lower heat resistance and higher mechanical brittleness than other plastics, nowadays there are ways to work around these problems, such as adding reinforcing phases [38].

However, PLA also has some drawbacks. Its biodegradability is frequently questioned because it varies depending on its composition, crystallinity and environmental conditions. A life cycle assessment (LCA) of two biodegradable materials showed that, in a 100-year horizon, PLA barely degrades on landfills when compared to other thermoplastic starch (TPS) polymers [39]. Nevertheless, another study of PS and PLA boxes' biodegradation on landfills had absolutely different results. After approximately 20 months, there were no signs of the PLA boxes [40]. These two examples show the importance of the landfill conditions on biodegradation variability periods. Despite these results, when considering PLA's long-term end-of-life degradation, landfilling exhibited the highest environmental impacts on both studies and a pre-composting before PLA landfill is suggested, in order to minimize its total global warming potential (GWP). These studies also mention that mechanical recycling is, with no doubt, the best alternative from the environmental point of view, when compared to landfill, composting and incineration in separate [39–41]. However, some authors mention that considering mechanical recycling might be a problem, because PLA has tendency to thermally degrade during its reprocessing when compared to other plastics, resulting in a final lower value material and contaminating relevant waste management streams if not well sorted, affecting the thermal and mechanical properties of other relevant recycling materials [42]. Given all of this, depending on the country, there are a lot of material recovery and industrial composting facilities that do not accept PLA and other biodegradable plastics. For example, *LIPOR,* an inter-municipal waste management entity in Portugal, was contacted to know more about its PLA acceptance and composting results. The responsible of the composting process mentioned that, in their composting process, PLA barely degrades hence, being considered as an inert in the final compost, in accordance with the national legislation. Giving this, other authors refer that chemical recycling[1] of PLA is a promising waste treatment solution and should be considered in any waste management system [43, 44]. Since PLA is produced by reversible polycondensation reactions, it can be depolymerized by a process called hydrolysis, carried out with water in a possible temperature range of 100-250 ^{o}C. The process is enhanced by a catalyst, and the residence times for PLA in the reactor are in the order

[1]General term used to describe innovative technologies where post-consumer plastic waste is converted into valuable chemicals, to be used as fuel or raw materials by the chemical industry [44].

of hours, depending on the process temperature as well as the used catalyst [43]. These said it is then possible to have much faster results when compared to landfilling or composting. Hydrolysis is also the primary mechanism of PLA's degradation during composting, that is why high moisture levels and temperature should be granted. It preferentially takes place on the ester groups of PLA's amorphous regions, leading to a decrease of its molar mass and an increase of its crystallinity [38, 45]. The polymer chains tend to split into smaller fragments and, in the end, lactic acid. The random cleavage of the ester bonds is controlled by four parameters [38], which are the rate constant, the amount of absorbed water, the diffusion coefficient and the solubility of the products resultant from degradation.

Regardless of all the previous achievements and conclusions, it is the most popular bioplastic, and some authors boost its production. In fact, a project conducted in Germany and supported by the Federal Ministry of Food and Agriculture, aimed for the study of two types of PLA wastes, one from industrial processes and other from post-consumer waste collections, focusing on its disposal, sorting and up-grading to recyclates. Some of the interesting conclusions are given below [46]:

- It is possible to apply near-infrared spectroscopy (NIR) identification and sorting of bioplastics, however, due to the lower PLA fluxes at the moment in the post-consumer mix, it is still not economical;
- Recycling of bioplastics is beneficial for the environment, where mechanical or chemical recycling of PLA contributes to the reduction of environmental impacts and for lowering the demand for non-renewable resources;

Moving to PE, it is the most well-known plastic in the world and has countless applications ranging from pipelines, plastic bags to storage vessels and kitchenware [47]. It has various grades depending on the structure of its molecules, resulting in different properties. As referred before, a biobased HDPE was selected because it has excellent chemical and thermal resistance, being capable of undergoing several thermal cycles. Furthermore, HDPE has a density of at least 941 kg/m^3, resulting in a more rigid product. It also exhibits excellent mechanical properties, such as tensile strength due to its low degree of branches resulting in strong intermolecular forces. On the other hand, higher densities result in higher crystallinities as well as lower impact strengths [48].

The used biobased HDPE is produced by polymerization of dehydrated sugarcane ethanol [49] and can be processed by a lot of industrial techniques, being injection moulding the one of interest in this project. Regardless having a natural or fossil origin, PE always has the same properties, so both versions can be recycled together in existing recycling streams [34] and, since it is a non-biodegradable material, it is the best end-of-life solution. Another advantage is that its processing parameters are the same, so its industrial implementation is quick and results in no extra

investments apart from buying the raw material, ensuring a final product with good quality. Finally, it is estimated that the production of 200 thousand tons of green PE, from sugarcane ethanol, results in an annual reduction of CO_2 in the atmosphere of 950 thousand tons [50].

Briefly talking about composites, they are a combination of two or more natural or synthetic materials, where the primary purpose is to form a stronger material, whether considering strength, efficiency or durability. They are constituted by a matrix and a dispersive phase. The matrix is frequently polymeric or metallic and the dispersive phase a fibre or a particulate load, depending on its size. The dispersive phase provides strength and stiffness to the matrix, and the latter protects the dispersive phase by transferring eventual applied external loads [51]. For this project, cork-polymer composites (CPC) were selected.

Cork is a natural, renewable and sustainable material with a lot of benefits. It has excellent elastic and compressive properties, low density ranging from 120 to 240 kg/m^3, low permeability to gases and liquids, good thermal insulation and high humidity resistance [52, 53]. Furthermore, its residues can be reused to produce new materials without limits, allowing to extend the retention of CO_2 once sequestrated from the atmosphere. Cork and wood have been competing for the composites' market, and their selection depends on the envisioned characteristics and application of the final material. Studies show that when compared to wood-reinforced materials, CPCs exhibit extremely low water absorption levels and really good dimensional stability [54], which means they maintain their dimensions when subjected to temperature and humidity changes. Furthermore, the same studies demonstrate that the addition of cork results in improving impact resistance and hardness of the neat materials.

Regarding biocomposites, according to some authors, it is stated that they should fulfil some requirements in order to be called sustainable [41]:

- Be produced from renewable or recycled sources;
- All the stages of their life cycle must be free of any hazardous environmental or toxicological effects;
- Have implemented waste management options.

Finally, recycling is considered to be one of the most advantage end-of-life solutions for them, because it ables to extend their life cycle, reducing potential environmental impacts due to decreasing the usage of raw materials and keeping CO_2 sequestrated for a more extended period.

2.4 Production method at *ATS*

At *ATS* unit, the focus is the production of plastic capsules by injection moulding, a time and cost-efficient process for industrial scale productions. Injection moulding is briefly the injection of the polymer in the molten phase, under high pressure, into a specified mould.

Apart from making the mould for the pretended product, injection moulding is a cyclic process, comprising 6 main steps: feeding, plasticization, injection, pressure holding, cooling and ejection [55]. The whole process can be briefly explained as follows:

1. The plastic, in pellet form, is feed into the injection hopper.
2. The pellets fall into the barrel, which has an endless screw pushing them forward. The screw is wrapped with resistances. Combining the screw rotation with the resistances, it is possible to keep the desired temperatures to melt the plastic material.
3. Once enough material reaches the front of the screw, it is injected into the mould cavity, under a certain defined injection pressure $P_{inj.}$.
4. A second pressure, called pack or holding pressure P_{back}, is applied to avoid the shrinkage of the material during the cooling step, forcing more material to flow into the mould, to ensure that a complete product is produced. Usually, this back pressure should not be lower than 50-60 % of the injection pressure.
5. During the cooling phase, a cooling system is responsible for maintaining the specified mould temperature. Water or oil are the most frequently used fluids for the purpose.
6. After a few seconds, the mould opens and releases the produced parts. Then, the process repeats as many times as desired.

In Figure 6, it is presented an example of an injection moulding machine.



Figure 6 – Injection moulding machine.

3 Materials and Methods

In this section, the different materials used are presented, as well as the tests conducted to each one of them. The studying raw materials with no cork granulates were not submitted to all tests but strategically selected depending on the studying characteristics. Moreover, some tests required specific samples so, the author had to perform a different injection production method, which is also briefly explained.

3.1 Materials

In this project, 9 materials were studied, each of them with different purposes. All materials and their reference names in this project, as well as a brief description of their content, are presented in the following Table 1.

Table 1 – Reference and content of the studied materials

Material reference	Description	Load content	Cork granulate dimensions / mm	Price / €·kg^{-1}
PLA	Pure PLA with a certified BCC = 100 %	-	-	2.95[a] (5[b])
PLA MF5	PLA blended with cork granulate	10-15 wt. % cork	0.3-0.6	4.50[c]
PLA MF8		5-10 wt. % cork	< 0.1	4.77[c]
HDPE	Pure HDPE with a BCC > 94 %.	-	-	2.19
HDPE MF5	Blend of HDPE with cork granulate	10-15 wt. % cork	0.3-0.6	3.93[c]
HDPE MF8			< 0.1	3.99[c]
PP-WF	Conventional PP blended with wood fibres.	30 wt. % wood fibres	-	1.97
High Impact PS (HIPS)	Pure HIPS with 2 wt. % black pigment	-	-	1.40
General Purpose PS (GPPS)	Pure GPPS with 2 wt. % black pigment	-	-	1.30

[a]price considering a purchasing amount of 750 kg;

[b]price considering a purchasing amount of 25 kg;

[c]price considering a purchasing amount of 675 to 1350 kg.

In Figure 7, it is presented one capsule of each material produced by injection moulding.

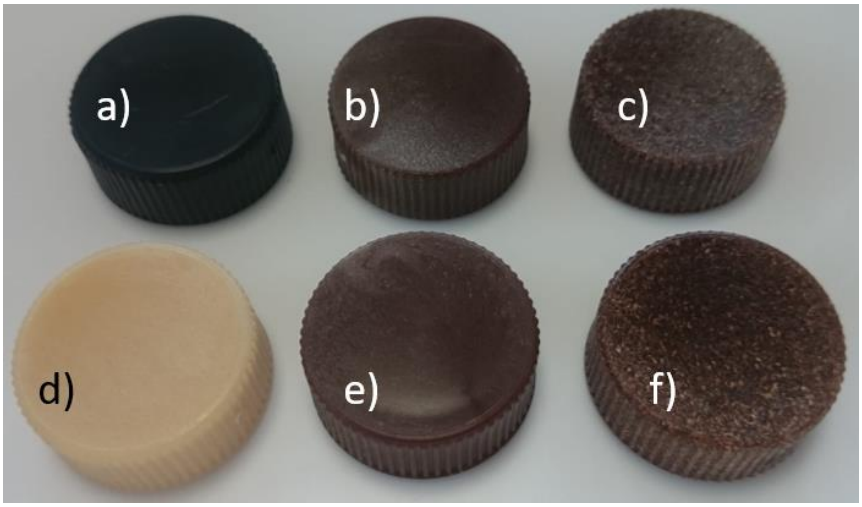


Figure 7 - Capsules produced: a) HIPS; b) HDPE MF8; c) HDPE MF5; d) PP-WF; e) PLA MF8; PLA MF5.

3.2 Samples production method

Apart from the capsules, it was also necessary to produce some specific samples to conduct certain types of tests. A Pharma melt double screw extruder Xplore 5 was used. The entire set is constituted by a 5 mL chamber where the material is fed in and mixed by two screws and a 5 mL barrel with a piston, which will be responsible for the injection of the material into the mould – Figure 8. The produced specimens had a length, width and height of (80 x 10 x 4) mm, respectively.

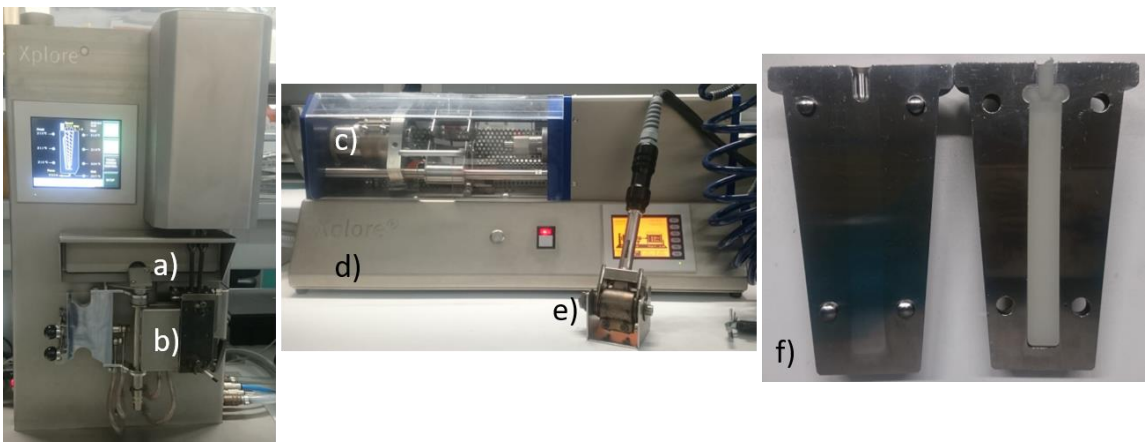


Figure 8 – Extruding apparatus: a) screws; b) chamber; c) mould container; d) extruder machine; e) barrel; f) open mould after extrusion.

The machine was turned on, and the working and mould temperatures and pressure were set. An initial rotation of the screws of 50 rpm is recommended until the temperature profiles stabilize. Previously, the rotation was increased to 100 rpm, the material fed in and left in the chamber for

around 1-2 minutes of residence time, ensuring a homogeneous mixture. The molten material was fed into the barrel at a specific rotation defined by the operator, depending on the viscosity of the outlet material, and then the injection process was manually activated. Before starting the extrusion of a different material, the machine needs to be cleaned appropriately. The produced specimens are shown below in Figure 9.

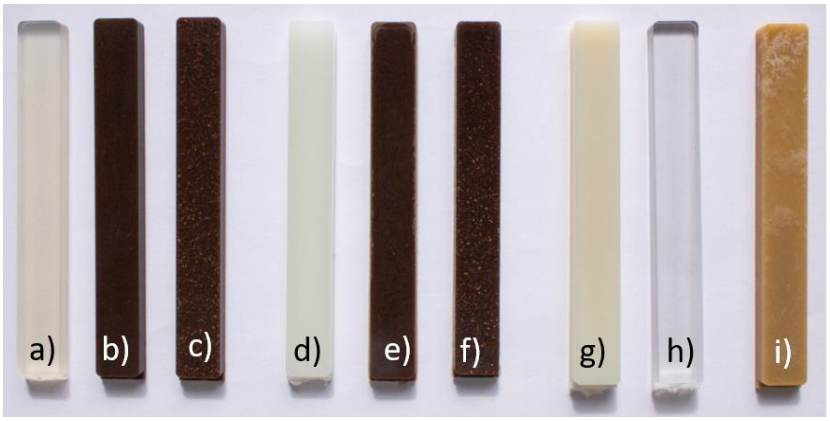


Figure 9 – Produced specimens: a) PLA; b) PLA MF8; c) PLA MF5; d) HDPE; e) HDPE MF8; f) HDPE MF5; g) HIPS; h) GPPS; i) PP-WF.

The chamber and mould temperature, injection pressure and screw rotation used for each material are presented in the following Table 2.

Table 2 – Conditions used during the extrusion of the samples

Material	Melt temperature / ºC	Mould temperature / ºC	Injection pressure / bar	Screw rotation / rpm
PLA	210	30	10	200
PLA MF5	200	30	8	200
PLA MF8				
HDPE	200	40	8	300
HDPE MF5	195	55	10	300
HDPE MF8				
PP-WF	200	40	8	350
HIPS	220	50	10	300
GPPS	230	50	10	350

For the CPCs, the temperatures and the residence times were lower than the ones observed for the neat materials, in order to avoid burning the cork.

3.3 Testing methods

The tests were divided into four main categories, depending on the studying properties: physical and mechanical, alcohol resistance, chemical stability and weathering tests.

3.3.1 Physical and mechanical tests

This group comprises tests and analysis required from the company to evaluate and validate the injection process and the capsules produced from it. Other tests were also applied to mimic the transport conditions and handling of the final product.

a. Dimensional analysis

In this analysis, the external and internal diameter $Ø_e$ and $Ø_i$, respectively, the height H and insertion height $H_{ins.}$ were measured in 15 capsules of each produced material with a calliper. The average values of each measured variable were also determined. The objective was to see if the capsules were respecting the tolerance intervals of ± 0.3 mm established by the company. If the tolerances are exceeded, it means that either the mould or the injection parameters must be reconsidered.

b. Density

The density of the developing materials is another significant value for the company because the price of the final product strongly depends upon it. Since cork has got a lot of air stored in its matrix and it is easily compressed, after injection moulding process it is expected a variation in the total density of the CPCs. The density of the produced materials was calculated by three different methods. One considering the theoretical volume given by the technical drawing of the capsule's mould, other using helium (He) gas pycnometer and the third one by mercury porosimetry.

For the first method, to have a more precise value, the average values obtained in the dimensional analysis were inserted in the program for the design of the capsules, and the theoretical volume was automatically given. The same 15 capsules from the dimensional analysis were weighted one at a time, and the density was calculated by the mass-volume ratio. In this method, the density was only calculated for the six materials used in the production of the capsules.

Gas pycnometry is a non-destructive technique to measure the volume of solid objects by following the volume-pressure relationships from Boyle's law[2]. He is frequently used because it can easily penetrate through the open pores of the materials, making it possible to calculate the

[2]Describes the pressure-volume relation based on the hypotheses that the gas has an ideal behaviour and that equilibrium is quickly reached after gas' expansion.

true[3] density of the materials. The constant volume pycnometer used is constituted by two chambers (sample and expansion chamber), three valves (fill, expansion and vent valve) and a pressure transducer linked to a manometer. A scheme of the system is presented in Figure C. 1 (Appendix C). First, two samples were placed in the sample chamber and then He was fed into the system keeping the vent valve closed. Then the fill valve was closed, and the vent valve opened to let He escape and return the whole system to atmospheric pressure. This initial process, called purge cycle was repeated several times, ensuring that both the sample and the equipment were cleaned. The initial pressure P_i observed was registered. Then the sample chamber was filled again with He until the pressure P_j stabilized. The expansion valve was opened, and the final pressure P_f of the whole system was registered. Three measurements were made for the same material and, having the pressures and knowing the volumes of the two chambers, it was possible to calculate the occupied volume of the studying samples V_s, applying the following Eq. (1) [56].

$$V_s = V_C + V_E \cdot \frac{P_f - P_j}{P_f - P_i} \quad (1)$$

Where V_c is the volume of the sample chamber = 43.54 cm^3 and V_E is the volume of the expansion chamber = 55.44 cm^3

Finally, the density of the CPC capsules measured was calculated for each material based on the weight and the volume obtained from Eq. (1).

Mercury porosimetry was also considered to verify the existence or absence of pores in the structure of the material. Since mercury (Hg) is a non-wetting liquid, it cannot penetrate the open pores of a material, unless an external force higher than its superficial tension is applied. Mercury pycnometry was applied to calculate the apparent[4] density of the materials with a Quantachrome PoreMaster 60 porosimeter. It is constituted by a low-pressure chamber (up to 4 bar) fed by gaseous nitrogen and a penetrometer, where the sample is put in up to 80 % of the penetrometer's volume. First, the sample and the empty penetrometer weight was taken. Then, the cell was filled with Hg and then weighted. Mercury was drained off, and the sample put in the cell. Finally, the equipment started a low-pressure cycle, in order to feed Hg again into the penetrometer. In the end, the mass of the penetrometer, mercury and sample set was measured. With all the measured masses and Hg density (13,593 kg/m^3), it was possible to calculate the apparent volume of the sample and then its density. Only the apparent density of the PLA materials was obtained by this technique.

[3]Volume occupied by a material divided by its mass, rejecting the existent pores.

[4]Volume occupied by a material divided by its mass, considering both open and closed pores.

c. Mass Flow Rate (MFR)

The MFR is a parameter that matters for the injection process and indicates the extruded mass of molten material over a specific time. This value allows the producer to identify what is the best process range temperature to operate. It is also an important parameter when considering recycling materials because if significant MFR changes are noticed, it can represent contamination in the stream or a mixture of different grades of the same raw material. Varying the temperature, different MFR are obtained. For this project, MFR values were determined based on the American Society for Testing and Materials (ASTM) 1238 Standard using a Ray-Ran 6MBA Advanced Melt Flow System. A scheme of the apparatus is represented in Figure C. 2 (Appendix C). The operating temperature and the load applied on the piston stem, which are the conditions that can be changed in the system, are prescribed depending on the material – Figure C. 3 (Appendix C). For the CPCs materials, a temperature of 190 ^{o}C and a load of 2.16 kg was selected. For the PP-WF blend, a temperature of 230 ^{o}C and a load of 2.16 and 5 kg was used.

Before the test, the materials were dried at 50 ^{o}C for 2 h for humidity removal. Then, the temperature was set, and the machine was left to stabilize for 15 minutes. After the material was fed in pellet form, the loaded piston was put on place, starting to descend under gravity into the cylinder. The test is only valid between the reference marks of the piston so, once the first mark reached the cylinder, the measurements started. One valid measurement consists of cutting-off a continuous and bubble-free filament in the defined time. Depending on the viscosity of the material and according to the standard, the time of the cut-offs was chosen, in order to have a filament of material between 10 to 20 mm according to Figure C. 4 (Appendix C). At the end of the test, at least three filaments were measured one at a time and their mass average $m_{av.}$ calculated. If the difference between the maximum and minimum value exceeds 15 % of $m_{av.}$, the results shall be discarded, and the test repeated. Finally, having the average mass of the cut-offs, Eq. (2) was applied to calculate the MFR.

$$\mathrm{MFR} = m_{av.} \cdot \mathrm{factor} \tag{2}$$

Where factor is the value mentioned in Figure C. 4 for the selected cut-off time.

The four CPCs presented in section 3.1 (page 13) had their MFR calculated, which was previously compared with their constituent neat polymers' MFR at the same test conditions.

d. Compression

The compression test was conducted to simulate storage and transport conditions, where several lots of bottles are packed on top of each other. Compressive resistance tests give an idea of the material's capacity to bear short-term loads. In this project, it was only pretended to conduct a comparative analysis of the materials. Thus it was not followed a standardized procedure neither

used the required tests specimens. Instead, the conditions of the test were established, and the capsules (final product) were used as sample tests. The testing material was placed between the two parallel plates of the compression machine, which exert a force perpendicularly to the surface area of the material at a specific velocity. The machine was connected to a computer, which collected the data (pressure vs. displacement) during the experiment. A picture of the compressive machine is presented in Figure C. 5 (Appendix C). A velocity of 1.5 mm/min was applied until a compression of 25 % of the initial sample height was achieved, and the recovery of the material after compression was then recorded. The test was done at least two times per material. In the end, it was possible to obtain the representative stress-strain curve for each material. From the curves, some parameters were estimated for each material, such as the compressive modulus[5], the yield point[6] and the compressive strength[7].

e. Hardness

Hardness is usually defined as the resistance of a material to permanent deformation such as indentation. Sometimes, tensile tests are replaced by hardness tests, because they are non-destructive, easier and faster to conduct[57], but should not be applied alone for product design specifications. There are different hardness tests with the correspondent scale but, since in this project hard plastics were studied, the most suitable one is known as Shore D. The equipment used for this test was a Shore D durometer, which as a sharper indenter – Figure C. 6 (Appendix C). This time, the specimens produced on section 3.2 (page 14) were used. The specimen was put under the indentation zone and, before applying the pressure, it was required to verify the presence of a flat surface, otherwise, the results might be compromised. The needle penetrates in the material as far as it can go and indicates immediately the corresponding hardness measurement. Ten measurements were made for each material and, in the end, a median of the values was calculated. The higher the value, the harder is the material.

f. Abrasion Resistance

The abrasion resistance is frequently considered as a critical property of packaging components. The material can be damaged during transportation, storage and handling, resulting in the poor appearance of the product. Moreover, abrasion impact may vary with time, temperature and humidity conditions. Some *ATS* clients have their own characterization and testing procedures to validate their purchased products. A similar procedure of an abrasion resistance test performed by a client was then implemented to assess the robustness of the capsules developed in this project. The client uses specific machinery, preparation of the samples and different harsh

[5]Ratio of stress to strain in the elastic domain (linear zone of a stress-strain curve).

[6]Point of a stress-strain curve where the deformation of a material can no longer be reversed.

[7]The maximum stress experienced by the material during the test.

surfaces in order to have a more in-depth analysis but, in this dissertation, a simple system was built as shown in Figure C. 7 (Appendix C), using an agitator, a wood stick, pieces of cardboard, 2 metal claws and an elevator. The client's procedure says to conduct the test at least 5 times for the same material, with a rotation of 44 cycles/min for 200 rubs [58]. In the built system, a rotation of approximately 50 rpm was set during 4.5 min. The test control material was PLA MF5 and, after testing the previously mentioned conditions, other rotations of 100, 150 and 500 rpm were further applied for a period of 2.5 min. After making a visual analysis of the control samples, it was decided to also conduct the test three times at 500 rpm for the rest of the materials, to evaluate the results in more extreme conditions than the proposed ones stated from the client. The marks were characterized, for both testing conditions, on a scale of 0 to 2, as described in Table 3.

Table 3 – Characterization levels of the abrasion marks

Scale Level	Description
0	No changes are noticed.
1	Light changes are noticed.
2	Significant changes are noticed.

3.3.2 Alcohol resistance tests

Alcohol resistance tests comprise, again, experiments required by the company to validate its products once in contact with alcoholic drinks.

1. Droplet test

The droplet test is a gentle experiment to mimic the deterioration a material can experience when in contact with alcoholic drinks. A solution of 50 % ethanol with 3 % of acetic acid was prepared and used to simulate the pH of an alcoholic drink. A single droplet was applied on the top of the capsule, which was then covered with a wristwatch glass. After 1 h the excess was removed, and the capsule was left at T_{room} for 24 h. In the end, the physical changes, such as colour and shine, were registered. The test was done to 3 capsules of the same material.

2. Spraying test

The Hennessy test is another example of an analysis required by certain *ATS* clients and is made to simulate handling situations when hands are wet or in case of spills on the capsule. The same solution of the droplet test was used, but, this time, it was vaporized 5 times around the capsule. Then, the capsule was massaged (to simulate handling) and left at T_{room} for 10 min. After this time and without rubbing, the excess solution was removed, and the changes registered. This sequence is then repeated 5 times, the equivalent of 1 h testing. The test was done to 3 capsules of the same material.

3.3.3 Chemical stability tests

This set of tests are more aggressive than the previously described alcohol resistance ones and were done to evaluate the behaviour of the studying materials when in contact with different substances at different temperature conditions.

a. Water and alcohol absorption

These tests were applied in order to evaluate the behaviour of the different materials in the presence of moisture and alcoholic solutions for longer periods, in order to study the worst possible case scenarios during transportation, storage and handling. Samples of each material were previously weighted and then immersed in the studying solutions. Two different types of measurements were made at room temperature T_{room} and 50 ºC:

- After immersed for a total continuous period of 15 days;
- From time to time, depending on the evolution of the test, for 22 days.

The conditions of each test, as well as the studying purpose, are presented in the following Table 4 for each material.

Table 4 – Conditions and purpose of each test

Solution	Conditions and purpose	Materials
Water or Alcohol 50 % V/V	• Samples studied at T_{room}; • Evaluate absorption levels and dimensional stability.	5 samples of: PLA MF5 PLA MF8 HDPE MF5 HDPE MF8 HIPS
	• Samples at 50 ºC; • Evaluate absorption levels and physical appearance.	
	• Samples studied at T_{room} pre and post-dried at 100 ºC for 2 h; • Evaluate possible mass losses and absorption levels.	

The tests involving a continuous exposure for 15 days were similar to the tests mentioned in Table 4, both in water and alcohol solutions. One involved the analysis of the dimensional stability of the materials as well as the absorption levels at T_{room}, to verify if the results were closer to the ones obtained with periodic measurements at the same conditions. In this case, 3 capsules of the different materials, including PP-WF, were studied, as well as a specimen of PLA and HDPE neat polymers.

The water and alcohol absorption X_{H2O} and X_{EtOH}, respectively, in % was calculated according to the following Eq. (3), which is written for X_{H2O} as an example.

$$X_{H2O}(\%) = \frac{m_t - m_i}{m_i} \cdot 100 \quad (3)$$

Where m_t is the sample mass at a specific time t and m_i the initial mass of the samples before immersion.

b. Morphological evaluation

Scanning electron microscopy (SEM) is a technique that allows to obtain the surface morphology of the materials with extremely high resolution. From captured images, it is possible to take some conclusions about the resistance of the material at certain conditions. The test was conducted to analyse the surface of the following materials:

- PLA MF5 and HDPE MF5 submitted to no tests;
- PLA MF5 and HDPE MF5 submitted to a water absorption test at 50 ºC;
- PLA MF5 submitted to an alcohol absorption test at 50 ºC.

Since the capsules are made of non-conductor materials, it was necessary to cover them with a thin gold layer to ensure conductivity during the analysis. It is important to mention that this additional layer does not change the surface of the material, hence, the analysis is not compromised. The morphological characterization was then performed using a desktop scanning electron microscope, Phenom XL. The sample was placed on carbon tape and then analysed at a voltage of 15 kV. Additionally, a sample of a fracture of the PLA MF5 material was also performed. For the effect, it was necessary to break the capsule at low temperatures using liquid nitrogen in order not to damage the structure of the material.

3.3.4 Weathering tests

This group comprises tests and analysis required from the company to evaluate the behaviour of the different materials under certain conditions of temperature and humidity in order to mimic the possible climatic scenarios that the materials might undergo during their lifetime and transportation. These conditions can vary from 60-90 % of relative humidity (RH) and temperature ranges from freezing to 60-70 ºC [59] in a single shipment, for example. A composting test was also conducted to analyse PLA's biodegradation in specific conditions.

a. Thermal resistance

This test is one of the required from the company and was done with the objective to test the response of the assembling surface of the material when submitted to thermal shocks, which can occur during transportation. The test was applied to 10 capsuled samples of each material, where a natural cork stopper was glued to the studying capsules with ethylene-vinyl acetate (EVA) adhesive. After stabilization, the thermal cycle began.

- First phase: the materials were put in a drying oven at 70 ºC for 16 h;
- Second phase: the materials were put in the freezer at approximately -20 ºC for 3 h;
- Third phase: the materials were put again in a drying oven at 70 ºC for 5 h.

In the end, the samples were left to stabilize at T_{room} for at least 2 h and, a glueing test on a tensile ruler was done to observe the type of break. There are 4 types of breaks: glue cohesive, substrate cohesive (pretended result), superficial or adhesive. Finally, the test ended with visual analysis.

b. Climatic ageing

Climatic ageing tests are applied to study extreme RH levels at considerably high temperatures in order to mimic shipments in containers with unfavourable conditions. In this test, 5 capsules were weighted, their dimensions taken ($Ø_e$, $Ø_i$ and H) and finally put on a climatic chamber (CC) at the pretended studying conditions: 95 ± 5 % RH and 60 ± 2 ºC for 20 h. In the end, the samples were immediately weighted, and the respective dimensions were taken one more time. Apart from visual and texture changes, the absorption level and the dimensional stability of each material was also analysed.

A compression test was also conducted to see if the climatic ageing had any impact on the testing samples' properties, by comparison with the values obtained with the capsules that were not submitted to any test apart from compression.

c. Composting

The composting experiment was conducted at *LIPOR* industrial composting facility in order to evaluate the biodegradation of the developed PLA materials. One specimen of pure PLA, PLA MF5 and PLA MF8, was previously weighted and its length, width and height measured. Additionally, a PLA MF8 capsule was also sent to check if the difference in shape and thickness of the material could influence the biodegradation process. After that, the samples were sent to *LIPOR*. There, the specimens were identified and put in a perforated bag along with organic residues, in order to avoid losing them in the composting tunnel. The composting process had two equal but separated phases. One phase consists of putting the materials in a closed tunnel for a period of 14 days and, in the end, the samples are recovered, and their state verified. Then the second phase begins following the same procedure. In the end, the samples were weighted again, to verify if any mass losses had occurred. The conditions experienced from the samples during composting, such as the average temperature, were also recorded.

4 Results and Discussion

This section presents the results and all the important collected data for their discussion. A slightly different distribution from section 3.3 (page 16) was made since some tests were possible to compare with each other.

4.1 Physical and mechanical properties

This section presents important results for the validation of the production process as well as the analysis of the mechanical properties.

4.1.1 Production results and MFR

In order to compare the parameters given by the manufacturers with the actual ones used, as well as making a comparison between the latter and the actual PS injection properties, the following information was displayed in Table 5. PLA MF5 and MF8 had the same injection parameters, thus they are referenced as PLA MF. The variables t_{cycle}, $t_{cooling}$, $V_{inj.}$, T_{max} and T_{mould} refer to the cycle time, cooling time, injection velocity, maximum temperature verified and mould temperature, respectively. The production of the PP-WF capsules was not followed by the author, so the parameters are not presented.

Table 5 – Injection moulding parameters registered for each studying material

Material	t_{cycle} / s	$t_{cooling}$ / s	$P_{inj.}$ / bar	P_{back} / bar	$V_{inj.}$ / mm·s^{-1}	T_{max} / ºC	T_{mould} / ºC
PLA MF	29	20	900[a]	450	40	175	16
HDPE MF5	32.5	20	900[a]	750	20	175	16
HDPE MF8	37.3	20	900[a]	750	20	175	16
HIPS	23.5	12	55[b]	58	45	210	15

[a]dynamic pressure

[b]hydraulic pressure

Before any further comparisons, HIPS was produced in a different machine and the process the $P_{inj.}$ was established as hydraulic pressure. To convert this value to dynamic pressure, it is required a specific dynamic-hydraulic pressure function characteristic from each machine, which the author did not have access.

From the presented values, it is possible to verify that HDPE materials took longer to produce registering the lowest $V_{inj.}$, and HIPS had the lowest t_{cycle} and the highest $V_{inj.}$. Regarding the maximum temperatures verified for each CPC, when compared to the ones recommended by the manufacturer, they are significantly lower. In PLA's technical data sheet, a melt temperature of

188-210 ºC is indicated, and the T_{max} displayed is of 205 ºC. The same goes for HDPE. In this case, cork is a limitation for the production process, because lower temperatures than the recommended need to be applied in order not to burn it (starts to degrade at 200 ºC). On the other hand, it was stated from the producers that cork acts like an expansion agent, helping to produce pieces with thicker walls.

Considering the P_{back}, it is responsible for avoiding the shrinkage of the materials during the cooling phase and should be equivalent to 50-60 % of $P_{inj.}$. The HDPE materials required a higher P_{back} because PE is known for having shrinkage values between 1.5 to 4.0 %, whereas PLA shrinkage reaches typically 0.5 % at maximum [60]. In fact, this HDPE shrinkage was verified after conducting the dimensional analysis of the produced capsules. As mentioned before, 15 capsules of each material had their dimensions were taken ($Ø_e$, $Ø_i$, H and $H_{ins.}$). The average values obtained for each variable are presented below in Table 6 for all produced materials as well the standard values of the used mould.

Table 6 – Standard and average dimensions of the produced capsules for each material

	$Ø_e$ / mm	$Ø_i$ / mm	H / mm	$H_{ins.}$ / mm
Standard	28.40 ± 0.30	19.40 ± 0.30	12.00 ± 0.30	9.30 ± 0.30
PLA MF5	28.49 ± 0.06	19.05 ± 0.19	11.94 ± 0.04	9.39 ± 0.07
PLA MF8	28.42 ± 0.09	19.18 ± 0.10	11.91 ± 0.04	9.35 ± 0.11
HDPE MF5	27.75 ± 0.09	18.85 ± 0.15	11.62 ± 0.05	9.21 ± 0.08
HDPE MF8	27.70 ± 0.08	18.73 ± 0.11	11.61 ± 0.04	9.15 ± 0.08
PP-WF	28.35 ± 0.06	19.24 ± 0.09	11.79 ± 0.03	9.15 ± 0.09
HIPS	28.34 ± 0.08	19.36 ± 0.08	11.94 ± 0.03	9.42 ± 0.09

As it can be seen, all the materials respect the tolerance value of 0.3 mm established by the company, except the HDPE materials. The higher differences are verified for the external and internal diameter. This means that the current mould used for HIPS cannot be used for the production of the HDPE composites, otherwise, some problems would arise. Since it is not possible to guarantee the standard dimensions of the used model, the client would have the right to claim, because dimensions out of the specifications may lead to problems on its bottling line. Moreover, at *ATS,* this lack of compliance on the dimensions can result in problems regarding the encapsulation of the stoppers.

Shrinkage is a phenomenon which varies depending on the type of the polymer, its properties, the applied processing conditions, mainly pressure, temperature and flow rate and also the design of the mould. Semi-crystalline polymers such as HDPE, always exhibited higher shrinkage rates, as verified, because while cooling down their chains try to rearrange in order to form well-organized structures, resulting in less volume occupied [60]. Moreover, higher molecular weights

also contribute to higher viscosities, leading to difficulties in filling the mould cavities, leading to higher pressure drops. Higher P_{back} needs to be applied to overcome this issue, as verified in the results obtained in the previous Table 5. The viscosity of a material is inversely related to its mass-flow rate, which can be concluded from the results presented below in Table 7.

Table 7 - MFR values for all materials

Material	Conditions	Determined MFR / g·10 min^{-1}	MFR given from manufacturer / g·10 min^{-1}
PLA	190 °C/2.16 kg	35-40	35
PLA MF5		20-25	-
PLA MF8		30-35	-
HDPE		-	20
HDPE MF5		7-10	-
HDPE MF8		10-15	-
HIPS	200 °C/5 kg	-	4.1
GPPS	200 °C/5 kg	-	12
PP-WF	230 °C/5 kg	9	-
	230 °C/2.16 kg	2	-

As it can be seen from the previous table, HDPE is more viscous than PLA, because the higher the MFR, the easier it is for the material to flow, as previously stated. It can also be concluded that cork loads affect the MFR value significantly, because they lead to materials with higher viscosities, thus interfering with the injection process. Finally, it was verified that the size of the granules is an important variable because, the bigger the loads, the lower the MFR.

In case of materials with high MFRs, PLA for example, it is recommended to use an automatic cutting system, to have more accurate measurements but, for this case, it was not possible to use such system. Another thing is that MFR is a very sensitive variable because it can easily vary between different grades of the same polymer. For example, considering a homo or copolymer, the values are completely different.

4.1.2 Density

The density of the materials was calculated based on three methods as mentioned before: the corrected theoretical volume of the capsule (with the average values obtained in the dimensional analysis) and by He and Hg pycnometry. The density values before injection of the CPCs were estimated based on the average values of the granulates' mass content and density given by the manufacturer and the density of each neat polymer, which can be seen in Table 8.

The purpose of the density test was to verify the impact of cork's compression on the CPCs' density during the injection moulding process. Even though the existence of pores will always be present, it is expected a reduction in their volume, leading to an increase in the density. The data obtained for each density is presented in Table 9.

Table 8 – Density of the neat polymers and range values of density and mass content of the different types of granulates

Material	Density / kg·m^{-3}	Mass content / wt. %	Granulate dimensions / mm
MF5 granulate	50-70	10-15	0.3-0.6
PLA MF8 granulate	75-95	5-10	< 0.1
HDPE MF8 granulate	75-95	10-15	< 0.1
PLA	1240	-	-
HDPE	955	-	-

Table 9 – Density values before and after injection for the three studied methods

Material	Density before injection / kg·m^{-3}	Density after injection / kg·m^{-3}		
		By theoretical volume	By He pycnometry	By Hg pycnometry
PLA MF5	1094[a]	1132 ± 12	1228 ± 7	1062[c]
PLA MF8	1154[a]	1129 ± 7	1235 ± 7	1082[c]
HDPE MF5	844[a]	814 ± 5	933 ± 2	-
HDPE MF8	848[a]	815 ± 5	951 ± 5	-
HIPS	1040[b]	944 ± 6	-	-
PP-WF	1050[b]	938 ± 6	-	-

[a]estimated values based on the cork weight content and density;

[b]given by the manufacturer;

[c]based on one single test.

As it can be seen, the cork loads have a significant impact on the density of the CPC, even though presented in low amounts. Taking a look to the values reached by the theoretical volume method, although the density of the CPC PLA materials had increased as expected when compared to their density before compression, all the other materials had their densities reduced, including HIPS. This cannot be correct, if considering that the polymer's density remains unchanged during the injection process, suggesting that the method is not adequate for the case. The estimation of the volume based on the schematic design of the mould can be complex.

However, He pycnometry was conducted to calculate the true density of the CPC materials, in order to verify the existence of pores in the material's matrix. It was verified that all densities increased, suggesting that free spaces were present. Furthermore, in order to have a more precise value, Hg pycnometry was done for the PLA composites, and it was verified a decrease

on the density, suggesting, again, the generation of free volume during the injection process. It was not possible to conduct the same test for the HDPE materials, but similar behaviour was also expected to be verified.

Although the values suggest the absence of cork's compression, a SEM analysis was conducted on a fracture of a PLA MF5 capsule, which was broken using liquid nitrogen. Images from the literature show that cork, in its normal condition, exhibits a representation similar to a honeycomb, once analysed by SEM [53]. In Figure 10, it is observed a warped cork granulate, suggesting that compression must have occurred.

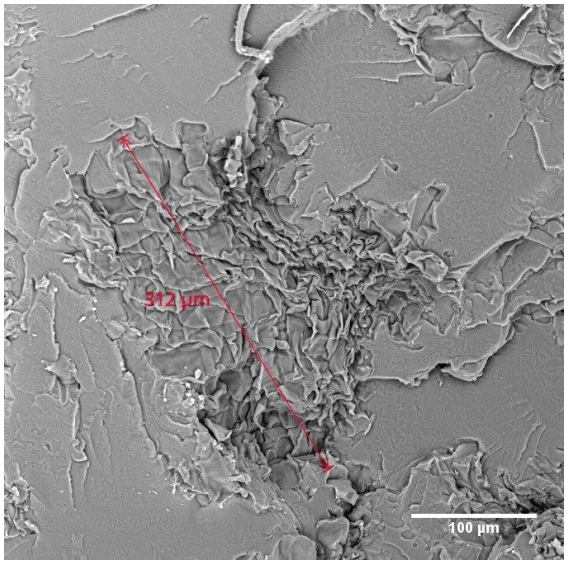


Figure 10 – Warped cork granulate with a visible length of approximately 312 µm captured from a fracture of a PLA MF5 capsule (600x).

4.1.3 Compression

The compression test was conducted to 3 capsules of each produced material at a velocity of 1.5 mm/min until 25 % strain of the initial thickness was achieved, as mentioned before. The collected data was in load-extension format. In order to obtain the stress-strain curves, the following Eq. (4) and (5) were applied to calculate the stress σ and the strain ε, respectively.

$$\sigma = \frac{F}{A_0} \tag{4}$$

$$\varepsilon = 1 - \frac{L_0 - L}{L_0} \tag{5}$$

Where F is the applied load at a specific deformation, A_0 the initial cross-sectional area of the capsules, L_0 the initial height of the sample and L the height of the sample at a specific deformation.

The representative stress-strain curve of each material is presented below in Figure 11. From the obtained curves, it was possible to verify that, PLA materials are stiffer than the other ones,

followed by HIPS, PP-WF and finally HDPE. This is possible to affirm, based on the slope of each curve, which is known as the elastic modulus and represents the ability of a material to resist deformation under stress. In other words, considering PLA and HDPE MF5 and fixing a specific deformation, the latter requires less stress to deform, thus being much less stiff than PLA.

A GPPS was also tested, and it did not tolerate a total deformation of 25 %, breaking nearly the beginning (≈ 4.5 to 7 % of strain). Deeper analysis was not undertaken, because the material was not injected in the same mould.

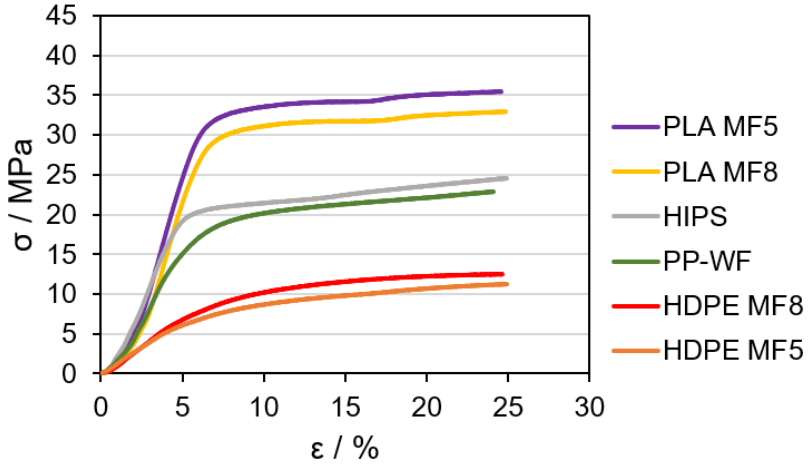


Figure 11 – Representative compressive stress-strain curve of each material.

The results obtained for the compression results before and after performing climatic ageing under specific conditions (95 ± 5 % RH and 60 ± 2 ºC for 20 h) in a CC are shown below in Figure 12.

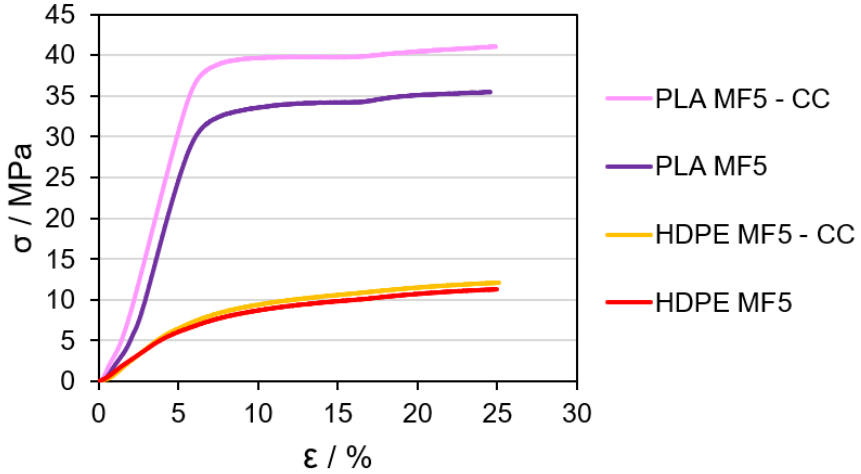


Figure 12 – Stress-strain curves of PLA and HDPE MF5 for the two studying conditions at 25 % strain.

As it can be observed, HDPE MF5 had a similar behaviour before and after the climatic ageing. The same results were verified for HDPE MF8, HIPS and PP-WF and are presented in Figure D.

1 (Appendix D). On the other hand, PLA MF5 experienced a significant increase in its compressive strength, as well as PLA MF8, which curve is presented in Figure D. 2 (Appendix D). This improvement on the mechanical properties cannot be clear and concisely explained but suggests that an interaction between cork and PLA's carbonyl groups (–C=O) might have occurred during the climatic ageing. Since the operating temperature was near PLA's glass transition temperature T_g (55-60 ^{o}C), the material shifted from a rigid to a soft phase, allowing for a readjustment of its chains, as well as eventual intermolecular interactions with cork, which became no longer an inert load. It is probable that hydrogen bonds were responsible for these interactions, a phenomenon known as crosslinking, promoting a change in the material properties. A similar interaction may not be verified for the rest of the materials, due to their chemical stability associated with their non-polar natures.

In order to have a more in-depth analysis between the different materials and between the two different studying conditions, an estimation of the compressive modulus, the yield point as well as the compressive strength experienced by the different materials was done.

- The compressive modulus is calculated from the slope of the linear zone of the stress-strain curve. The calculation only considered the stress-strain pared values contained in a window range of $[(1.1\cdot\varepsilon\text{-}1.4\cdot\varepsilon),(1.1\cdot\sigma\text{-}1.4\cdot\sigma)]$ from the beginning of the linear zone, to ensure a more accurate value.
- For the yield point, which marks the transition from the elastic to the plastic domain, since it is not well-defined due to the shape of the stress-strain curve, it was suggested to estimate the offset yield point. For the effect, a parallel line to the linear zone was drawn and intercepted with the horizontal axis at 0.2 % of plastic strain [61, 62]. This means that, upon load's removal, an irreversible (plastic) deformation of 0.002 would be experienced from the material. An example of this technique is presented in Figure D. 3 (Appendix D). The offset yield point is marked as $(\varepsilon_y^*,\sigma_y^*)$.

The achieved results are shown in Table 10, where the compression values from the samples tested after the climatic ageing are presented in parenthesis, to promote a straightforward analysis. Before any further comparisons, it is important to mention that since the samples used to perform the compression tests were not standardized as well as the testing conditions, the values cannot be compared to the ones in the literature. Moreover, the capsules are not whole solid bodies, having a different base from its top. This can be observed in the initial phase of the stress-strain curves, where a non-linear relationship is verified and might be explained due to an uneven cross-sectional area, which required some extent to stabilize the stiffer the material was. Despite this, it is mentioned in the literature [31] that for biobased polyesters like PLA, if a CPC material has a lower density than its original neat polymer, worse mechanical properties are expected in general, such as the decrease in the tensile modulus. Tensile and compressive

modulus are not the same for most of the materials but, if one decreases, it is expected the other to follow the same pattern. In fact, it makes sense, due to the cork's low resistance to deformation (low elastic modulus ≈ 8 to 13 MPa depending on the calibre and applied compression force direction) [53].

Table 10 – Compression test results for the two testing conditions. In parenthesis are presented the values of the materials after tested in the CC

Material	Compressive Modulus / MPa	Strain at yield / %	Compressive Yield Strength / MPa	Compressive Strength at 25 % strain / MPa
PLA MF5	722 ± 4 (704 ± 5)	3.8 + 0.1 (5.3 ± 0.5)	27.8 ± 0.5 (36.7 ± 0.5)	35.3 + 0.2 (41.1 ± 0.5)
PLA MF8	707 ± 2 (722 ± 9)	3.6 ± 0.4 (4.7 ± 0.1)	24.7 ± 0.2 (32.1 ± 0.5)	33.5 ± 0.5 (38.8 ± 0.1)
HDPE MF5	147 ± 7 (155 ± 6)	4.4 ± 0.1 (4.2 ± 0.2)	5.7 ± 0.1 (6.1 ± 0.2)	11.2 ± 0.1 (12.3 ± 0.2)
HDPE MF8	173 ± 8 (160 ± 13)	4.3 ± 0.2 (4.3 ± 0.4)	6.8 ± 0.5 (6.3 ± 0.2)	12.5 ± 0.2 (12.4 ± 0.2)
HIPS	515 ± 5 (517 ± 2)	3.8 ± 0.3 (3.9 ± 0.2)	18.1 ± 0.9 (18.5 ± 1.0)	24.0 ± 0.4 (26.1 ± 0.2)
PP-WF	436 ± 6 (451 ± 4)	3.2 ± 0.1 (3.7 ± 0.2)	13.2 ± 0.3 (13.3 ± 1.1)	22.6 ± 0.3 (23.5 ± 0.1)

Moving to the values displayed in Table 10, it is verified that the offset yield point was maintained for all materials, except for the PLAs, where a significant increase of the σ_y* was verified, meaning they could handle heavier loads. It is important to mention that the strain at yield verified for the materials experiencing an initial non-linear behaviour was corrected by subtracting a correction value to the determined ε_y* (see Figure D. 3 on Appendix D). In the same line of thought, the compressive strength, which is the maximum strength a material experiences, had a significant increase for PLA MF5 and MF8 but remained basically the same for the other materials. Finally, it is also possible to conclude that, in this case, neither the size nor the amount of the granulates is a crucial variable, because the obtained parameters for the HDPE and PLA CPCs, respectively, are not significantly distant. Furthermore, their response to climatic ageing was the same, considering each type of CPC individually.

Finally, the recovery of each material was also recorded, and it was possible to verify that HDPE materials were the ones exhibiting a better elastic behaviour with recoveries of ≈ 50 %, followed by PP-WF with ≈ 30 % and then HIPS and PLAs with similar recoveries of ≈ 20 %. This behaviour was repeated after climatic ageing, where the recovery values remained basically the same, except for the PLA materials, which exhibited slightly higher recoveries.

Figure D. 4 (Appendix D) shows an example of the stress-strain curves and the respective recovery for PLA and HDPE MF5 materials. The recovery values were estimated based on the ratio between the final deformation after load's removal and the total expected deformation of

0.25·L_0. The exact values obtained for all materials at the two studying conditions can be consulted in Table D. 1 (Appendix D). Just for curiosity, considering the yield point of the different materials and assuming a standard A_0 of 633.5 mm^2 (using a standard diameter of 28.4 mm), it is possible to calculate the approximate maximum weight that each material can handle until starting to deform plastically. Considering HDPE MF5, which is the less stiff material, it can handle a weight around 360 kg. In the case of PLA MF5, which has the highest stiffness, it is able to handle weights around 1760 kg, which corresponds to approximately 5 times more weight than HDPE MF5.

In spite of these verified differences, all materials perform well under compression and are good alternatives for the company's purposes.

4.1.4 Hardness

The hardness test was conducted to all the materials mentioned in section 3.1 (page 13), meaning that also the neat polymers were tested. As previously mentioned, specific specimens were used this time, to at least ensure better surface conditions. The average hardness values obtained for each material are presented below in Table 11.

Table 11 – Hardness results for each material

Material	PLA	PLA MF5	PLA MF8	HDPE	HDPE MF5	HDPE MF8	PP-WF	HIPS	GPPS
Hardness	81 ± 1	81 ± 1	81 ± 1	59 ± 1	61 ± 0	62 ± 2	75 ± 2	77 ± 3	82 ± 1

From these results, it is possible to prove that hardness is related to the stiffness of the material, because the greater it is, the higher resistance to deformation is verified. All the studying materials are comprised in the hard-extra hard range of the Shore D scale as it can be seen in the following Figure 13.

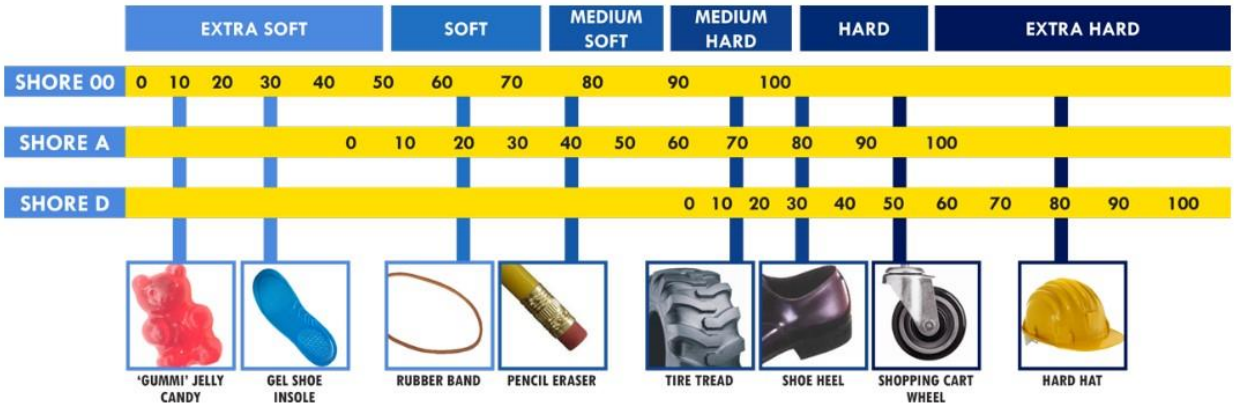


Figure 13 – Shore D Hardness scale.

Again, and as also concluded from the compression test results, apart from GPPS, PLA materials are the hardest ones, followed by the HIPS and PP-WF, which exhibited similar compressive modulus, and finally the HDPEs in the bottom of the ranking. The PLA composites exhibited the same hardness, maybe because PLA is already extra hard itself, and the low cork content did not affect the material. The Shore D Hardness value of HDPE indicated by the manufacturer was of 64, which is slightly far from the one obtained, maybe due to unfavourable processing conditions during specimens' extrusions. The PLA manufacturer does not mention the hardness value.

Despite these variations, it was only pretended to make a comparative analysis between the different materials, as in the compression test.

4.1.5 Abrasion resistance

The abrasion resistance test, as mentioned before in section 3.3.1 (page 19), is an adaptation of a client's test and it was conducted in an improvised system (Figure C. 7) where two conditions where used. First, a rotation of 50 rpm for 4.5 min was tested on 5 capsules of the same material. Then, a second condition with a rotation of 500 rpm for 2.5 min was applied to 3 capsules of the same material, to test their response to extreme conditions. The results were analysed in a three-degree scale, where 0 means that the material did not exhibit any changes, 1 was used to evaluate light changes and 2 means that significant changes were detected. One important note is that just because two different materials have a 2 classification, it does not mean they had similar scratch patterns. The only factor being evaluated in this test is the detection of light or deep marks or their absence. The following Table 12 presents the obtained results.

Table 12 – Classification attributed to each material: Condition 1 – 50 rpm for 4.5 min; Condition 2 – 500 rpm for 2.5 min

Material	Condition 1	Condition 2
PLA MF5	0	1
PLA MF8	0	1
HDPE MF5	1	1
HDPE MF8	1	2
HIPS	1	1
GPPS	2	2
PP-WF	0	0

The observed marks were verified in the outer zones of the capsule for the PLA and HIPS materials, suggesting the existence of higher borders than the middle section. The opposite was verified for the HDPE materials where round marks were noticed in the middle zone. Some of these marks were only visible depending on the light and inclination of the studying surface. Given

this, only the on-camera visible changes were presented below in Figure 14. The PP-WF material had no noticeable changes. PLAs only show slightly visible marks for extreme conditions. HDPE MF5 had a similar behaviour on both conditions, but HDPE MF8 had a poor response when the rotation was 10 times higher. HIPS had similar behaviour as the PLAs and GPPS was the material with the lowest performance. It was also concluded that the higher dimension granules (MF5) allowed to better camouflage eventual marks.

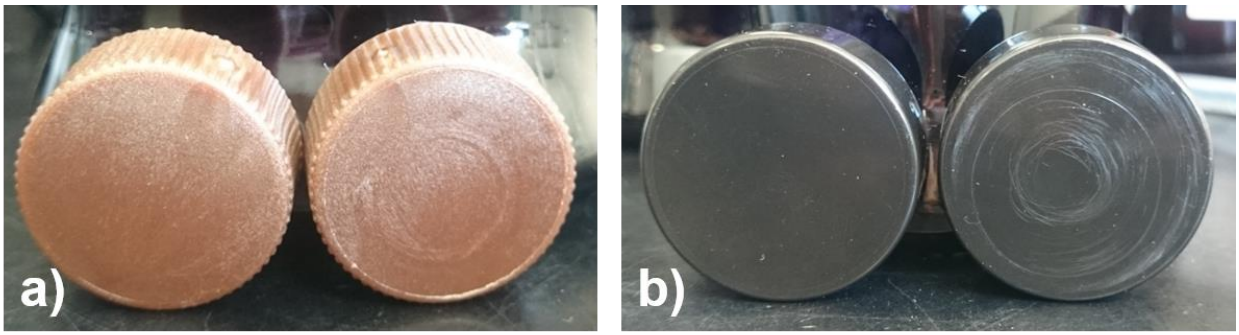


Figure 14 - Visual changes observed after a resistance abrasion test with a rotation of 500 rpm for 2.5 min: a) HDPE MF8; b) GPPS.

4.2 Alcohol resistance

The alcohol resistance tests were conducted to validate the different materials upon real scenarios of light spills and handling. Both the droplet and spraying test resulted in no physical and visual changes for any material, maybe due to the low exposure time and amount of alcoholic solution. It was possible to conclude that all materials perform very well under the studied conditions.

4.3 Chemical stability

The chemical stability tests included water and alcohol absorption measurements at different temperatures and a SEM analysis of some chosen capsules. As mentioned before, the purpose of this analysis was to evaluate the dimensional stability of each material, calculate their average absorption levels and verify the occurrence of visual and textural changes during storage and transport.

Starting off with dimensional stability, the variation values obtained for $Ø_e$ and H of each material after being immersed in water and in alcohol were basically the same and did not surpass 0.1 mm, respecting the tolerances established by the company – Table D. 2 and Table D. 3 (Appendix D). The values of the internal diameter were not calculated because the measurements were difficult to conduct due to irregularities on the inside wall of the capsules.

Moving on to the absorption levels, the following Figure 15 summarizes the results obtained for alcohol and water immersion during 22 days at T_{room} and 50 ^{o}C.

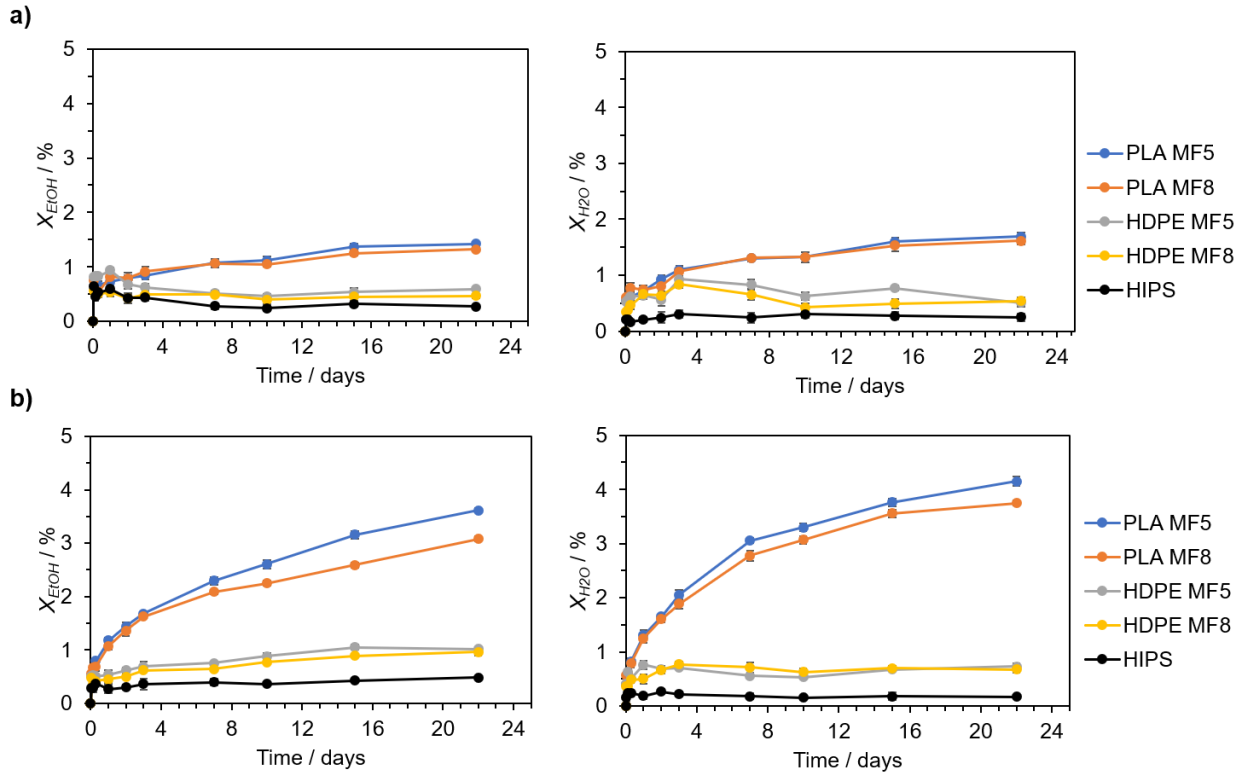


Figure 15 – Absorption profiles for each material in a 50 % V/V alcohol solution (on the left) and water (on the right) at different temperatures: a) T_{room}; b) 50 ºC.

From the analysis of the graphics displayed above, it is possible to verify that the absorption level depends on the type of material, exposure time and temperature. It is clear that only PLA materials exhibited an absorption profile, which is better defined in the case of 50 ºC, proving that temperature is one of the controlling factors of absorption. Despite the temperature, the higher values for PLA materials were registered for water absorption. The rest of the materials had a similar evolution throughout the entire experience for the 4 different conditions studied, suggesting that temperature and immersion environment do not influence the absorption levels, at least in the studied conditions.

This absence of water or alcohol profiles of HDPE and HIPS materials can be explained based on their chemical structure, which is presented below in Figure 16.

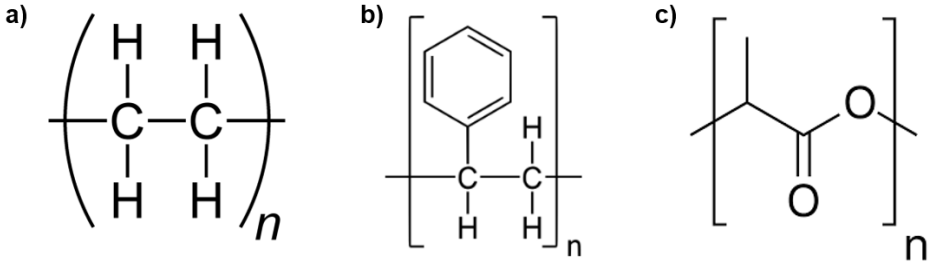


Figure 16 – Chemical structures: a) PE; b) PS; c) PLA [48].

From the previous illustrations, it is possible to understand the chemical resistance of PE and PS to polar solvents, such as water and alcohol in this case. They exhibit non-polar and stable groups over its entire chain. Moreover, a high-density polymer such as HDPE present long-linear chains, making difficult the diffusion of the solvents in their matrix. On the other hand, PLA is constituted by ester groups (RCOOR') along its chain, revealing a clear affinity for polar solvents as observed in the absorption profiles. A spectroscopy study on water diffusion in PLA films states that diffusion starts with bound water (reactive water) interacting with the amorphous regions of PLA and creating hydrogen linkages with –C=O groups. Then more water diffuses into free spaces forming more hydrogen bonds [63].

Proceeding with the analysis of the profiles, it is also possible to conclude that, for the HDPE materials, the size of the cork granulates was not a determinant parameter. However, cork content may be contributing to raise the absorption levels. A study of the degradation of HDPE during long term ageing in water at 80 ºC for 1 year time shows that the maximum value of water uptake was of 0.50 %, reaching values close to 0.10 % after the first month [64]. Another study, involving the analysis of water absorption on boards made of PE with 50 wt. % cork powder, demonstrated a water uptake of 3.7 % [54], suggesting that cork promotes water absorption to some extent. In this project, the obtained values were in between the two mentioned previous ones as it can be confirmed by consulting Figure 15. HIPS follows the same pattern as HDPE, having the lowest absorption levels for every scenario. The PLA materials with different granulates and amounts exhibited similar behaviours, which again suggests that cork does not play a key role in the absorption levels because PLA itself is known for its ability to absorb moisture. However, materials with the same cork load size and in different amounts should be studied for better analysis. All materials, including neat PLA and HDPE, were studied under two same type conditions: immersion in alcohol and water at T_{room} for 15 days. For the neat polymers, instead of capsules, the produced specimens mentioned in section 3.2 (page 14) were used. These results are presented below in Table 13.

Table 13 – Absorption levels after 15 days of continuous immersion in water and alcohol

	X_{H2O} / %	X_{EtOH} / %
PLA	0.87*	0.69*
PLA MF5	1.23 ± 0.01	1.14 ± 0.09
PLA MF8	1.16 ± 0.06	1.12 ± 0.03
HDPE	0.04*	0.17*
HDPE MF5	0.88 ± 0.06	0.59 ± 0.08
HDPE MF8	0.67 ± 0.10	0.68 ± 0.02
HIPS	0.21 ± 0.05	0.34 ± 0.08
PP-WF	1.32 ± 0.05	0.88 ± 0.01

*representative values of a single test.

For all the materials, it is not possible to compare with accuracy the values mentioned on the literature, because many factors can be influencing them, mainly the type and grade of the polymer and the injection process, where temperature and cooling times can be defined, resulting in different chain organizations. Moreover, the specimens used for testing the neat polymers were produced from a completely different process when compared to the capsules, as mentioned in section 3.2 (page 14). Additionally, only one sample was used, so the obtained values might not be conclusive for comparison. Despite this, the value for the neat HDPE is similar to the ones mentioned in the literature, as stated above.

The measurements obtained at the end of the 15th day of T_{room} immersions, were not significantly different for both continuous or interrupted immersions, concluding that quick interruptions do not influence absorption levels. The differences observed are relative to measurement errors. An example of PLA MF8 material can be seen in Figure D. 5 (Appendix D). Moreover, it was verified that pre-drying did not influence the absorption levels conducted at T_{room}, because similar profiles and values were observed, as shown in Figure D. 6 (Appendix D).

Moving on to visual and physical changes (colour and texture), PLA materials were the ones exhibiting the most modifications either in colour or texture. In fact, the HIPS capsules did not experience any changes, neither the HDPE materials, except for some little lost in coverage, conceiving a little harsh sensation. In the following Figure 17, the final state of each material after 22 days of exposure can be analysed for the 4 studied scenarios.

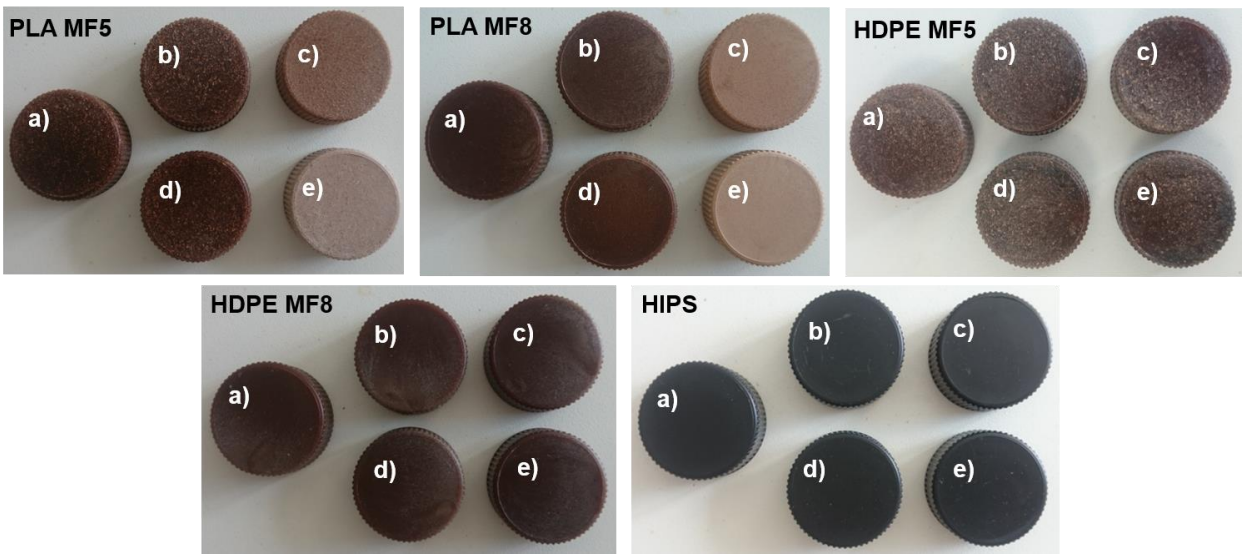


Figure 17 – Visual changes verified for every material at each condition: a) no test; b) alcohol at T_{room}; c) alcohol at 50 ^{o}C; d) water at T_{room}; e) water at 50 ^{o}C.

From Figure 17 presented above, it is possible to verify that no visual modifications were noticed for the HDPE and HIPS materials, as stated before. Nevertheless, during the measurements, it was verified that HDPE materials became slightly darker when wet, but once left to stabilize at room temperature, they returned to their initial state.

Considering PLA materials, it is possible to conclude that the more significant changes were verified for a temperature of 50 ºC, including a harsh and dull surface, suggesting degradation. Some losses in coverage and shine were also noticed at T_{room}, but less significant. Furthermore, these materials started to exhibit this behaviour after 6 days of exposure to all conditions.

In order to verify effectively if any degradation occurred, the more damaged materials were analysed using SEM. Since PLA MF5 and MF8 exhibited similar changes, only one of the materials was analysed, assuming that the same conclusions would be verified. For the effect, one capsule of PLA MF5 after immersed in water at 50 ºC and alcohol in the same conditions was analysed and compared to a PLA MF5 capsule not submitted to any test.

The captured images from the PLA analysis are displayed in Figure 18. It is possible to see that the capsule immersed in water exhibits some kind of droplets, suggesting specific local attack points. This phenomenon was also verified in a study of the hydrolytic degradation of PLA reinforced with rice hulls for 25 days at 51 ºC [45]. On the other hand, the capsules exposed to alcohol clear reveal the existence of fractures of small and high dimensions, indicating that, in this case, the chemical attack was more spread when compared to the water exposure situation. The capsule without being tested shows the injection profile of the polymer and also indicates the presence of free spaces, favouring the solvent's diffusion into the material. It also explains the results achieved on the density measurements, proving the presence of void spaces.

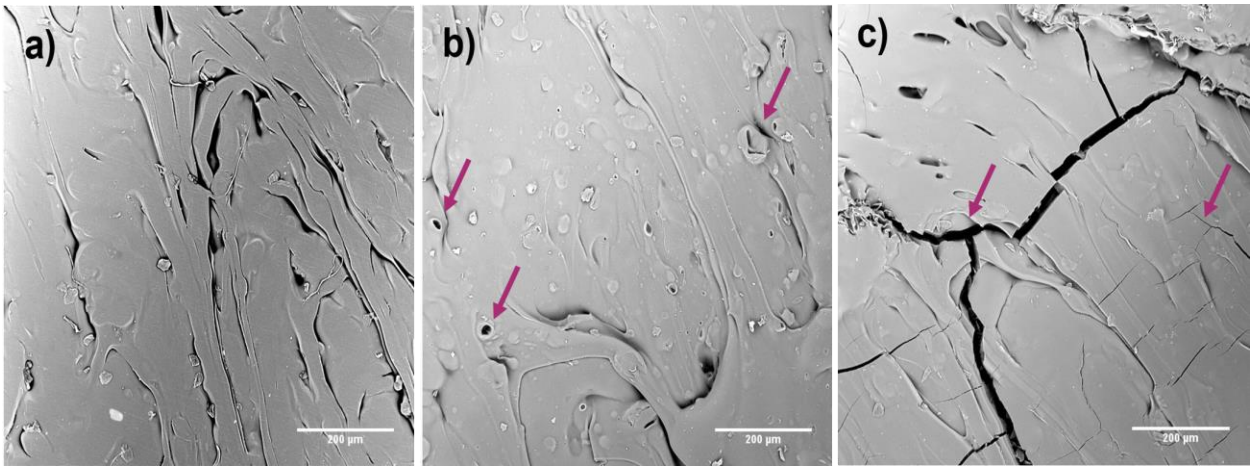


Figure 18 – SEM analysis of PLA MF5 surfaces: a) no test; b) water at 50 ºC; c) alcohol at 50 ºC (310x).

Furthermore, one capsule of HDPE MF5 after being immersed in water at 50 ºC was also analysed and compared with another one not submitted to any test. The results are presented in the following Figure 19. Again, apart from visualizing the injection profile of the polymer and suggesting the existence of free spaces, no changes where verified when compared the two different samples.

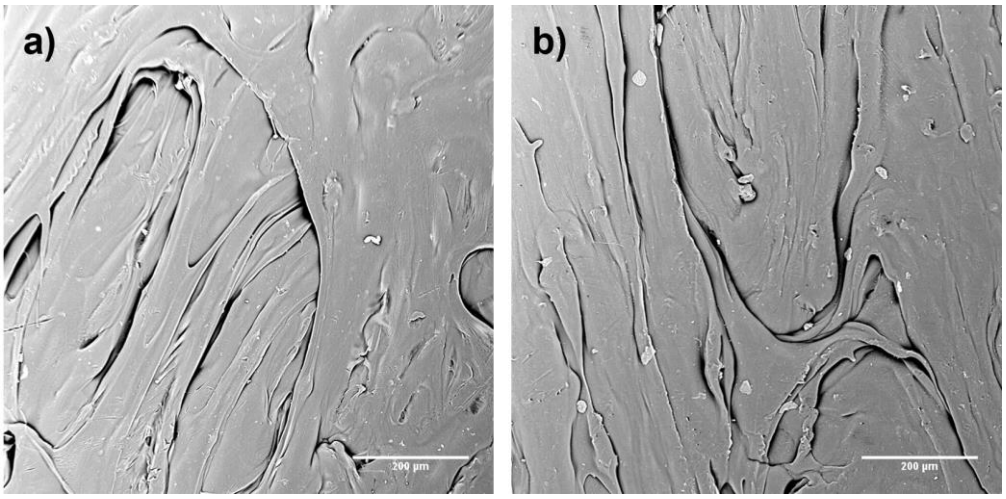


Figure 19 – SEM analysis of HDPE MF5 surfaces: a) no test; b) water at 50 °C (320x).

Since the tests were not conducted at the same time and, after the obtained SEM analysis, it was decided to study the behaviour of PLA and its composites at 50 °C with a continuous immersion for 15 days in water and alcohol 50 % V/V, with a pre and post-drying at 100 °C for 2 h. These tests were performed in order to calculate the absorption levels of the materials and to investigate the occurrence of degradation. Although mass losses were expected, due to the conclusions taken from the SEM analysis, the mass variation was kept positive, as it is presented in Table 14. A second dry was also done after some days at 50 °C for 24 h, to verify if the absorption levels would decrease.

Table 14 – Absorption values for the dried capsules after 15 days of immersion at 50 °C: (1) absorption right after immersion; (2) absorption after drying at 100 °C for 2 h; (3) absorption after drying at 50 °C for 24 h

	Water			Alcohol 50 % V/V		
Material	X_{H2O} **(1) / %**	X_{H2O} **(2) / %**	X_{H2O} **(3) / %**	X_{EtOH} **(1) / %**	X_{EtOH} **(2) / %**	X_{EtOH} **(3) / %**
PLA MF5	2.87 ± 0.04	0.74 ± 0.02	0.34 ± 0.01	3.10 ± 0.06	0.47 ± 0.06	0.44 ± 0.05
PLA MF8	2.32 ± 0.06	0.63 ± 0.03	0.29 ± 0.02	2.87 ± 0.07	0.49 ± 0.03	0.47 ± 0.02
PLA	0.93 ± 0.05	0.29 ± 0.05	0.19 ± 0.05	1.64 ± 0.05	0.37 ± 0.05	0.35 ± 0.05

After analysing the previous table, it is possible to see that this type, pre-drying affected the absorption levels. This time, X_{EtOH} 1 is greater than X_{H2O} 1, which did not happen for the same conditions without pre-drying (see Figure 15). Furthermore, after the first drying, absorption levels were kept higher both for the water and alcohol cases. After the second drying, X_{H2O} halved suggesting that PLA was returning to its equilibrium state of moisture absorption. However, X_{EtOH} values were maintained, suggesting that strong permanent bonds were created between the material and the solvent, probably due to the fractures observed in the morphological analysis.

4.4 Weathering responses

The weathering tests consisted on required tests from the company to evaluate the response of the developed materials under extreme conditions of temperature and humidity, simulating different possible climatic case scenarios. A composting test in *LIPOR* industrial composting facility was also undertaken and the results briefly interpreted.

4.4.1 Thermal resistance

This test was conducted to 10 capsulated samples of each material in order to study the adhesion efficiency of the EVA hotmelt adhesives in the surface of the developed materials. After the thermal cycle, which was described in section 3.3.4 (page 22), a glueing test was conducted with the auxiliary of a tensile ruler. The results observed for the PLA MF5 and HIPS capsules are presented below in Figure 20.

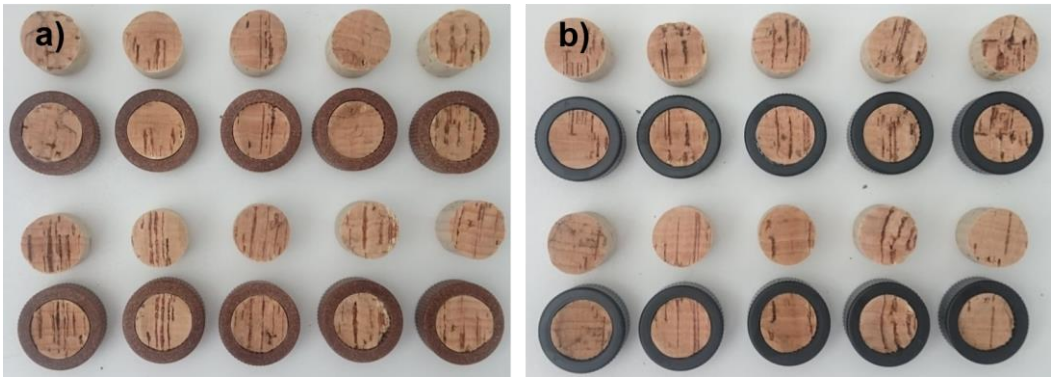


Figure 20 – Gluing test results after the thermal cycle: a) PLA MF5; b) HIPS.

It is possible to verify that both materials exhibit the pretended result, which is a substrate-cohesion break. The same result was obtained for the other materials.

4.4.2 Climatic ageing

The climatic ageing test was conducted using a climatic chamber with the objective to study extreme case conditions that the final product might undergo during shipment. For the purpose, 5 capsules of each material were weighted, their dimensions were taken ($Ø_e$, $Ø_i$ and H) and, finally, put on a CC at the pretended studying conditions: 95 ± 5 % RH and 60 ± 2 ^oC for 20 h. In the end, the samples were immediately weighted again, in order to analyse if there was any kind of absorption. The final dimensions were taken and compared to the initial ones. Apart from moisture uptake and dimensional stability, the visual and texture changes were also analysed.

Table 15 – Mass variations verified immediately after climatic ageing

	PLA MF5	PLA MF8	HDPE MF5	HDPE MF8	HIPS	PP-WF
Mass variation / %	0.69 ± 0.01	0.68 ± 0.01	0.11 ± 0.00	0.12 ± 0.00	0.05 ± 0.00	0.57 ± 0.01

The resulting increase in mass follows the same trend as the absorption results obtained in water and alcohol ageing tests, although considerably lower values for the HDPE and HIPS cases were verified. This might be explained considering that this time, no water excess was needed to be removed from the surface of the capsules, decreasing the fluctuations of the values and measurement errors. The value reached for HIPS is in compliance with the one stated by the manufacturer, where a moisture absorption at equilibrium (23 ºC and 50 % RH) of < 0.1 % is granted. Thus, with higher humidity and temperature, this value remains lower, indicating that HIPS is a very stable material. The same can be concluded for HDPE.

Moving on to the dimensional analysis, the variations obtained for $Ø_e$ and H of each material after the climatic ageing were not significant, which can be seen in Table D. 4 (Appendix D). As mentioned for the ageing tests in alcohol and water, the values of the internal diameter were not calculated due to the non-uniform inside wall surface of the capsules.

Regarding visual and textural changes, they were only verified for the PLA materials, were a loss in coverage and shine was verified, resulting in slightly harsh and lighter surfaces, respectively. These visual changes can be seen below in Figure 21 for the PLA materials and also HDPE MF5 for comparison.

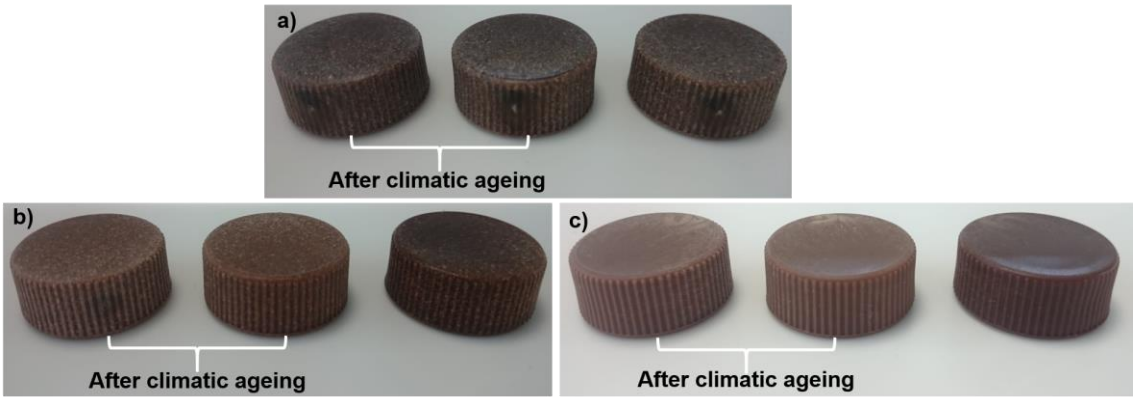


Figure 21 – Visual changes verified after climatic ageing: a) HDPE MF5; b) PLA MF5; c) PLA MF8.

As presented in section 4.1 (page 28), a compression test was also done to the capsules submitted to this test. The results suggested that, for PLA materials, a rearrangement followed by a polymer-cork interaction might have occurred, improving the material's mechanical properties, mainly its compressive strength at 25 % compression. The rest of the materials did not experience any significant modifications.

4.4.3 Composting

The composting test made in an industrial facility was conducted to evaluate the biodegradability of the PLA materials. One specimen of pure PLA, PLA MF5 and PLA MF8 were previously weighted and its length, width and height measured. A capsule of a PLA MF8 material was also

considered for this analysis to see if the size and conformation of the material would interfere on the degradation level. A visual analysis after 28 days was made in order to verify any possible changes. The samples were only sent back to *ATS* after the end of the whole process. In Figure 22 below, it is possible to verify the observed modifications. A change in colour is noticed, and the materials are also deformed and broken, thus final measurements were not possible to be done. The materials exhibited a fragile behaviour, breaking easily with low applied forces, suggesting that degradation from hydrolysis might have occurred, due to the verified maximum average temperature of 65 ºC and high characteristic moisture levels of the process – Figure D. 7 (Appendix D). Moreover, although it was expected a mass decrease of the samples, this was not verified, as presented below in Table 16.

Table 16 – Mass variation of the materials after industrial composting for 28 days

Material	Mass variation / %
PLA	0.10
PLA MF8[a]	0.85
PLA MF5	1.12
PLA MF8[b]	0.87

[a]PLA MF8 specimen (2); [b]PLA MF8 casule (4).

As it can be concluded, the mass variation was positive, and the type of sample did not have interference on the variation values.

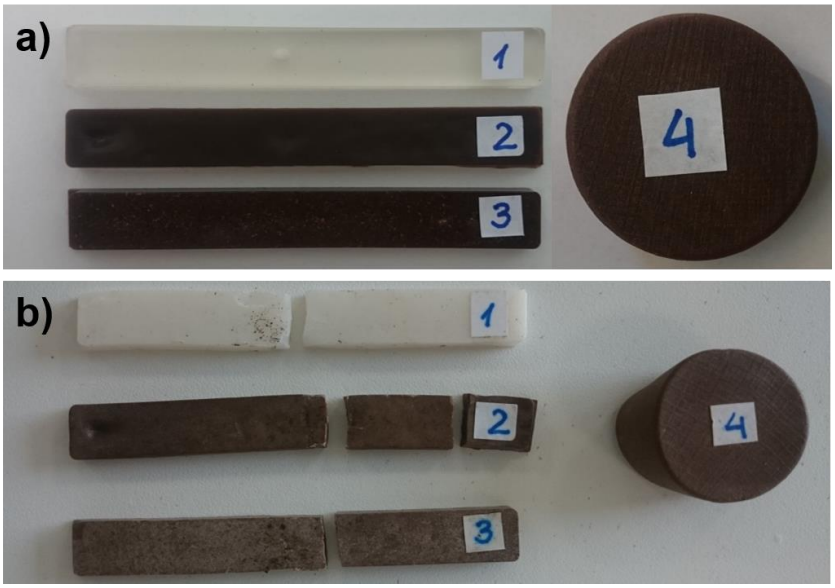


Figure 22 – Visual changes verified for each material after composting: a) before composting; b) after composting; 1-PLA; 2-PLA MF8; 3-PLA MF5; 4-PLA MF8.

Although these results may be verified, composting conditions can vary from country to country as well as from composting facility conditions. In *LIPOR* facility, PLA needs to return to the tunnel for more composting cycles. For this reason, *LIPOR* does not accept such kind of materials,

because it is difficult to sort them at the end of the process, hence, being considered as contaminants in the final compost, lowering its quality level.

4.5 Cost analysis of the final products

The total cost of the developed products based on the production and raw materials' cost was estimated. The production costs involve the number of cavities of the used mould (12), the t_{cycle} for each material and the hourly working cost of the injection moulding machine and the respective labour work, which was considered as 16.50 €/hr. The cost of the raw materials considered was the one presented in Table 1 (page 13), for the highest possible amount. In the case of HIPS, it has a masterbatch content of 2 wt. %, with a cost of 2.20 €/kg. The results are presented below in Table 17 to produce a thousand (ML) capsules of each material.

Table 17 – Total cost of the final products considering a thousand-unit basis (ML)

Material	Material cost / €·kg^{-1}	Average unit mass[a] / g	t_{cycle} / s	Material cost / €·ML^{-1}	Operational costs / €·ML^{-1}	Total cost / €·ML^{-1}
PLA MF5	4.50	5.28	29	23.76	11.08	34.84
PLA MF8	4.77	5.27	29	25.14	11.08	36.21
HDPE MF5	3.93	3.65	33	14.34	12.60	26.95
HDPE MF8	3.99	3.66	37	14.60	14.13	28.74
HIPS	1.60	4.33	24	6.98	9.17	16.15
PP-WF	1.97	4.26	37[b]	8.39	14.13	22.52

[a]based on 15 measured capsules;

[b]the highest value verified was considered because the author did not follow the production of this material.

From the results, it is possible to conclude that HIPS has the lowest material and operational costs, also resulting in the lowest cost, followed by the HDPE materials and, finally, the PLAs. Although these cost differences, PLA materials are valuable alternatives in the environmental point of view but need to have lower prices than the companies' wooden range, which is 100 % natural and biodegradable without needing to call for industrial composting.

4.6 End-of-life solutions

Considering the two different raw materials, PLA and HDPE, and the CPCs produced from them, there are a variety of possible end-of-life alternatives to choose from.

Biobased HDPE can be recycled along with the conventional HDPE, offering the possibility to be reprocessed and applied in new products without losing its properties. PLA, known for its ability

to biodegrade on specific conditions can be sent to industrial composting facilities but, as seen before, accelerated conditions or many repetitions of the composting cycle are required for faster results and, in the end, the result is a compost, which can no longer be used to produce new materials. Given this, aside from composting, many authors suggest chemical recycle as the best end-of-life treatment for PLA and support that any waste management system considering in receiving such material should implement it [43]. Any type of manufacturing waste or post-consumer PLA materials can be chemically recycled by a process called hydrolysis, where much higher temperatures than composting facilities are present, and the reactions are enhanced by a catalyst. The results are fully functional PLA monomers (lactic acid), without compromising their properties and ready to be fed again in new processing streams. Besides this, chemical recycle has low economic costs and impacts on the environment, contributing to PLA's sustainable production [43].

Considering the composite materials, at the moment, material recovery and composting facilities consider cork as a contaminant for their waste management streams so, the only way to recover and reintroduce these products on new process lines is by creating internal collecting and processing systems.

5 Conclusion

In this dissertation, it was proposed to develop more sustainable bartops for the spirit drinks market by an injection moulding process. PLA and biobased HDPE were blended with cork loads with content from 5 up to 15 wt. % and then studied under different conditions.

Physical and mechanical tests were conducted in order to simulate transport and handling conditions which the final product might undergo. Moreover, the injection process of each material was also evaluated and compared to the current parameters applied in the production of PS capsules. For the physical and mechanical tests, the PLA materials exhibited higher stiffness, hardness and abrasion resistance than HIPS and HDPE composites. After the production process, dimensional analysis was performed, and all materials were approved, but a new mould or adaptions to the existent ones need to be made for the HDPE composites, which exhibited a high shrinkage rate. Moreover, the MFR of each material was determined, revealing that cork loads increase the viscosity of the materials when compared to the neat polymers but, on the other hand, cork acts as a blowing agent, avoiding the formation of surface deformations.

From the alcohol resistance tests, it was possible to conclude that all materials remained the same. However, once exposed to more extreme conditions, the results were different. The PLA composites exhibited modifications once immersed in water and alcohol solutions, both at room temperature and 50 ^{o}C for 22 days. The most remarkable changes were verified for both water and alcohol exposures at 50 ^{o}C, where the materials' coverage was lost entirely, and the colour changed drastically. The other materials did not experience any sort of changes. Furthermore, high water and alcohol uptakes were obtained for the PLA materials, and again significantly higher for a temperature of 50 ^{o}C. The absorption levels of the rest of the materials remained low, as expected. This group of tests allowed to conclude that PLA and its composites have poor chemical stability in relation to the other materials studied. Similar behaviours were registered on the weathering tests. PLA materials were also sent to a composting facility but, composting time and conditions were not sufficient to verify strong signs of degradation, apart from colour and brittleness of the samples.

Finally, an economic analysis was made for thousand-unit production basis, where the production time and the acquisition cost of the raw materials were taken into consideration. None of the developed materials revealed to be cheaper than HIPS. Regarding the four developed CPCs, HDPE materials had lower production costs, although exhibiting higher production times. Summarizing, the best alternative to replace PS is one of the HDPE materials, depending on the purpose and aesthetical preferences. However, an optimization of the production parameters or a redesign of the mould should be made, in order to avoid high shrinkage levels and comply with the established tolerances.

6 Assessment of the Work Done

6.1 Objectives Achieved

The objective of this dissertation was to develop new sustainable alternatives to replace PS. For the effect, four different CPCs were developed. The developed HDPE composites reveal to be the best option to choose from. However, it is necessary to rethink the injection moulding parameters or redesign the current used PS moulds.

6.2 Other Work Carried Out

At the end of the project, some pigments were also added to the produced HDPE CPCs for aesthetical analyses. Apart from the developed solutions, a PP-cork blend was initially considered. PP has similar properties as PE and can also be a better alternative to PS. However, it is not currently being produced from renewable sources at industrial scale, so this option had to be postponed. In the future, if interest for PP persists, anticipating its optimization in the production systems by using conventional PP, will allow *ATS* to be one step ahead of the other companies by the time biobased PP hits the market.

6.3 Limitations and Future Work

In the future, the developed PLA composites could be sent to international composting facilities, which exhibit different composting conditions, in order to evaluate its degradation.

Considering the recycling process of the CPCs, an internal recycling system should be created, because cork, although an inert, is considered as a contaminant either on mechanical recycling and composting facilities. Specific collection systems may be created from the Amorim Group or *ATS* at least, to recover the end-of-life bartops and reprocess them. In this way, *ATS* is creating its own circular economy, recovering the original materials and transforming them into new products.

6.4 Final Assessment

The work developed during this dissertation was interesting and allowed me to extend my knowledge in different areas, which I did not have the opportunity to learn in college.

Furthermore, it was an enriching experience, introducing me to the professional world and its environments. There I understood the importance of learning how to deal with different people every day and try to adapt to any circumstances readily.

7 References

[1] E. Bioplastics, “Circular Economy – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/policy/circular-economy/. [Accessed: 01-Apr-2019].

[2] Amorim, “Presentation, Amorim Group, Who are we - Corticeira Amorim, Cork Sector World Leader.” [Online]. Available: https://www.amorim.com/en/who-are-we/amorim-group/presentation/. [Accessed: 26-Apr-2019].

[3] Amorim, “Corticeira Amorim, Cork Sector World Leader.” [Online]. Available: https://www.amorim.com/en/. [Accessed: 26-Apr-2019].

[4] Amorim, “Top Series Amorim | Top Series.” [Online]. Available: https://www.amorimtopseries.com/. [Accessed: 30-Apr-2019].

[5] E. Bioplastics, “Bioplastics – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/. [Accessed: 01-Apr-2019].

[6] E. Bioplastics, “Materials – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/materials/. [Accessed: 15-Feb-2019].

[7] TÜV AUSTRIA, “OK biobased.” [Online]. Available: http://www.tuv-at.be/certifications/ok-biobased/. [Accessed: 06-May-2019].

[8] TÜV AUSTRIA, “TUV Austria OK Biobased Certification, ASTM D6866.” [Online]. Available: https://www.betalabservices.com/biobased/ok-biobased.html. [Accessed: 06-May-2019].

[9] E. Bioplastics, “What are bioplastics?” [Online]. Available: https://www.european-bioplastics.org/bioplastics/. [Accessed: 18-Apr-2019].

[10] NaturePlast, “End-of-life of bioplastics - NaturePlast.” [Online]. Available: http://natureplast.eu/en/the-bioplastics-market/end-of-life-of-bioplastics/. [Accessed: 23-Apr-2019].

[11] E. Bioplastics, “EN 13432 CERTIFIED BIOPLASTICS PERFORMANCE IN INDUSTRIAL COMPOSTING,” 2015.

[12] E. Bioplastics, “What are the required circumstances for a compostable product to compost? – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/faq-items/what-are-the-required-circumstances-for-a-compostable-product-to-compost/. [Accessed: 18-Feb-2019].

[13] TÜV AUSTRIA, “OK compost & Seedling.” [Online]. Available: http://www.tuv-at.be/certifications/ok-compost-seedling/. [Accessed: 06-May-2019].

[14] E. Bioplastics, “Labels – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/standards/labels/. [Accessed: 06-May-2019].

[15] NaturePlast, “History of bioplastics.” [Online]. Available: http://natureplast.eu/en/the-bioplastics-market/history-of-bioplastics/. [Accessed: 04-Apr-2019].

[16] A. Barrett, “The History and Most Important Innovations of Bioplastics – Bioplastics News.” [Online]. Available: https://bioplasticsnews.com/2018/07/05/history-of-bioplastics/. [Accessed: 04-Apr-2019].

[17] WRAP, “A Roadmap to 2025 - The UK Plastics Pact | WRAP UK,” *Wrap*, p. 11, 2018.

[18] PCA, “Towards Sustainable Packaging,” 2007. [Online]. Available: https://www.cisl.cam.ac.uk/resources/circular-economy/towards-sustainable-packaging-a-plan-to-eliminate-plastic-packaging-waste-from-uk-bottled-water-and-soft-drinks. [Accessed: 02-Mar-2019].

[19] APA, “Estratégia Europeia sobre Plásticos.” [Online]. Available: https://www.apambiente.pt/?ref=x254. [Accessed: 08-Apr-2019].

[20] European Comission, “Plastic waste - Environment - European Commission.” [Online]. Available: http://ec.europa.eu/environment/waste/plastic_waste.htm. [Accessed: 08-Apr-2019].

[21] E. Bioplastics, “Waste Management – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/waste-management/. [Accessed: 08-Apr-2019].

[22] NaturePlast, “Types of bioplastics: biobased and/or biodegradable - NaturePlast.” [Online]. Available: http://natureplast.eu/en/the-bioplastics-market/types-of-bioplastics-biobased-and-or-biodegradable/. [Accessed: 16-Apr-2019].

[23] E. Bioplastics, “New market data: The positive trend for the bioplastics industry remains stable – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/new-market-data-the-positive-trend-for-the-bioplastics-industry-remains-stable/. [Accessed: 24-Apr-2019].

[24] Fabri-Kal, “Greenware Cups.” [Online]. Available: http://www.fabri-kal.com/products/Greenware-Cups. [Accessed: 23-Apr-2019].

[25] FoodIngredientsFirst, “Greenware Cold-Drink Cups, Lids and Portion Cups Awarded USDA Certified Biobased Product Label.” [Online]. Available: https://www.foodingredientsfirst.com/news/greenware-cold-drink-cups-lids-and-portion-cups-awarded-usda-certified-biobased-product-label.html. [Accessed: 24-Apr-2019].

[26] BioMass Packaging, “Biodegradable Cups & Lids | BioMass Packaging.” [Online]. Available: http://www.biomasspackaging.com/portfolio_category/cups-lids/. [Accessed: 23-Apr-2019].

[27] Tetra Pak, “Tetra Top - a better bottle for JUST Water.” [Online]. Available: https://www.tetrapak.com/sustainability/cases-and-articles/just-water. [Accessed: 23-Apr-2019].

[28] Tetra Pak, “First Tetra Top carton bottle with bio-based plastic hits the market with JUST® water.” [Online]. Available: https://www.tetrapak.com/about/newsarchive/first-tetra-top-carton-bottle-with-bio-based-plastic. [Accessed: 23-Apr-2019].

[29] Packaging Europe, “Bottle Caps Made from Sugarcane - Packaging Europe.” [Online]. Available: https://packagingeurope.com/united-caps-adds-bottle-caps-made-from-sugarcane-portfolio/. [Accessed: 23-Apr-2019].

[30] Bioplastics NEWS, “The Future Bottle Caps will be made from Bioplastics.” [Online]. Available: https://bioplasticsnews.com/2018/08/29/bioplastics-bottle-caps-closures/. [Accessed: 23-Apr-2019].

[31] E. M. Fernandes, V. M. Correlo, J. F. Mano, and R. L. Reis, “Cork–polymer biocomposites: Mechanical, structural and thermal properties,” *Materials & Design*, vol. 82, pp. 282–289, 2015.

[32] Bioplastics NEWS, “The Future of Polystyrene.” [Online]. Available: https://bioplasticsnews.com/2018/08/08/future-of-polystyrene/. [Accessed: 24-Apr-2019].

[33] E. Bioplastics, “Biodegradable – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/materials/biodegradable/. [Accessed: 24-Apr-2019].

[34] E. Bioplastics, “Biobased – European Bioplastics e.V.” [Online]. Available: https://www.european-bioplastics.org/bioplastics/materials/biobased/. [Accessed: 24-Apr-2019].

[35] PlasticsEurope, “Thermoplastics :: PlasticsEurope.” [Online]. Available:

https://www.plasticseurope.org/en/about-plastics/what-are-plastics/large-family/thermoplastics. [Accessed: 10-May-2019].

[36] NatureWorks, “How Ingeo is Made.” [Online]. Available: https://www.natureworksllc.com/What-is-Ingeo/How-Ingeo-is-Made. [Accessed: 14-Apr-2019].

[37] E. Castro-Aguirre, F. Iñiguez-Franco, H. Samsudin, X. Fang, and R. Auras, “Poly(lactic acid)—Mass production, processing, industrial applications, and end of life,” *Advanced Drug Delivery Reviews*, vol. 107. pp. 333–366, 2016.

[38] M. A. Elsawy, K. H. Kim, J. W. Park, and A. Deep, “Hydrolytic degradation of polylactic acid (PLA) and its composites,” *Renewable and Sustainable Energy Reviews*, vol. 79, pp. 1346–1352, 2017.

[39] V. Rossi, N. Cleeve-Edwards, L. Lundquist, U. Schenker, C. Dubois, S. Humbert, and O. Jolliet, “Life cycle assessment of end-of-life options for two biodegradable packaging materials: Sound application of the European waste hierarchy,” *Journal of Cleaner Production*, vol. 86, pp. 132–145, 2015.

[40] T. Leejarkpai, T. Mungcharoen, and U. Suwanmanee, “Comparative assessment of global warming impact and eco-efficiency of PS (polystyrene), PET (polyethylene terephthalate) and PLA (polylactic acid) boxes,” *Journal of Cleaner Production*, vol. 125, pp. 95–107, 2016.

[41] A. Soroudi and I. Jakubowicz, “Recycling of bioplastics, their blends and biocomposites: A review,” *European Polymer Journal*, vol. 49, no. 10, pp. 2839–2858, 2013.

[42] M. Arrieta, M. Samper, J. López-Martínez, D. Bertomeu, and J. Ferri, “Interference of Biodegradable Plastics in the Polypropylene Recycling Process,” *Materials*, vol. 11, no. 10, p. 1886, 2018.

[43] D. W. Farrington, J. Lunt, and S. Davies, “Poly(lactic acid) fibers,” in *Biodegradable and Sustainable Fibres*, R. S. Blackburn (Ed.), Cambridge: Woodhead Publishing, 2005, pp. 191–220.

[44] Plastics Recyclers Europe, “Chemical Recycling.” [Online]. Available: https://www.plasticsrecyclers.eu/chemical-recycling. [Accessed: 14-Jun-2019].

[45] B. S. Ndazi and S. Karlsson, “Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures,” *Express Polymer Letters*, vol. 5, no. 2, pp. 119–131, 2011.

[46] FNR, “PLA in the waste stream,” 2017. [Online]. Available: https://www.umsicht.fraunhofer.de/content/dam/umsicht/en/documents/press-releases/2017/pla-in-the-waste-stream.pdf. [Accessed: 21-Mar-2019].

[47] British Plastic Federation, “Polymer Thermoplastics.” [Online]. Available: https://www.bpf.co.uk/plastipedia/polymers/polymer-thermoplastics.aspx#polyethylenehd. [Accessed: 13-May-2019].

[48] A. J. Peacock, *Handbook of polyethylene : structures, properties, and applications*. New York: Marcel Dekker, 2000.

[49] Braskem, “Etanol - Braskem.” [Online]. Available: http://plasticoverde.braskem.com.br/site.aspx/Etanol-pe. [Accessed: 11-May-2019].

[50] Braskem, “How it is produced - Braskem.” [Online]. Available: http://plasticoverde.braskem.com.br/site.aspx/How-it-is-produced. [Accessed: 20-May-2019].

[51] CompositesLab, “What Are Composites? - Composites 101 | CompositesLab.” [Online]. Available: http://compositeslab.com/composites-101/what-are-composites/. [Accessed: 14-Apr-2019].

[52] Amorim, “Características, A Cortiça - Corticeira Amorim, Líder Mundial Setor Cortiça.” [Online]. Available: https://www.amorim.com/a-cortica/caracteristicas/. [Accessed: 02-Mar-2019].

[53] S. P. Silva, M. A. Sabino, E. M. Fernandes, V. M. Correlo, L. F. Boesel, and R. L. Reis, “Cork: properties, capabilities and applications,” *International Materials Reviews*, vol. 53, no. 4, pp. 256–256, 2008.

[54] E. M. Fernandes, V. M. Correlo, J. A. M. Chagas, J. F. Mano, and R. L. Reis, “Properties of new cork–polymer composites: Advantages and drawbacks as compared with commercially available fibreboard materials,” *Composite Structures*, vol. 93, no. 12, pp. 3120–3129, 2011.

[55] Prototech, “The 5 keys stages of plastic injection or injection molding.” [Online]. Available: https://prototechasia.com/en/injection-molding/stages-injection-molding. [Accessed: 21-May-2019].

[56] S. Tamari and A. Aguilar-Chávez, “Optimum Design of Gas Pycnometers for Determining the Volume of Solid Particles,” *Journal of Testing and Evaluation*, vol. 33, no. 2, p. 12674, 2005.

[57] Buehler, “Non-Destructive Hardness Testing.” [Online]. Available: https://www.buehler.com/nondestructive-testing.php. [Accessed: 22-May-2019].

[58] DIAGEO, “Sutherlan Rub Test – Specification Management Decorated Stopper Heads and Closures,” 2000.

[59] AbsorboPAk, “Moisture in Shipping Containers - Absorbopak Moisture and Condensation Damage.” [Online]. Available: https://www.absorbopak.co.uk/moisture-in-shipping-containers/. [Accessed: 19-Apr-2019].

[60] Omnexus, “Shrinkage Value of Plastics Material & Injection Molding - Chart.” [Online]. Available: https://omnexus.specialchem.com/polymer-properties/properties/shrinkage. [Accessed: 27-Jun-2019].

[61] INSTRON, “Offset Yield Strength - Instron.” [Online]. Available: https://www.instron.com.br/pt-br/our-company/library/glossary/o/offset-yield-strength. [Accessed: 11-Jun-2019].

[62] Quality Magazine, “Tensile Testing Principles: Fundamentals, Methods and Challenges | 2018-08-01.” [Online]. Available: https://www.qualitymag.com/articles/94867-tensile-testing-principles-fundamentals-methods-and-challenges. [Accessed: 11-Jun-2019].

[63] Y. Jin, W. Wang, and Z. Su, “Spectroscopic study on water diffusion in poly(lactic acid) film,” *Polymer Chemistry*, vol. 3, no. 9, p. 2430, 2012.

[64] I. Kriston, E. Földes, P. Staniek, and B. Pukánszky, “Dominating reactions in the degradation of HDPE during long term ageing in water,” *Polymer Degradation and Stability*, vol. 93, no. 9, pp. 1715–1722, 2008.

[65] International Organization for Standardization, “ISO 1133-1:2011 - Plastics -- Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics -- Part 1: Standard method,” *Geneva*, vol. 2011, p. 24, 2011.

[66] ASTM D1238-10., “Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer,” *ASTM International*, vol. West Consh, no. PA, 2010.

Appendix A – *ATS* business unit

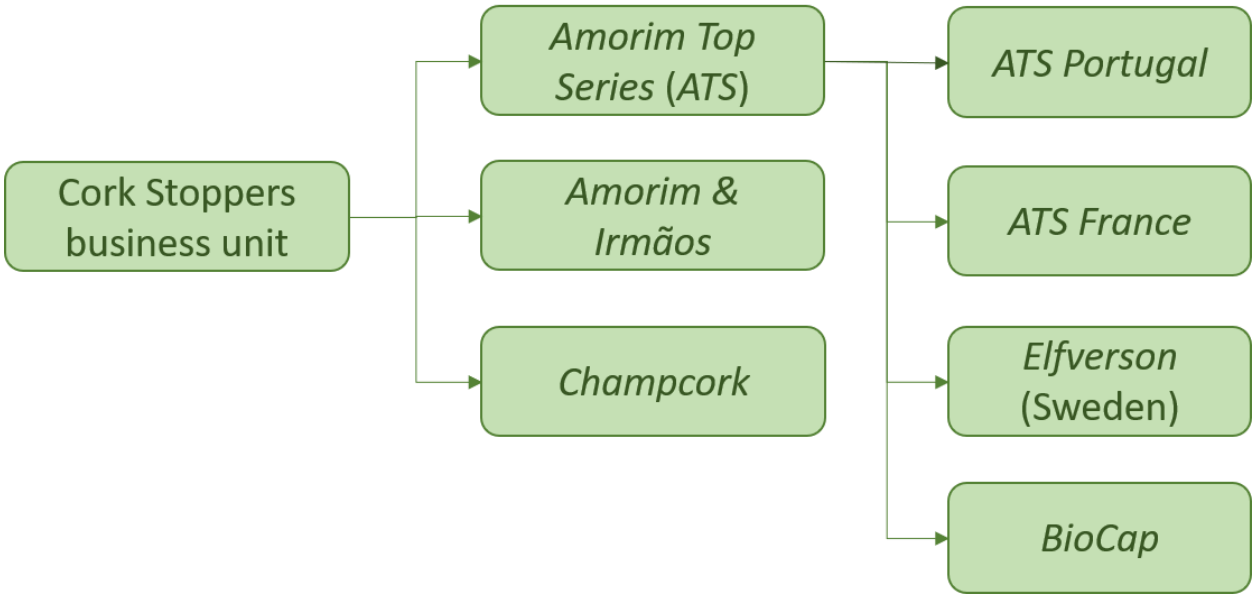


Figure A. 1 – Cork stoppers business unit chart.

Appendix B – Labels

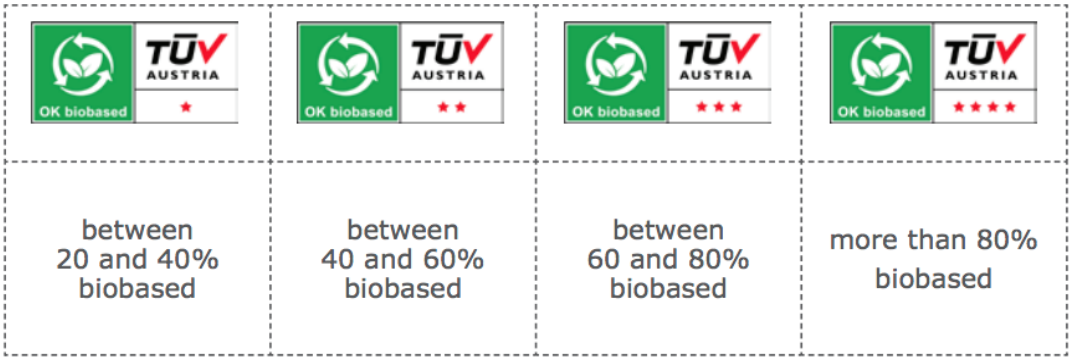


Figure B. 1 – OK Biobased labels [7].



Figure B. 2 – OK compost INDUSTRIAL and HOME labels [13].

Appendix C – Apparatus and Testing Information

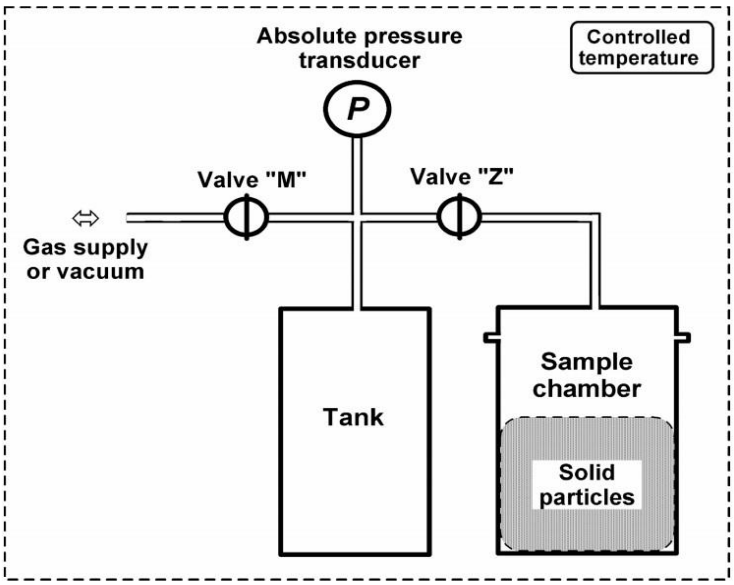


Figure C. 1 - Diagram of a constant-gas pycnometer system [56].

Note: In this project, the tank and the sample chamber were assembled in the reverse order, as seen in Figure C. 1, as the description of the method suggests.

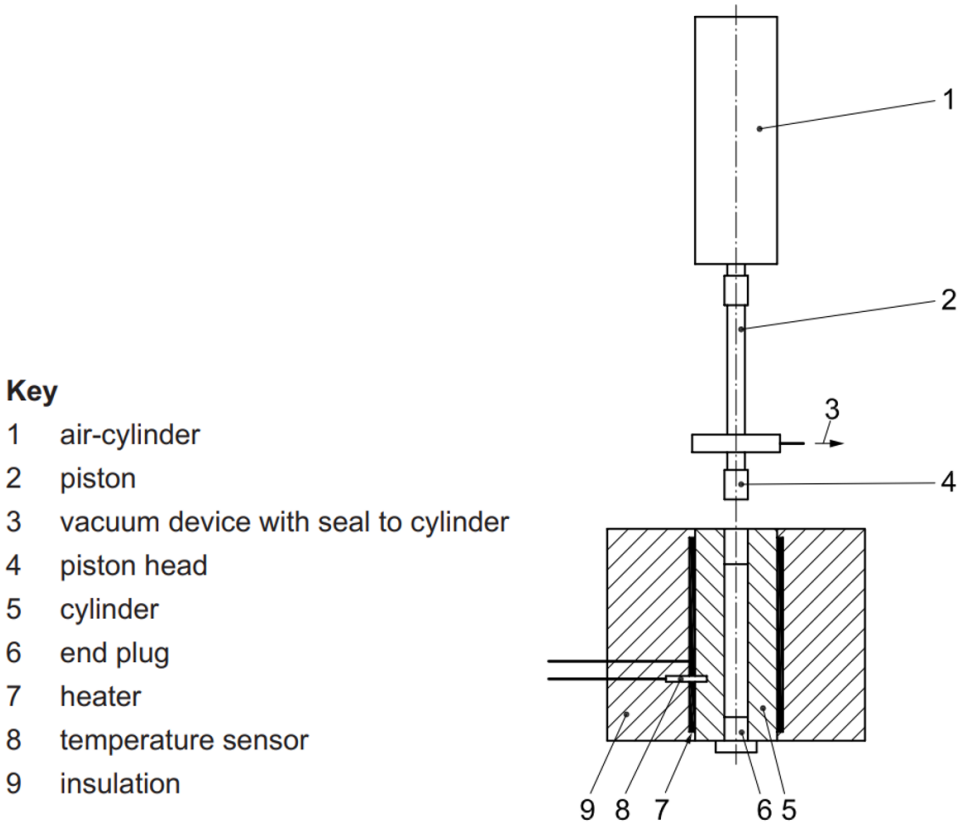


Figure C. 2 - Example apparatus for an MFR charge by compression [65].

Material	Condition	
Acetals (copolymer and homopolymer)	190/2.16	190/1.05
Acrylics	230/1.2	230/3.8
Acrylonitrile-butadiene-styrene	200/5.0	230/3.8
	220/10	
Acrylonitrile/butadiene/styrene/polycarbonate blends	230/3.8	250/1.2
	265/3.8	265/5.0
Cellulose esters	190/0.325	190/2.16
	190/21.60	210/2.16
Ethylene-chlorotrifluoroethylene copolymer	271.5/2.16	
Ethylene-tetrafluoroethylene copolymer	297/5.0	
Nylon	275/0.325	235/1.0
	235/2.16	235/5.0
	275/5.0	
Perfluoro(ethylene-propylene) copolymer	372/2.16	
Perfluoroalkoxyalkane	372/5.0	
Polycaprolactone	125/2.16	80/2.16
Polychlorotrifluorethylene	265/12.5	
Polyether sulfone (PES)	380/2.16	360/10
	343/2.16	
Polyethylene	125/0.325	125/2.16
	250/1.2	
	190/0.325	190/2.16
	190/21.60	190/10
	310/12.5	
Polycarbonate	300/1.2	
Polymonochlorotrifluoroethylene	265/21.6	
	265/31.6	
Polypropylene	230/2.16	
Polyphenyl sulfone (PPSU)	365/5.0	380/2.16
Polystyrene	200/5.0	230/1.2
	230/3.8	190/5.0

Figure C. 3 – Standard conditions of temperature and load for MFR tests [66].

Flow Range, g/10 min	Suggested Mass of Sample in Cylinder, g	Time Interval, min	Factor for Obtaining Flow Rate in g/10 min
0.15 to 1.0	2.5 to 3.0	6.00	1.67
>1.0 to 3.5	3.0 to 5.0	3.00	3.33
>3.5 to 10	4.0 to 8.0	1.00	10.00
>10 to 25	4.0 to 8.0	0.50	20.00
>25	4.0 to 8.0	0.25	40.00

Figure C. 4 – Standard conditions of mass, cut-off time and factor for MFR measurements [66].

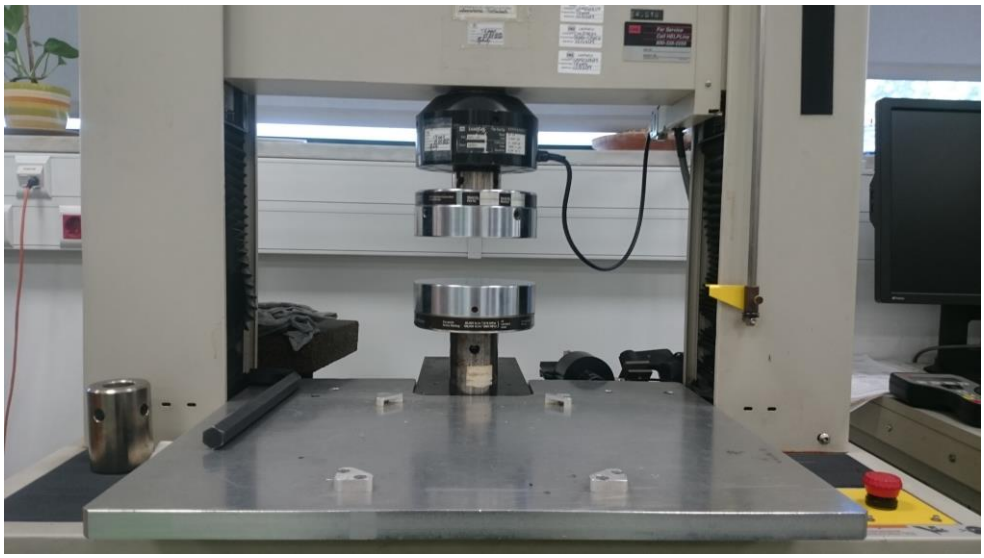


Figure C. 5 - Compression machine.



Figure C. 6 - Shore D durometer.



Figure C. 7 - System built for the abrasion resistance test.

Appendix D – Complementing Results

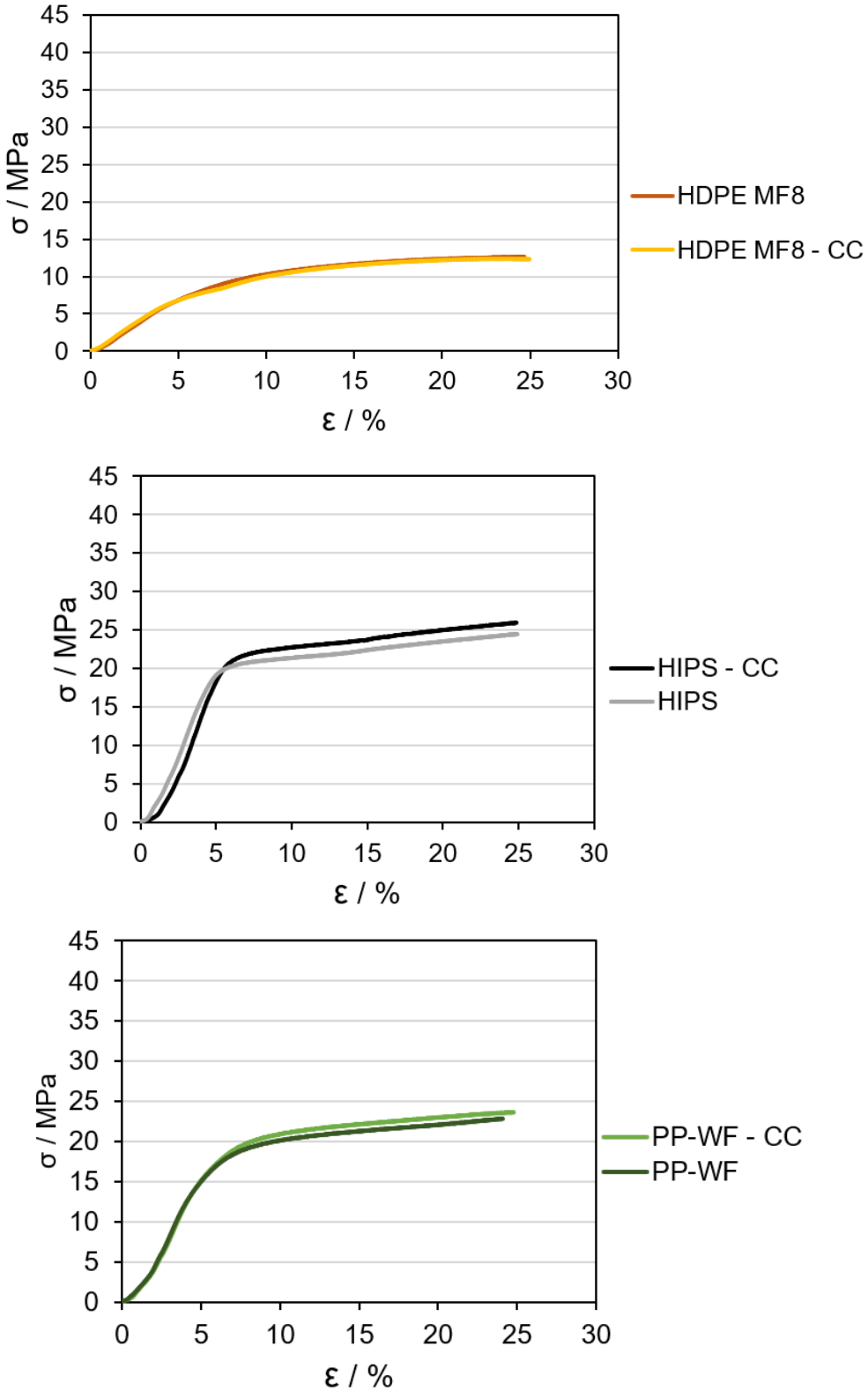


Figure D. 1 – Stress-strain curves of HDPE MF8, HIPS and PP-WF for the two studying conditions.

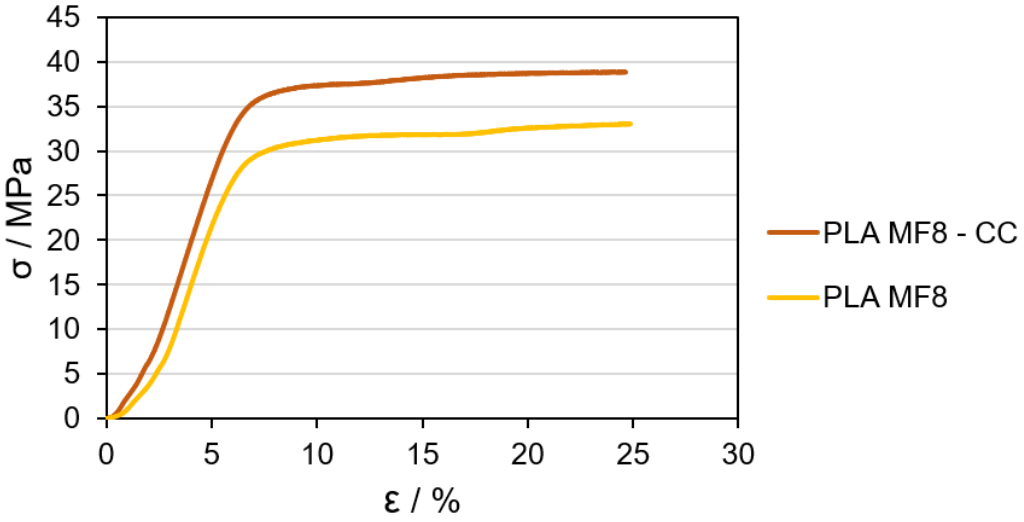


Figure D. 2 – Stress-strain curve of PLA MF8 for the two studying conditions.

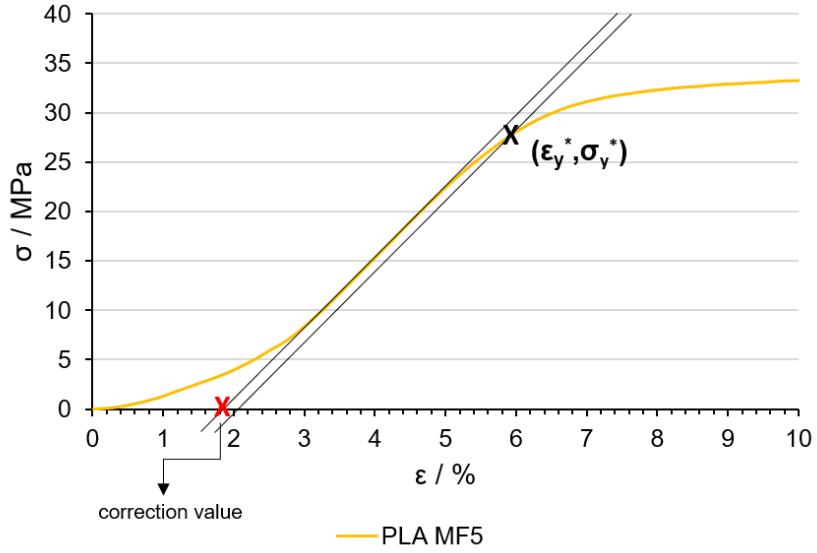


Figure D. 3 – Determination of the offset yield point and the correction value.

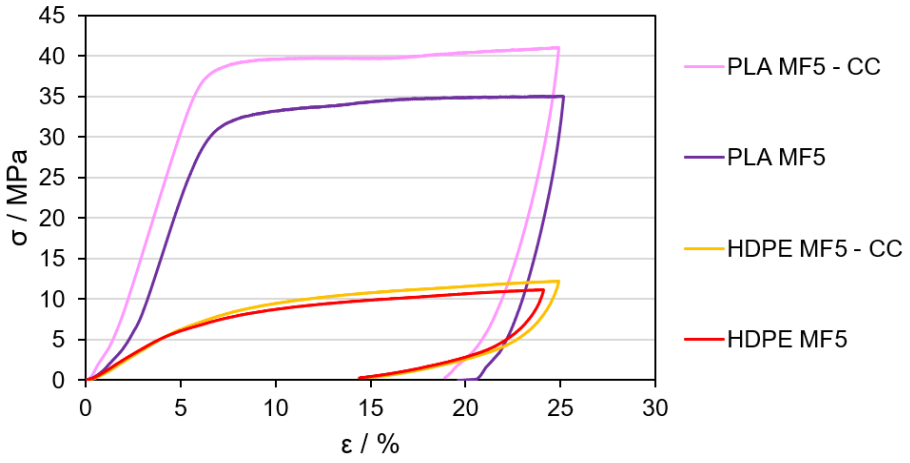


Figure D. 4 – Recovery curves for PLA and HDPE MF5.

Table D. 1 – Recovery values of each material for the two testing conditions

Material	Recovery 1 / %	Recovery 2 / %
PLA MF5	19.6 ± 0.7	26.2 ± 0.5
PLA MF8	18.8 ± 0.3	24.8 ± 0.4
HDPE MF5	48.1 ± 1.3	47.5 ± 0.5
HDPE MF8	47.0 ± 0.5	48.5 ± 1.1
HIPS	20.2 ± 0.5	22.5 ± 0.9
PP-WF	32.9 ± 1.0	30.7± 0.2

Where 1 is in respect to the capsules compressed without any previous test being applied and 2 the capsules compressed after climatic ageing.

Table D. 2 – External diameter and height variations verified in water ageing

	PLA MF5	PLA MF8	HDPE MF5	HDPE MF8	HIPS	PP-WF
$Ø_e$ variation / mm	0.10 ± 0.02	0.07 ± 0.04	0.02 ± 0.02	0.04 ± 0.02	0.03 ± 0.00	0.03 ± 0.03
***H* variation / mm**	0.04 ± 0.01	0.05 ± 0.01	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.04 ± 0.00

Table D. 3 – External diameter and height variations verified in alcohol ageing

	PLA MF5	PLA MF8	HDPE MF5	HDPE MF8	HIPS	PP-WF
$Ø_e$ variation / mm	0.05 ± 0.01	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.06 ± 0.02
***H* variation / mm**	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.00	0.03 ± 0.02	0.03 ± 0.02	0.07 ± 0.01

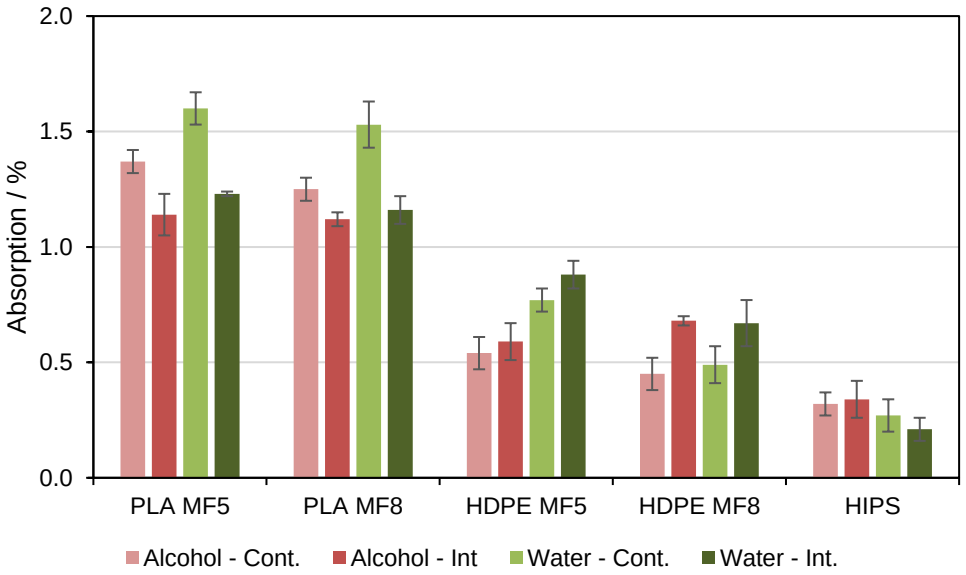


Figure D. 5 – Impact of continuous and interrupted immersions on absorption levels.

Where Cont. is referred to a continuous immersion and Int. to an interrupted immersion.

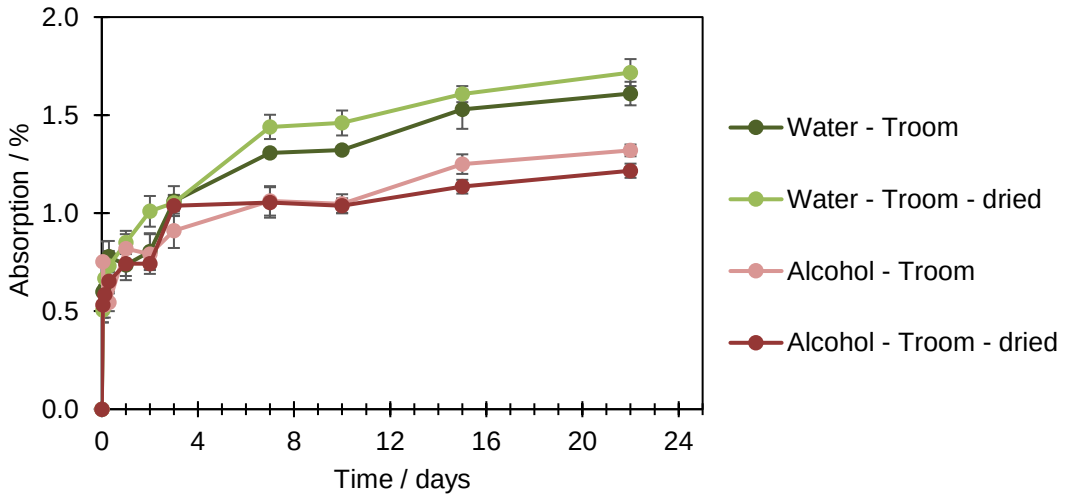


Figure D. 6 – Differences between pre and no pre-drying for PLA MF8.

Table D. 4 – External diameter and height variations verified after climatic ageing

	PLA MF5	PLA MF8	HDPE MF5	HDPE MF8	HIPS	PP-WF
$Ø_e$ variation / mm	0.05 ± 0.03	0.06 ± 0.03	0.03 ± 0.02	0.03 ± 0.02	0.01 ± 0.01	0.03 ± 0.03
***H* variation / mm**	0.05 ± 0.03	0.03 ± 0.01	0.04 ± 0.02	0.06 ± 0.02	0.01 ± 0.01	0.01 ± 0.01

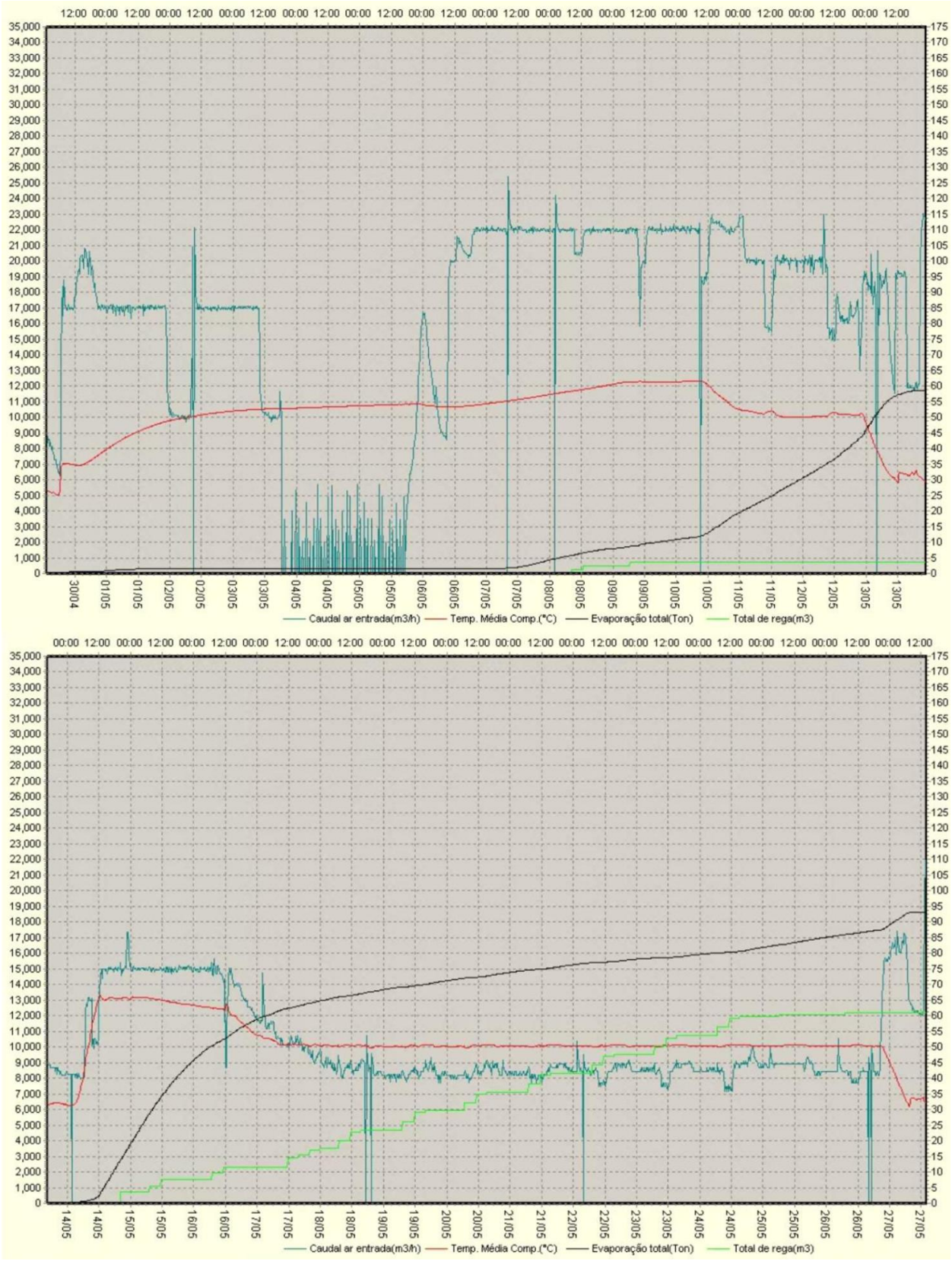


Figure D. 7 – Evolution of the composting variables during the 28 days.