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**BIOPLASTICS BIODEGRADABILITY THROUGH COMPOSTING
PROCESSES: IMPACT IN WASTE MANAGEMENT SYSTEMS**

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“As viagens são os viajantes.

O que vemos, não é o que vemos, senão o que somos”.

Fernando Pessoa

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ABSTRACT

The present dissertation aimed to study two types of biodegradable bioplastics available on the Portuguese market, one certified as compostable, made from 'Bioplast' (BA) and another presenting an indication of compostability, made from Mater-Bi® (BB). Both materials, in the form of strips (5x1 cm), were submitted to simulated industrial composting (sIC) and simulated home composting (sHC), at a laboratory scale, for 12 weeks. The same materials were submitted to industrial composting (IC, 3 weeks of active composting + 3 weeks of maturation), either in the form of strips (3 weeks, only active phase) or in their original appearance as bags (6 weeks). The disposal of these bags in the environment was also analysed, through their incubation in the soil for 12 weeks. A selective collection route for organic waste was also inspected. In all studies performed, a High-Density Polyethylene (HDPE) plastic material was used for comparison and cellulose filter paper as control. The strips and bags submitted to the different composting processes were characterized (before, during and after the process) visually, physically by weight loss, mechanically (tensile properties), morphologically (scanning electron microscopy - SEM) and chemically (infrared radiation spectroscopy - FTIR).

After the end of the trials, it was observed a significant change in colour and integrity in both BA and BB strips and bags after sHC and IC, with a more profound change for BA, and a total fragmentation for BA strips after sIC. In terms of weight loss, 35% and 15% was recorded for BA and BB after sHC, 95% for BA after sIC, 50% and 60% for BA and BB strips after IC (active phase) and 22% and 18% for BA and BB bags (after maturation), respectively, in all cases. In terms of mechanical properties, tensile strength losses of 85% for BA strips after sIC, and 86% for BA and 77% for BB under sHC conditions were verified. In addition, a total loss in strain at break for BA after sIC and 98% for BA and BB after sHC were observed. SEM images allowed confirmation of morphological changes after sHC, sIC and IC for both BA and BB, and the presence of biological activity. FTIR analysis confirmed a decrease in the intensity of the characteristic peaks of BA and BB polymers under all conditions. The mentioned results allowed demonstrating that the studied bioplastics started a process of biodegradation by composting when submitted to sHC and IC. However, it is noteworthy that the degree of biodegradation of these is reduced at the end of the studies carried out. Effectively, these constitute a contamination for the industrial process to which they were submitted, considering the process conditions established, raising questions of operational disruptions and quality of the compost obtained. The sIC studies did not guarantee the necessary composting conditions, leading to the presence of a thermal disintegration of these products, thus raising questions about the dissemination of meso- and microplastics by these products in the environment. The incubation studies in soil enabled to conclude that these materials allow the vegetation development, not inhibiting their growth; regarding physical changes, only slight signs of disintegration/degradation for both BA and BB bags were observed. The inspection of one selective collection route of organic waste confirmed the presence of these types of bags in the routes of the collection systems.

In short, the present study allowed to conclude that the studied compostable bioplastics represent contaminations for the current composting processes in use, namely industrial ones.

Keywords: Biodegradable bioplastics; Biowaste; Compostable bioplastics; Composting; Municipal Waste Management

RESUMO

A presente dissertação teve como objetivo estudar dois tipos de bioplásticos biodegradáveis disponíveis no mercado português, um certificado como compostável, fabricado a partir de 'Bioplast' (BA) e outro que apresenta a indicação de ser compostável, fabricado a partir de Mater-Bi® (BB). Os dois materiais, sob a forma de tiras (5x1 cm), foram submetidos a uma compostagem industrial simulada (sIC) e a uma compostagem doméstica simulada (sHC), à escala laboratorial, durante 12 semanas. Os dois materiais foram também submetidos a uma compostagem industrial (IC, 3 semanas de compostagem ativa + 3 semanas de maturação), quer sob a forma de tiras (3 semanas, apenas fase ativa), quer no seu aspeto original de sacos (6 semanas). Foi também analisado o descarte não controlado destes sacos no ambiente, através da sua incubação no solo durante 12 semanas. Por último, um circuito de recolha seletiva de resíduos orgânicos foi inspecionado. Em todos os estudos realizados foi utilizado um material plástico de Polietileno de Alta Densidade (PEAD) para comparação e papel de filtro de celulose como controlo. As tiras e sacos submetidos aos diferentes processos de compostagem foram caracterizados (antes, durante e após o processo) visualmente, fisicamente por perda de peso, propriedades mecânicas (resistência à tração e alongamento à rotura), morfológicamente (microscopia eletrónica de varrimento - SEM) e quimicamente (espectroscopia de infravermelhos com transformada de Fourier - FTIR).

Após o final dos ensaios, observou-se uma alteração significativa da cor e da integridade das tiras e sacos de BA e BB após sHC e IC, com uma alteração mais profunda para BA e uma fragmentação total das tiras de BA após sIC. Em termos de perda de massa, foram registados 35% e 15% para o BA e BB após sHC, 95% para o BA após sIC, 50% e 60% para as tiras de BA e BB após IC (fase ativa) e 22% e 18% para os sacos de BA e BB (após maturação), respetivamente, em todos os casos. Em termos de propriedades mecânicas, foram verificadas perdas de resistência à tração de 85% para as tiras de BA após sIC, e de 86% para BA e 77% para BB em condições de sHC. Para além disso, foi observada uma perda total do alongamento à rotura para o BA após sIC e de 98% para o BA e BB após sHC. As imagens SEM permitiram confirmar alterações morfológicas após sHC, sIC e IC para BA e BB, bem como a presença de atividade de degradação biológica. As análises por FTIR confirmaram uma diminuição da intensidade dos picos característicos dos polímeros de BA e BB em todas as condições. Os resultados mencionados permitiram demonstrar que os bioplásticos estudados iniciaram um processo de biodegradação por compostagem quando submetidos a sHC e IC. É de salientar que o grau de biodegradação dos materiais foi reduzido no final dos estudos efetuados. Efetivamente, estes constituem uma contaminação para o processo industrial a que foram submetidos, tendo em conta as condições de processo estabelecidas, levantando questões de perturbações operacionais e de qualidade do composto obtido. Os estudos de sIC não garantiram as condições de compostagem necessárias, tendo-se apenas verificado uma desintegração térmica do BA, levantando assim questões sobre a disseminação de meso- e microplásticos por estes produtos no meio ambiente. Os estudos de incubação no solo permitiram concluir que estes materiais permitem o desenvolvimento da vegetação, não inibindo o seu crescimento; relativamente às alterações físicas, apenas se observaram ligeiros sinais de desintegração/degradação para os sacos de BA e BB. A inspeção de uma rota de recolha seletiva de resíduos orgânicos confirmou a presença deste tipo de sacos nos percursos dos sistemas de recolha.

Em suma, o presente estudo permitiu concluir que os bioplásticos compostáveis estudados representam contaminações para os atuais processos de compostagem em uso, em particular os industriais.

Palavras-Chave: Bioplásticos Biodegradáveis; Bioplásticos compostáveis; Biorresíduos; Compostagem; Gestão de Resíduos Urbanos

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ACRONYMS

AD	Anaerobic Digestion
BA	Bioplastic A
BB	Bioplastic B
CEAP	Circular Economy Action Plan
EPS	Expanded Polystyrene
EU	European Union
FTIR	Fourier Transform Infrared
HDPE	High-Density Polyethylene
IC	Industrial Composting
LPDE	Low-Density Polyethylene
PAHs	Polycyclic Aromatic Hydrocarbons
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
SEM	Scanning Electron Microscopy
sHC	Simulated Home Composting
sIC	Simulated Industrial Composting
SUP	Single-use Plastics
UN	United Nations

1. FRAMEWORK

1.1. Relevance and Presentation of the work

Plastics have acquired a significant role in modern society's metabolism, being their use nowadays nearly indispensable [1, 2]. Their application can be observed among the most distinct sectors such as packaging, construction, textiles, transport, electricity and electronics [3].

The packaging sector has been one of the most impacted by the emergence of plastics. Their lightness, capacity to preserve perishable food for long times, safety and hygiene advantages, and easy handling have made plastics “the preferred packaging material for all sorts of commercial and industrial users” [4]. However, one of the main problems associated with the use of plastics is related to the packaging sector, mainly due to the production of consumer plastics designed for single use (Single-Use Plastics – SUP), representing around 50% of all plastic consumption [5, 6].

SUP are defined as those that fulfil the purpose for which they were designed only once, or for a very short time (less than a year), being after disposed of. Typical examples consist of fast-food containers, beverage bottles, plastic bags, cutlery, plates, straws, and cigarette butts [7].

Even though plastics' ability to single usage might be essential in some fields, such as for medical and public health applications, their increasing production represents an unquestionable environmental threat. Most plastics, including SUP, are produced from fossil hydrocarbons, having their most common end-of-life in landfills (79%) and incinerators (12%) [8]. These alternatives are by no means the most desirable. Landfilling leads to both the material and energy contained in plastics being lost, implies the use of soil that could be destined for more noble purposes, potentially leading to environmental contamination through the production of leachates, containing not only disintegrated plastic materials but also other substances by contact with other products. Landfilling also enhances water source contamination, raising questions related to the bioaccumulation of

plastics in living organisms [9]. Incineration, although having the possibility for energy recovery, relies heavily on emissions control technologies, having negative effects such as the emission of greenhouse gases and other pollutants such as dioxins and polycyclic aromatic hydrocarbons (PAHs) into the environment [10].

Multi-material recycling has been increasingly considered as the best alternative to face the limitations associated with the previously mentioned end-of-life alternatives [11]. Through recycling, a reduction in the use of fossil fuels and soil use is promoted, contributing to preserve plastic value as secondary material, through its incorporation into new materials. However, recycling is dependent on several factors to assume itself as an advantageous and efficient process. It depends on a correct materials separation at source and efficient transportation to avoid downstream contamination, which can make their incorporation into new materials unfeasible [12]. In addition, it should be noted that most recycled materials still have presently lower quality compared to virgin materials (downcycling). Moreover, not all types of plastics are recyclable, which reinforces the importance of effective separation techniques and innovative recycling technologies [13].

Therefore, their fossil origin, allied to their high resistance and durability, large-scale production, as well as inappropriate social behaviour, such as littering, the referred end-of-life options for plastics appear not to be sufficient, leading to the accumulation of plastics in environmental compartments, mainly soil and water, at an alarming rate [14]. Their increasing prevalence in the environment is such that plastic sedimentary deposits are already considered a stratigraphic indicator of the Anthropocene - a geological epoch that marks the period when human activities have had a significant impact on the Earth's ecosystems and geological systems [15, 16].

Among the main impacts related to plastics accumulation are modifications to nutrients cycles, diffusion of plastics debris and consequent (bio)accumulation and ecotoxicity, changes in habitats and ecosystems, biological impacts on endangered or keystone species and social impacts such as health issues and disruption of food production capabilities [17, 18].

Over the recent years, and in order to mitigate the observed environmental problems, the terms bioplastics and biodegradable plastics have gained media and scientific attention. However, the meaning given to them is not always the most correct, being the terminologies used not consensual. Later in this document (section 2.3), the different terminologies will be addressed objectively. The introduction of these terms reveals,

nevertheless, that efforts have been made towards the development of materials which have, globally, the same already mentioned characteristics and advantages, as those of conventional plastics (flexibility, lightness, etc.), but with substantial modifications in their production (non-petroleum biological origins), and/or in their end-of-life due to their biodegradability, i.e., in their capacity to biologically decompose [19].

Solutions to overcome some of the problems associated with the production and waste management options for this type of material, such as the reduction of fossil fuel consumption, contamination of soil and water resources, as well as the reduction of its perseverance in the environment considering their possible reintegration through its biodegradation are thus of high relevance. Although the field related to biodegradable plastics seems promising, given that it is still a developing and relatively new area, it is important to analyse in detail all the implications associated with their production and widespread use, and above all, to effectively assess their biodegradability conditions. It is also important to evaluate how the current collection and sorting systems are affected by the presence of these new materials and what possible constraints and modifications are required to ensure that these systems' quality and reliability are maintained.

In agreement, the present dissertation aims to evaluate the biodegradability of plastic bags available in the Portuguese market, both at a simulated home process and at industrial composting conditions, by monitoring their physical/mechanical properties over time. The direct and uncontrolled disposal of this type of bags into the environment (littering) was in addition simulated through soil incubation assays. Finally, the presence of these materials at the reception of selective organic waste in a waste management plant was evaluated.

1.2. Scope and Objectives

The present dissertation was presented as a documental exigence to obtain the Master's Degree in Environmental Engineering, by the Faculty of Engineering of the University of Porto (FEUP).

This dissertation was developed in an academic environment, at FEUP, with the collaboration of two external entities: LIPOR - Municipalities Association for Sustainable Waste Management of Greater Porto and Porto Ambiente – “Empresa Municipal de Ambiente do Porto, E.M., S.A.”.

The laboratory studies were performed in different laboratories of FEUP, while studies at the industrial level (industrial composting), were performed in a subunit of LIPOR. Incubation tests in soil were performed in an agricultural field, at Paços de Ferreira municipality, Porto district. All the studies were performed between March and June of 2023.

All the studies conducted were performed in order to fulfil the following outlined general objective:

- Assessment of the biodegradation of bioplastic materials labelled as compostable, available in the Portuguese market, through composting.

For that, the following specific objectives were established:

- Performing biodegradation under laboratory simulated industrial and home composting conditions and further evaluating changes in physical/mechanical and chemical properties overtime;
- Performing biodegradation at a selective collection industrial composting plant and further evaluating changes in physical/mechanical and chemical properties overtime.

1.3. Brief description of the external entities

1.3.1. LIPOR

LIPOR is an organisation that was founded by the association of eight municipalities from continental Portugal: Espinho, Gondomar, Maia, Matosinhos, Porto, Póvoa de Varzim, Valongo and Vila do Conde. Its field of activity comprises the management, recovery and treatment of municipal waste produced by the above-mentioned municipalities, while also conducting environmental awareness campaigns and exchange of good practices.

The population served is about 1 million inhabitants, equivalent to an annual production of 500 thousand tons of waste, corresponding to a daily production of 1.38 kg.

LIPOR facilities comprise a Sorting Plant, a Waste-to-Energy Plant (incineration), a Landfill and a Composting Plant, through industrial composting in tunnels, the last included in the scope of this dissertation [20].

1.3.2. Porto Ambiente

Porto Ambiente, E.M., S.A. is the municipal environment company of the municipality of Porto, Portugal. Its field of activity is related to municipal waste management through the distribution of containers for unsorted and selective collection and ensuring its respective collection either at collection points, or through door-to-door collection systems for commercial establishments and certain residential areas. Additionally, Porto Ambiente is responsible for urban cleaning, and maintaining levels of cleanliness and hygiene at Porto municipality. It also plays a role of social responsibility in raising the awareness of the whole community to environmental issues, more specifically the reduction of waste and its correct separation [21].

Currently, citizens are informed not to dispose bags (of any kind) containing biowaste, since they represent contamination for the subsequent composting process. However, the use of plastic bags to accommodate the biowastes produced in households is highly appreciated among citizens, since it avoids odours and guarantees greater comfort and hygienic conditions. The increasingly mediatised topic of biodegradable bioplastics through composting has recently attracted attention, since this type of material could in principle transport the biowaste inside, and with it follow the process of organic valorisation, thus presenting itself as a solution for the issues mentioned. The company has necessarily high interest in providing convenient solutions to the citizens since it is a key issue to maintain their participation in the selective collection of biowaste. However, citizens tend to be discouraged by some discomfort given by current restrictions which might lead to reduce citizens' participation. Thus, there is a high current relevance and pertinence of this theme, as well as the need to effectively evaluate the assumptions presented by this type of materials in order to have basis for ways of action to improve the system performance.

1.4. Dissertation outline

The present dissertation is divided in six chapters.

In the first chapter, a general overview of the topic concerning bioplastics and its relevance is presented. The scope and objectives of the work carried out are outlined, as well as the external entities that contributed to its realisation are presented.

In the second chapter, a theoretical introduction on the most diverse topics intrinsically related to the subject of bioplastics is presented. Firstly, the current production and disposal of conventional plastics is analysed, as well as their associated problems. An approach to the most diverse concepts and terminologies related to bioplastics is also described, together with current standards and certifications related. The various end-of-life routes for these types of plastics are also addressed, along with their implications for current recycling processes. Finally, the composting process was described, including the conventional technologies employed and the main parameters that affect the process.

Chapter three covers a detailed description of all materials and methods used. The laboratory set-up and the respective composting mixture are specified, and the samples used are characterised. The different composting processes performed are defined, as well as their operational and monitoring conditions. Finally, the methods used for the characterisation of the samples after the studies performed are defined.

Chapter four presents all the obtained results, together with their interpretation and discussion, whenever possible supported by literature. The results of visual inspection, weight loss, mechanical properties analyses as well as analyses of scanning electron microscopy and Fourier transform infrared spectroscopy are presented. Similarly, the main considerations regarding soil incubation studies and inspection of a selective biowaste collection route are described.

In chapter five, the main conclusions from the work carried out are presented.

At last, chapter six, lists the main limitations identified throughout the development of the work, along with suggestions for future and complementary work.

2. INTRODUCTION

2.1. Global Plastic Production and Management

Plastics can be defined as fully synthetic or semi-synthetic polymeric compounds, generally derived from fossil carbon sources, such as crude oil and natural gas [22]. Their cost-effectiveness, durability, and lightweight, among other properties, have made them the most widely used polymer, mainly for packaging purposes [23].

Global plastics production has assumed massive proportions, growing at an annual average rate of 9%. As presented in Figure 2.1. , and complemented by more recent data, global plastic production has increased from around 1.7 million tons in 1950 to around 391 million tons in 2021, a 230-fold increase in 71 years [24]. Furthermore, current forecasts indicate that in the next two decades, plastic production should double, making the plastics industry responsible for 20% of annual oil consumption [25].

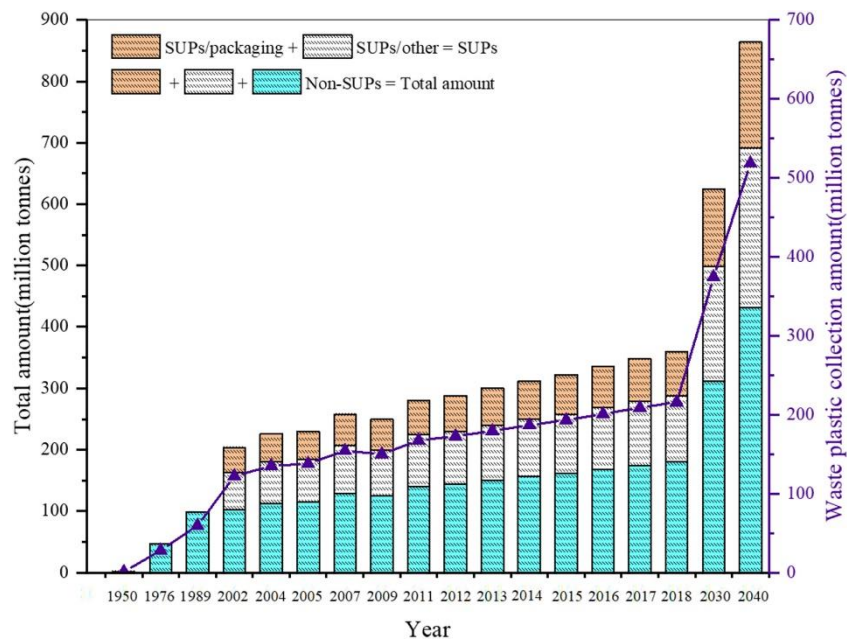


Figure 2.1. Global plastic and SUP production growth trends [25].

Packaging industry is primarily responsible for the SUP production and its introduction in the market. SUP are plastics that are intended to be used only once, often as a protective layer, outer packaging, or containers for transporting food and drink, such as water bottles [7].

As seen in Figure 2.1, SUP have gradually assumed a greater representation in global plastics production. In fact, it is estimated that they currently account for 50% of all annual plastics production [25, 26]. Accordingly, the industrial sector that consumes the most plastics is packaging, with about 36%. However, other sectors also present a relevant contribution, namely, building and construction with 16% and textiles with 14% [8, 27].

On the other hand, it can be observed that the industries which consume the most plastics are not necessarily the ones which lead to the generation of the largest quantities of plastic waste. It is therefore important, taking into account the theme under study, to approach the generation of plastic waste in more detail.

By analysing Figure 2.2, which refers to the evolution of plastic waste generation by industrial sector, it can be seen that although the industrial sector that contributes most to the generation of plastic waste continues to be packaging (141 Mt), the construction sector, which occupied second place in the industries that consume the most plastics, is not, however, one of the sectors that contributes most to the generation of waste from these materials, being surpassed by the textile sector (42 Mt) and other sectors (38 Mt).

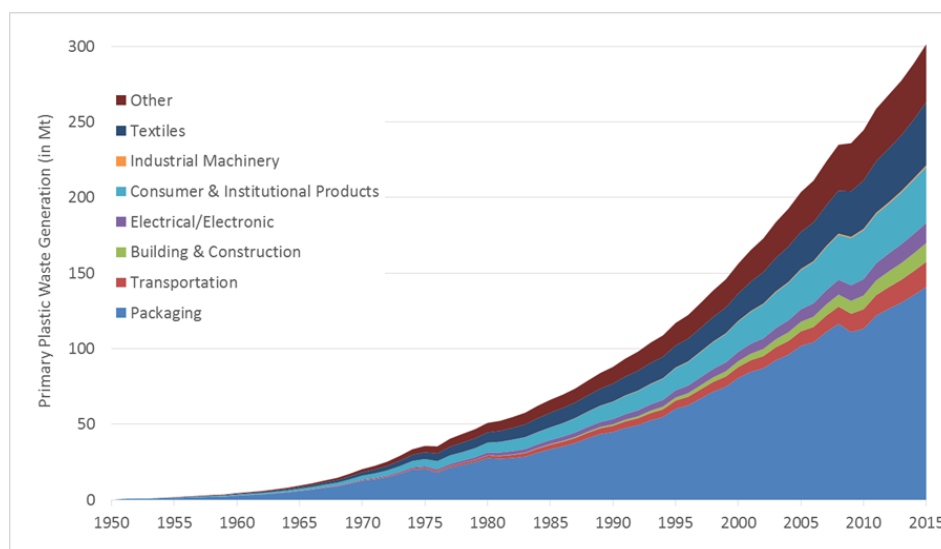


Figure 2.2. Global primary plastics waste generation (in million metric tons) according to industrial use sector from 1950 to 2015 [8].

One of the main reasons associated with the discrepancy between plastic consumption and its release as waste by several industrial sectors is its useful lifespan. In 2015, plastic products consumed by the packaging industry averaged a lifetime of only 0.5 years, followed by consumer & institutional products with 3 years and textiles with 5 years [8]. The problems related to textiles should be highlighted considering their relevance for plastic waste generation, as their recyclability is still very low, as well as the ways to recycle them, with incineration and landfill being the most common end-of-life for these products [3].

In addition to the segregation of plastic waste according to its production and use, it is crucial to distinguish plastics according to their properties, in thermoplastics and thermosets. This distinction is essential, as only thermoplastics can be mechanically recycled, namely melted, moulded and cooled successively to produce new materials. By contrast, thermosets, after being heated and thus formed, cannot return to the processing cycle [27].

The most used thermoplastics to produce SUP, consist of the following polymers [27]:

- **LDPE – Low-Density Polyethylene** (e.g., bags and films for food packaging);
- **HDPE – High-Density Polyethylene** (e.g., milk and shampoo bottles);
- **PET – Polyethylene Terephthalate** (e.g., water bottles and other beverages);
- **PS – Polystyrene** (e.g., plastic cutlery, plates and cups);
- **EPS – Expanded Polystyrene** (e.g., insulated food packing such as shielding packing);
- **PP – Polypropylene** (e.g., bottle caps).

As presented in Figure 2.3, the majority of produced plastic waste is within the thermoplastic category, with LD, LPDE being the most generated plastic waste (57 Mt), followed by PP (55 Mt). However, polymers such as PUR (Polyurethane), which fall into the thermoset plastics category, accounted for a production of 16 Mt in 2015. More recent data (2021), reports that globally, thermoset plastics represent 12.6% of all plastics produced [24].

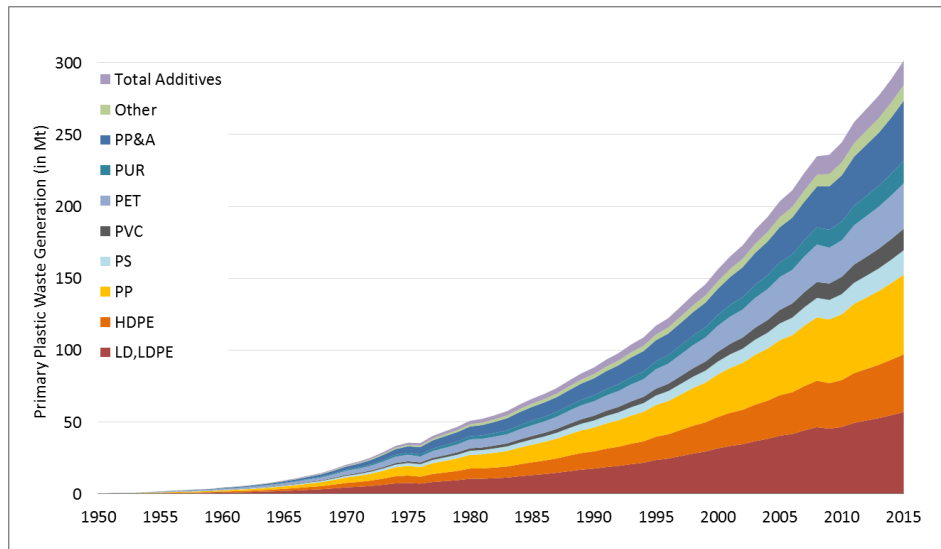


Figure 2.3. Global primary plastics waste generation (in million metric tons) according to polymer type, from 1950 to 2015 [8].

One of the biggest problems associated with the production of plastic waste is its mismanagement. In fact, recent studies report that about 79% of all plastic waste ever produced was landfilled, or can be found in the environment, whereas only 12% was incinerated and 9% was recycled (Figure 2.4) [3, 27].

In addition, an analysis of the Figure 2.4, also reveals that only 30% of all the primary plastics produced are still currently in use. In addition, from the 9% of recycled plastics (500 Mt), only 20% are still in use (100 Mt), with 20% having already been incinerated (100 Mt) and the remaining 60% being discarded (300 Mt).

Furthermore, in what concerns packaging waste production per capita, projections indicate an increase from 174 kg (in 2018, real values) to 209 kg in 2030 and 245 kg in 2040, being plastic packaging waste responsible for 41% of the increase between 2018 and 2040 [28].

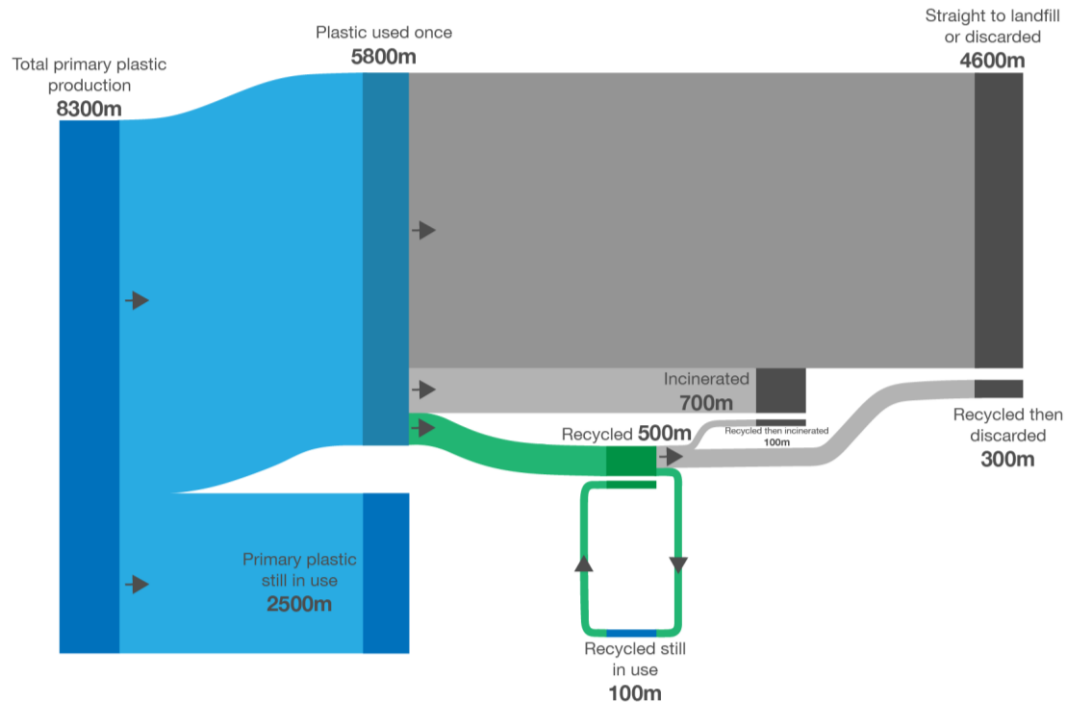


Figure 2.4. Global plastic production and its fate (1950-2015) (m represents million metric tons (Mt)) [3].

2.2. Brief Description of the Plastic Pollution Problematic

As a result of the plastic stream mismanagement, pollution due to plastic waste is currently "one of the most threatening environmental issues" facing today's society [29].

Due to its non-biodegradable characteristics, if not recovered, plastic waste can remain in the environment up to a few thousand years. During this time, their presence can lead to several changes in terrestrial and aquatic ecosystems. Plastic bags, for instance, can worsen natural disasters by blocking waterways. They also obstruct sewers and provide ideal breeding conditions for pests and mosquitoes that may constitute disease vectors like malaria [27].

Plastic waste, particularly residues of mulching film, which is widely used to limit water loss through evaporation and preserve soil moisture, reducing weed growth, creates a significant threat to agricultural areas as it disrupts water and air movement through the soil. This obstruction can have a negative impact on the productivity of agricultural land by preventing plants from taking up essential nutrients [25].

Additionally, in developing countries, plastic waste is often burned in open-air pits for heat or cooking, releasing harmful gases that damage human health and contribute to pollution and climate change [27].

Since Earth's aquatic and terrestrial ecosystems are interconnected, changes in one can easily affect the other. Thus, plastic debris can also be found in the ocean due to land-based activities such as urban and stormwater runoff, littering, industrial activities, and inadequate waste management; and also due to ocean-based activities like fishing, aquaculture and nautical activities [30]. Therefore, marine and coastal pollution due to plastic waste production have become a crucial problem, with currently 14 million tons of plastic ending up in the oceans every year, making up 80% of all marine pollution [30].

Plastic waste has negative impacts on marine life, and when ingested can cause suffocation, and entanglement for hundreds of species as marine animals often confuse plastic debris with food, resulting in starvation, infections, lacerations, and internal injuries. The presence of floating plastics also facilitates the transportation of invasive marine species, endangering marine biodiversity and disrupting the food chain. Marine organisms that ingest plastic debris also ingest toxic chemicals used during plastic production, which can transfer to animal tissue and accumulate in the food chain over time, eventually reaching the human food chain [30, 31].

Finally, plastic pollution is also associated with serious economic impacts. Plastic debris in the Asia-Pacific region alone is estimated to represent a cost of \$1.3 billion yearly on how it affects its tourism, fishing, and shipping sectors. Across Europe, the cost of clearing plastic waste from coasts and beaches reaches approximately €630 million per year. Research indicates that plastic pollution causes a minimum of \$13 billion/year in economic damage to the planet's marine ecosystem [27].

Resuming, plastic pollution aligns perfectly with the United Nations (UN) definition of a disaster, as it consists of “a serious disruption of the functioning of a community or a society at any scale due to hazardous events interacting with conditions of exposure, vulnerability and capacity, leading to one or more of the following: human, material, economic and environmental losses and impacts” [32, 33].

However, it is imperative to mention that, as previously stated, plastics have been and continue to be an enormous vector of development in today's society. The actual problem associated with them derives largely from their misuse, mainly in single-use products, or in products with a very short lifespan, as well as in their poor management as waste, often resulting in their uncontrolled disposal in the environment. Accordingly, in 2015, 16 of the 20 most polluting countries for marine plastics had economic development that could not be matched by waste management infrastructures [27].

2.3. Bioplastics and associated terminologies

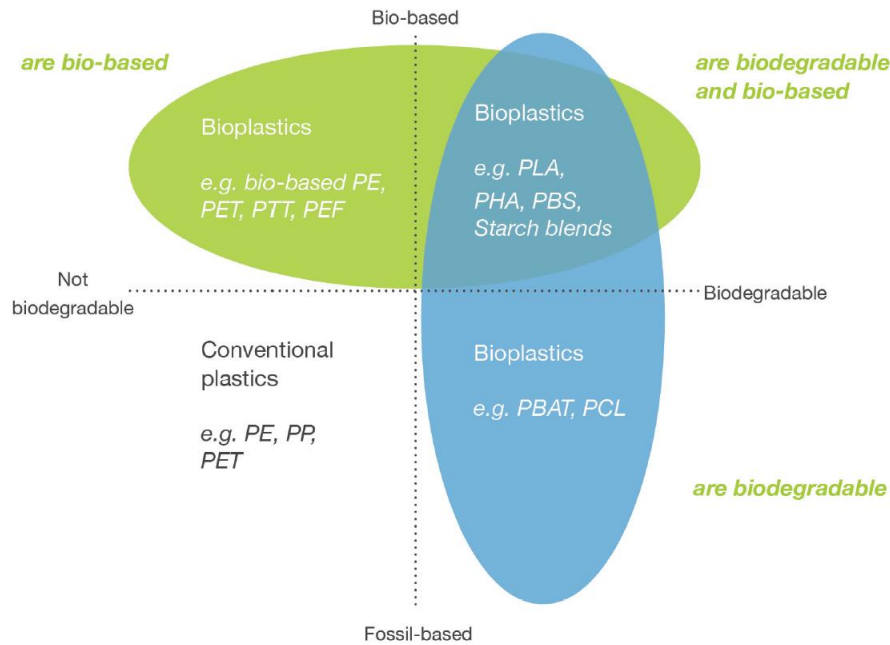
The problem of plastic waste has naturally raised many concerns in society. From the scientific community to social pressure, the problem is an increasingly current issue. Accordingly, the European Union (EU), has in recent years established legislation on different themes to address this issue. The EU Strategy for Plastics in the Circular Economy aims to promote plastic products with high recyclability, determining that by 2030, all plastics must be mechanically recycled. Furthermore, the Circular Economy Action Plan (CEAP), introduced by the European Commission aims at eliminating landfilling as a waste treatment option. Recently, The EU's Directive on single-use plastics (2019/904), introduced market and consumer restrictions on SUP products, oxo-degradable plastics and fishing gear containing plastics, including their ban from the market [7, 34].

The way that plastics are approached in terms of production, usage, and disposal, needs to be rethought and multiple options have been put forward, among which, are bioplastics, including biodegradable bioplastics. However, and despite the term being increasingly popular, there is still great confusion and lack of knowledge regarding the various terminologies. Moreover, and regardless of being generally perceived by the general public as a better solution than conventional plastics, this option has its “own sustainability challenges and trade-offs, that should be well understood and duly taken into account” [35].

2.3.1. Definitions

Firstly, it is imperative to mention that the terminology ‘bioplastic’, does not relate to a single type of material, but rather covers a wide range of materials with different properties and uses [36].

A plastic material is considered a bioplastic if it is totally or partially, of bio-based origin (non-fossil), or if it is biodegradable, or if it comprises both (bio-based and biodegradable), as shown in Figure 2.5.



.Figure 2.5. Material coordinate system of bioplastics [36].

According to Figure 2.5, bioplastics can be divided into three major groups, considering if they are fossil or bio-based and their biodegradability:

- **Bio-based and non-biodegradable**

These types of plastics consist of materials or products that are totally or partially produced from biomass, such as plant-based (wheat, sugar cane or starch), or from organic waste and by-products (cooking oil, bagasse and tall oil). These materials offer therefore a renewable carbon feedstock, instead of the conventional fossil origins [35]. Some typical examples are bio-based polyethylene (PE), bio-based polyethylene terephthalate (PET) and bio-based polyamides (PA). Some of its applications are in textile fibres (seat covers and carpets) as well as in the automotive industry in foams and cables [36].

- **Fossil-based and biodegradable**

These plastics are produced from fossil fuels, however, unlike conventional plastics, which do not decompose when they reach the end of their life, these types of plastics are designed to decompose “by the microbial conversion of all its organic constituents to carbon dioxide (CO₂), new microbial biomass and mineral salts under oxic conditions (in the presence of oxygen) or to carbon dioxide (CO₂), methane (CH₄), new microbial biomass and mineral salts under anoxic conditions

(in the absence of oxygen)”[37]. Materials like polybutylene adipate terephthalate (PBAT) and polycaprolactone fall into this category [38].

- **Bio-based and biodegradable**

These types of materials are both organic in origin (bio-based) and capable of decomposing by microorganisms (biodegradable). Biodegradable polymers such as polylactic acid (PLA), polyhydroxyalkanoates (PHAs) and starch blends made from thermoplastic starch (TPS) are part of this group. Typical applications involve their use in short-life products, such as packaging.

2.3.2. Biodegradation as a ‘system property’

The biodegradation of plastic materials is a biochemical process in which the organic component of the plastic materials is organically metabolised [37]. However, this process is strongly dependent not only on the material, but also on the conditions in which it occurs, which should be explicitly stated when referring to the biodegradability of a given material. Thus, different standards have been developed to regulate the conditions and environments under which a material biodegrades, as will be presented in section 2.4 [35].

The use of the terminology '**compostable plastic**' shows the need to specify the conditions under which biodegradation occurs. Compostable plastics are thus a subcategory of biodegradable plastics, in which their decomposition assumes a set of certain factors inherent to the composting process, which will be analysed in more detail in section 2.6 [39].

Additionally, it is important to make a clear distinction between the term biodegradation and degradation. Degradation encompasses not only biotic but also abiotic processes, i.e., in the absence of microorganisms. Thus, fragmentation and alteration of plastic properties due to UV radiation (photodegradation), or due to heat (thermo-oxidative degradation) is also a type of degradation [40]. Such degradation leads to the generation of small plastic particles from plastic fragmentation, called mesoplastics (5 to 10 mm), microplastics (<5 mm) and nanoplastics (1 nm to 1 mm), which accumulate in the environment, becoming a source of pollution and contamination, also leading to problems for human health and other living beings [41]. The emission of toxic gases into the environment in the case of thermo-oxidative degradation also constitutes an environmental issue associated with this process.

Biodegradation, through biotic processes, on the other hand, does not lead to the accumulation of plastic particles in the environment, as these should decompose completely in the receiving environment by the action of microorganisms [35].

2.4. Standards and labelling

Standardization is the process of establishing agreed guidelines and criteria for describing products, services, and processes in order to overcome communication barriers and promote fair competition and growth. Standardization also introduces benchmarks for quality requirements and prevents fraudulent market behaviour.

Although adherence to standards is voluntary, it is generally recognized as a good practice that can benefit both companies and consumers. By establishing and adhering to standards, market participants can establish a level competitive field that benefits everyone involved.

As regards bioplastics, there are two major categories of certification, one related to their origin (fossil or bio-based) and another to their ability to biodegrade.

It is also important to note that, currently, producers are not obligated to reveal the precise quantity of bio-based materials in their products when advertised as such; however, they can do so voluntarily.

As previously mentioned, biodegradability is related with a set of conditions and the environment in which it takes place. Thus, in what concerns the decomposition of bioplastics, it can be standardized in what concerns to the conditions in which it occurs, such as composting conditions, or in the medium in which it takes place: soil, marine or in water.

Table 2.1 and Table 2.2 summarise the main standards and respective labelling regarding the certification of bioplastics.

Table 2.1. Standards and labelling concerning bio-based plastics [42].

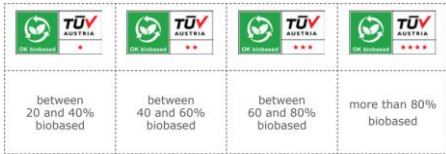
Labelling	Standard(s)	Description
	CEN/TS 16137	OK biobased Issued by TÜV Austria, based on the ^{14}C -method for measuring the bio-based carbon content in relation to total carbon as a percentage.
	ASTM 6866	
	ASTM 6866	DIN CERTCO bio-based certification
	CEN/TS 16137	Issued by the German certifier DIN CERTCO, based on the ^{14}C -method for measuring the bio-based carbon content in relation to total carbon as a percentage.
	ISO 16620	

Table 2.2. Standards and labelling concerning biodegradable plastics [39, 42].

Labelling	Standard(s)	Description
 compostable	EN 13432	Seedling
	EN 14995	Either issued by DIN CERTCO or TÜV Austria, concerns to products which comply with all the criteria present in EN 13432, relating industrial compostability .
	EN 13432	DIN CERTCO industrial compostable & OK compost Issued by the German certifier DIN CERTCO and Belgian certifier TÜV Austria, relating to compliance with EN 13432, compostability in industrial composting installations .
	NF T51-800	DIN CERTCO home compostable & OK compost HOME
	AS 5810	Issued by DIN CERTCO based on the mentioned standards and issued by TÜV Austria on a certification scheme by them developed. Both regard compostability at environment temperatures, under home composting conditions .

Table 2.2. Standards and labelling concerning biodegradable plastics (cont.).

Labelling	Standard(s)	Description
 	EN 17033	<i>DIN CERTCO biodegradable in soil & OK biodegradable SOIL</i> Issued by DIN CERTCO, applies to products manufactured to be used in or on soil, such as mulch films – EN 17033. Issued by TÜV Austria on a certification scheme by them developed, regarding products that fully biodegrade in soil.
	ASTM D7081	<i>OK biodegradable MARINE</i> Certification developed by TÜV Austria regarding the mentioned standard, demanding a 90% biodegradation in six months.
	---	<i>OK biodegradable WATER</i> Certification scheme developed by TÜV Austria, regarding biodegradability in natural freshwater environments.

Currently, EN 13432 and EN 14995 are the two European standards concerning the biodegradability of plastics through industrial composting.

The EN 13432 standard relates to "Requirements for packaging recoverable through composting and biodegradation", whereas EN 14995 outlines a broader approach, relating to "Plastics – evaluation of compostability – Test scheme and specifications [42-44].

It should be highlighted that EN 13432 covers both to composting (aerobic degradation) as well as treatment under anaerobic conditions. Nevertheless, both routes require certain conditions such as temperature, humidity, aeration, material size and carbon to nitrogen ratio (C/N) [45]. As the focus of the present dissertation is on composting of packaging plastics classified as compostable, the corresponding European standard was analysed in more detail, as follows.

According to standard EN 13432, to consider a plastic material biodegradable, four parameters must be analysed and fulfilled [44], namely:

Biodegradability:

A minimum of 90% of the compostable material should be converted to CO₂ and biomass due to the action of microorganisms in no more than 6 months, at 58 °C ± 2 °C, under dark or diffused light environment, in static composting vessels as in ISO 14855:1999.

Disintegration during biological treatment:

No more than 10% of the original material after 3 months of composting should be retained in a 2 mm sieve.

Effect on the biological treatment process:

Negative effects in the composting process should not occur, such as the presence of toxic, hazardous substances and heavy metals beyond concentrations thresholds defined by the standard.

Effect on the quality of the resulting compost:

No decline in agronomic value or ecotoxicological effects on plant growth should occur in the obtained compost.

Furthermore, the standard also refers to criteria regarding possible additives that the product may contain.

At the time the present document was written, there was no European standard focusing at home composting, although being highly relevant, has recognised by the European Parliament and Council [46].

In fact, home composting conditions are more challenging to ensure the complete biodegradation of compostable plastics and demand more caution. Agreement with industrial composting requirements does not guarantee the decomposition in home composting as temperature, aeration and humidity which can be obtained at industrial composting systems are not generally achievable in home composting. On the other hand, the conditions needed for home composting closely depend on the local climate and consumer habits [35]. Nevertheless, properly performed, home composting can have relevant benefits compared to landfilling and incineration, as less biodegradable waste collected from households can lead to a significant reduction in waste management costs and also in the production of compost for agricultural purposes [47].

Although there are no European or International standards, several countries have their own, such as Australia - AS 5810 "Biodegradable plastics - biodegradable plastics suitable for home composting" and France - NF T 51-800 "Plastics - Specifications for plastics suitable for home composting".

The already mentioned Belgian certifier TÜV Austria has developed its own certification, which states as a condition that at least 90% degradation should be achieved in no more than 12 months at ambient temperature [48].

2.5. Bioplastic waste management

Although bioplastics account for less than 1% of annual plastics production, their increased and widespread availability on the market brings problems regarding waste management [49]. Moreover, their recent appearance means that consumers are still largely unaware of the appropriate end-of-life routes for these products. The identification of the products as 'biodegradable' or 'compostable' should not lead the consumer to think that any end-of-life option is acceptable, and certainly not their uncontrolled disposal into the environment (littering).

It is generally thought that bioplastics, namely biodegradable, have only organic recycling as an appropriate end-of-life solution; however, and according to the CEAP and the European Waste Framework Directive (Directive 2008/98/EC) amended by Directive (EU) 2018/851, other routes are preferable if feasible. Waste prevention and management must follow a hierarchy, also known as the waste hierarchy, which comprises, as shown in Figure 2.6: (i) prevention; (ii) preparing for re-use; (iii) recycling; (iv) other forms of recovery (such as energy recovery) and (v) disposal.



Figure 2.6. Waste hierarchy according to the European Waste Framework Directive (Directive (EU) 2018/851) [50].

Bioplastics can follow three main routes, strongly influenced by consumer behaviour, which naturally leads to challenges for collection and sorting systems:

- **Route 1:** Multi-material recycling;
- **Route 2:** Organic recycling;
- **Route 3:** Other forms of recovery and landfill.

Such routes are described as follows.

2.5.1. Route 1 – Multi-material recycling

If a bioplastic is not biodegradable and is mechanically recyclable, according to the waste hierarchy already analysed, it should follow the selective collection route in order to be mechanically recycled. It should be highlighted that materials which recyclability is not referred should not follow this route, as they can severely affect the recycling process, damaging it and affecting the quality of the obtained materials or products [51].

According to European Bioplastics [38], non-biodegradable bioplastics can be mechanically recycled using already existing technologies for traditional plastic waste streams. Thus, a bio-PET material can be recycled together with a PET material. Therefore, a selectively collected bioplastic product suitable for mechanical recycling would follow the naturally conventional steps of sorting, grinding, washing, drying, re-granulating, and compounding [38]. It should be noted that the literature indicates that the mechanical recycling of bioplastics, such as bio-based plastics, can itself sometimes constitute a contamination for the process, damaging it; so it will depend largely on the characteristic of each bioplastic. The subject in question is therefore not yet consensual [52].

There is already technology in use capable of separating and identifying bioplastic materials, such as Near-Infrared spectroscopy (NIR). However, like other methods, it still has strong capacity and material size limitations, as mentioned by Wojnowska-Baryła, Kulikowska [52]. The presence of physical indicators in the biopolymer products such as printings or labelling could be an effective solution when manual separation is performed. Furthermore, it should be addressed that, as with fossil-based plastics, a product cannot be mechanically recycled indefinitely due to the successive loss of mechanical properties. The quality presented by bioplastics regarding their mechanical properties and effective recyclability is still a controversial and non consensual topic [53, 54].

In short, the conventional selective collection systems constitute an opportunity for bioplastics collection, as they can integrate the conventional plastics chain. However, it is evident from the literature that this topic still needs further research and development.

2.5.2. Route 2 - Organic Recycling

Bioplastic products that are biodegradable should follow the organic recycling route. As expected, the separate collection of organic waste plays a crucial role in the effectiveness of this route. Mixed Municipal Solid Waste (MSW) schemes employ a fully mixed waste collection approach, which has drawbacks in terms of cost and quality for accurate sorting and cleaning of severely contaminated recyclable material streams and biowaste. Thus, biowastes obtained through MSW schemes and subsequent sorting, impairs the composting process, affecting the quality and marketability of the resulting compost [34].

According to the CEAP and the European Waste Framework Directive (2018/851), the selective collection of biowaste will be mandatory from the end of 2023 onwards, in an attempt to avoid contamination of biowaste, leading to more effective separation, and also seeking to increase the recyclability rates of EU member states. This fact, combined with the EU's pressure to reduce landfilling, will increase the demand for organic recycling plants, as well as the need for redesign waste collection systems.

The organic recycling of biodegradable bioplastics is not a consensual topic. Composting plants differ in their processes, strongly influenced by their biomass source (feedstock), microorganisms involved and composting conditions [34]. Additionally, and as already mentioned, since techniques to distinguish conventional plastics from bioplastics are not yet widely developed, in most cases all types of plastics end up being removed from the streams heading for organic recycling to avoid contamination of the process.

It is therefore crucial to evaluate the effectiveness and efficiency of current organic recycling plants to deal with biodegradable plastics, which is expected to increasingly appear in organic waste streams. Furthermore, it is important to assess what possible technological advances or modifications in the existing composting or anaerobic digestion (AD) processes will be necessary to implement in order to ensure the incorporation of biodegradable bioplastics [55]. In addition, operational processes are subjected to an economic analysis, and thus the modifications required to the

incorporation of biodegradable plastics in existing procedures cannot affect their profitability [34, 56].

2.5.3. Route 3 – Other forms of recovery and disposal

Bioplastics that are neither biodegradable nor recyclable, will necessarily have to follow the path of energy recovery or disposal, usually associated with unsorted collection.

Although incineration is not the ideal option, it seems not to be affected by the presence of these materials in the process, being reported that 56% of all energy obtained comes from municipal organic waste [52].

Bio-based plastics that follow this route will release CO₂ that has been accumulated in the biomass used for their manufacture, which will be retained again in the manufacture of new similar materials. In that sense, the incineration of bio-based materials may provide a better alternative to the incineration of fossil-based plastics, since as polymers with high amounts of carbon and hydrogen, they lead to an acceptable heat output, thereby not interfering with the process [51]. However, the emission of greenhouse gases, among other noxious gases and other contaminants by this route, makes it, as mentioned in the waste hierarchy, a route neither preferable nor advisable.

In what concerns to landfilling, apart from the direct implication of increasing the volume of landfill sites, non-biodegradable and non-recyclable bioplastics should not cause relevant contamination due to the absence of biodegradability; although physical disintegration into meso- and microplastics should not be ignored. However, biodegradable bioplastics reaching this destination could lead to an increase of leachate and biogas production as they could start their degradation process [51].

2.5.4. Main challenges

Effective waste separation is crucial for a successful recycling. Currently, consumer behaviour regarding the purchase, use and disposal of bioplastics is not yet well known and there is a great lack of knowledge regarding these products by the population.

In addition, the idea that a bioplastic material has as its end-of-life pathway composting or AD is not true. It is therefore necessary that these products clearly identify the end-of-life route for which they were intended. Hence, there is a great lack of knowledge

and unclear planning about the routes and how the management of this waste should be carried out, which demands an urgent and more thorough analysis by the scientific community. Also, the adaptability and effectiveness of multi-material and organic recycling plants in relation to the handling of these products could be a constraint. It is essential to guarantee that these plants are technologically prepared to incorporate these new products in their processes, without damaging them.

Thus, some of the main challenges faced regarding the transition to the use of bioplastics are:

- Lack of knowledge by the consumers regarding the appropriate end-of-life solutions for each product;
- Poor and misleading labelling;
- Difficulties in sorting after collection;
- Discrepancy between lab-scale assays and industrial composting conditions, leading to a real behaviour of the material that differs from that experimentally perceived, such as its effective compostability;
- Discrepancy between compostable packaging designs and what composting facilities are prepared to accept;
- Technological advances in the packaging industry are not matched by respective technological advances;
- Separated collection routes are missing or insufficient, particularly for organic waste;
- Insufficient number of organic recycling plants;
- Need to ensure the absence of contaminants;
- Lack of life cycle assessments of these products.

2.6. Composting

Composting is the aerobic decomposition and stabilization of organic substrates due to microbial activity, under controlled conditions. It consists in the consumption of organic matter carried out by microorganisms in the presence of oxygen (O_2) and leads to the emission of carbon dioxide (CO_2) and water (H_2O), while resulting in a stable and agronomically valuable product known as compost [57, 58].

Globally, about 50% of the municipal waste fraction is biodegradable organic fraction, with a positive evolutionary trend [59]. European legislation on waste management has reinforced the need for effective treatment of the municipal waste biodegradable organic fraction (biowaste – food and garden waste), instead of its landfilling. Composting processes have gain attention as part of the solution for biowaste management and treatment. In fact, they are already considered as one of the most efficient and effective in the treatment of the organic fraction of solid waste, being economically achievable and environmentally sustainable [60].

Composting has been practised since ages, with essentially two major objectives: as a method of waste prevention (home composting); and as a recovery solution for biowastes, producing a product (compost), with the aim to improve soil conditions. The process allows the recovery of biowaste such as food waste, manure and crop residues, which would otherwise be wasted as they would be perceived as having low value. However, through composting, resources in the form of organic matter, minerals, nutrients and energy are thus recovered from biowastes and transformed into soil-building products. In most cases, these products resulting from the composting process, have a higher value compared to the feedstock that originated them [56].

2.6.1. Industrial versus Home Composting

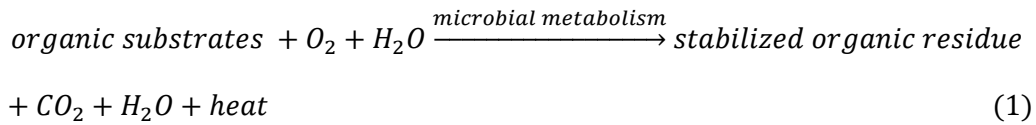
Industrial composting is carried out in large installations designed for such purpose, with the aim of treating large quantities of organic waste. They involve continuous monitoring and adjustment of the optimum conditions for composting, enabling rapid degradation and ensuring that a high-quality product is obtained [61].

In contrast, the term home composting is associated with a biowaste composting process on a small scale, usually carried out at home composting bins, where the resulting product is essentially used in private gardens. It is a slower process, and occurs at lower temperatures (mesophilic range) [62].

However, home composting translates into certain benefits as it leads to waste prevention, thus reducing the pressure on collection and treatment systems, which may translate into lower energy and material costs [63].

2.6.2. The composting process

In overview, the biological equation describing the composting process can be represented as follows [64]:



Composting can thus be seen as a mineralisation process in which microorganisms degrade organic matter into stabilised inorganic compounds and organic residues as seen in equation (1). The process leads to a high mass reduction (40-50%), together with a volume reduction of up to 90%, largely due to the mentioned mass loss and the release of CO₂ and water during the process [58, 65].

The aerobic decomposition process associated with composting can be achieved in a variety of ways, resulting in different technologies being employed. In general, there are two types of composting: open systems and in-vessel systems.

2.6.1.2. Open systems

In this type of composting, the waste is traditionally composted in piles or open beds exposed to the atmosphere. However, the piles can also be placed inside warehouses or under roofs [66].

The most common open systems are:

Turned windrows: These consist of long narrow compost piles, also called 'windrows' that are mechanically aerated frequently in order to control factors such as aeration/oxygenation, temperature and humidity. The active phase of composting lasts between 8 to 16 weeks, depending on the material being composted and the frequency of turning. Piles can reach heights of up to 4 m and widths of up to 8 m [66, 67].

Aerated static pile: This type of system relies on forced aeration of the compost pile through the use of drainage pipes and fans. The increased airflow results in more efficient composting by limiting excessive temperature rise, maintaining good oxygen levels and removing excess moisture as well as gases such as carbon dioxide and ammonia. Active composting time lasts between 18 and 21 days. An advantage of this type of system is that if aeration is by suction, the air can be redirected to biofilters in order to treat odours from the process [66, 68].

2.6.1.2. Closed systems

The closed systems consist of the composting process carried out in containers or vessels, thereby confining the composting mixture.

The most common closed systems are:

Agitated bays/bed: Long channels bordered by side walls in which a revolving machine circulates automatically and continuously. Forced aeration is usually used, and the typical composting period is 2 weeks [69].

Rotating drums: These consist of horizontal cylinders which slowly rotate on themselves in order to aerate, mix and rewind the composted materials. They are fed in at one end and the compost is extracted at the opposite end. The use of forced aeration is common and the usual residence time of the material is 3 to 5 days [69].

Composting tunnels: Closed containers or concrete tunnels that are fed in batches. Aeration is forced by an upward current of air over the pile with the exhaust air being recovered and treated. There is no agitation or stirring, and the retention time of the waste is about 2 weeks [69].

In general, there is a wide variety of composting processes, as exemplified above, ranging from simple, low-maintenance methods to specially designed reactors. Naturally, several factors are involved in deciding which method is best to use, including the type of material to be composted, the scale of the process, economic constraints, rules and regulations and proximity to populations. In almost all methods, the experience and knowledge of the process operators is critical for an effective composting process [66].

Given the composting process is a biological process, it is naturally affected by several factors, that also influence the microbial activity. The most relevant parameters that affect the composting process will be addressed below.

Temperature

Temperature is considered one of the most important factors for process control, since it reflects the biological equilibrium and efficiency of the whole process, also indicating the end of the process [58]. In fact, the composting process can be divided into three stages, encompassing four different temperature ranges observed during the process, as presented in Figure 2.7.

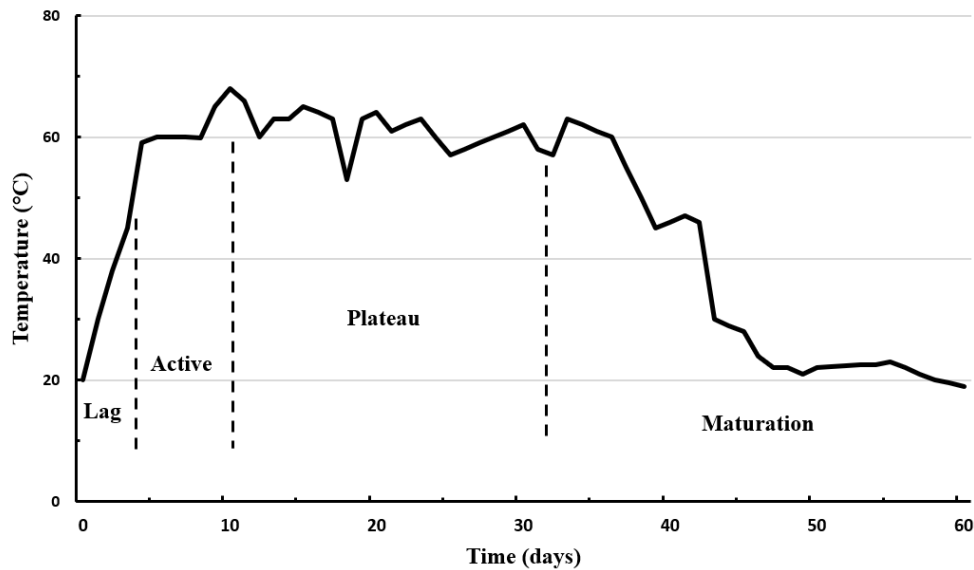


Figure 2.7. Typical temperature curve observed during the compost process [70].

The first stage, known as the 'lag phase', starts as soon as the composting conditions occur and consists of a period of adaptation for the microorganisms present in the waste. As the microbial community begin to grow through the degradation of the organic compounds, the temperature increases as an effect. This phase is characterised by a mesophilic range of temperatures (20-45 °C).

When an exponential increase in temperature is observed, the 'active phase' of the process is entered. In this phase, there is intense microbial activity and a continuous increase in temperature, resulting from the breakdown of easily degradable organic matter. A thermophilic range of temperatures is thus reached (45-75°C), allowing disinfection and elimination of potential pathogens present in the material. With the depletion of easily degradable matter, the temperature begins to stabilise, reaching a 'plateau'.

In the 'maturation phase' or curing phase, there is a decrease in microbial activity and a consequent decrease in temperature until mesophilic ranges, eventually reaching room temperature. At this point, the composting process is considered completed [58, 70].

It is relevant to note that when referring to in-vessel composting systems, they are generally in reality, a combination of in-vessel and open composting, the vessel being reserved for the active phase of composting, with maturation occurring in open systems [70].

Aeration/Oxygenation

Being an aerobic process, the metabolic activity of microorganisms involved in composting is strongly dependent on oxygen consumption. As the process develops and the microbial population grows, increasing oxygen consumption occurs. Composting is thus a process that leads to high oxygen demand. Thus, aeration of the mixture is essential to avoid anaerobic conditions, which can strongly affect the process, since they are associated with other types of microorganisms and biochemical reactions. Furthermore, aeration is essential to avoid excessive temperature values as well as odour control.

It should be noted that bulking agents are often used to ensure the structural integrity of the compost material and to enable the formation of pores, thus providing a pathway for the diffusion of oxygen. Examples of bulking agents are materials that do not easily biodegrade due to their high lignin content, such as shredded green wastes, bark and wood chips [58, 62, 70, 71].

Moisture

The medium in which the reactions inherent to the composting process unfold is aqueous. Water is essential to the process, allowing the diffusion of nutrients, the movement of microorganisms and their metabolic process. It should be noted however, that high moisture contents (> 65%) can lead to anaerobic conditions that compromise the process, since under these conditions the water occupies the interstitial spaces of the composting materials, limiting the diffusion of oxygen [62].

pH

The high diversity of microorganisms present in the process makes a wide range of values acceptable. Typical ranges are 5.5 to 8.0 for fungi and 6.0 to 7.5 for bacteria. Certain materials such as wastepaper raise the pH, while food waste lowers it. Usually, pH adjustment is not attempted, as autoregulation processes are performed by the microorganisms (e.g. assimilation of organic acids) [71, 72].

Nutrients (Carbon-to-Nitrogen ratio (C/N))

The main nutrients required by the microbial population in the composting process are carbon (C), nitrogen (N), phosphorus (P), potassium (K) and sulphur (S). Among those, the nutrients that most influence the process, are carbon and nitrogen. Carbon is used by microorganisms for energy and growth, while nitrogen is essential for proteins and

reproduction. Thus, a balance between these, known as the carbon to nitrogen ratio (C/N), is often the indicator used to assess the presence and correct amount of nutrients required for the process [58, 72].

Very high C/N ratios often lead to longer composting times, due to insufficient nitrogen needed for the growth of microbial populations, while at very low C/N ratios, excess nitrogen is bound in the form of ammonia gas, affecting the composting process and generating odours [58, 72].

Particle Size

Particle size is essential as it is directly related to the surface area of contact between the microorganisms and the organic waste to be composted. In general, smaller particle sizes lead to larger surface areas and therefore to a decrease in composting time. However, it should be noted that smaller particles also lead to a reduction of porosity, which delays the circulation of oxygen and water. Therefore, the particle size should not be excessively reduced [62].

In summary, the main factors and corresponding reasonable and preferred ranges to be considered in the composting process are presented in Table 2.3.

Table 2.3. Range of reasonable and preferable conditions for composting [58, 62, 71, 72].

Condition	Reasonable Range	Preferred Range
Temperature* (°C)	45 – 70	50 – 65
Aeration/Oxygenation (concentration inside the pores)	> 5%	> 10%
Moisture (%)	40 – 65	50 – 60
pH	5.5 – 9.0	6.5 – 8.0
C/N ratio	20:1 – 60:1	25:1 – 40:1
Particle Size (mm)	3 – 50	**

*Relating the active phase. **Dependent on the waste to be composted, type of technology and/or atmospheric conditions.

2.6.3. Compostable Bioplastics

Compostable bioplastics can now be defined as plastics that are biologically degraded under conditions of a composting process (such as those previously detailed) and that when introduced together with other organic waste in the composting process, do not lead to any negative impact on the process, quality of the final product and the environment [34, 73].

2.6.4. Literature on laboratory scale composting trials

In order to perform the laboratory composting trials, a bibliographic review was carried out in order to objectively analyse the methods and methodologies employed by other authors, as well as the process conditions and monitoring conducted relative to a laboratory scale composting.

Technical aspects such as the volume and size of the composting reactors, the composition and relative proportion of the composting mixture, as well as its characterisation such as moisture, volatile solids, pH and C/N ratio were sought. Similarly, information regarding the shape and size of the bioplastic samples to be used as well as their proportion with the compost mix was searched. Operational procedures such as assays temperature and duration as well as moisture conditions were also explored in the literature.

The studies considered most relevant, taking into account the targeted factors and the scale of the trials, are compiled in Table 2.4. These constituted the basis for the structuring and assembly of the laboratory process employed. Regarding the results obtained, a high variability is denoted among the studies analysed. This discrepancy reveals once again how the theme concerning bioplastics is still a recent and developing topic and highlights how biodegradation processes are intrinsically dependent on the conditions in which they occur. Note that even for the same material, such as Mater-Bi[®], the disintegration values varied from 45% to 94-99% between Ruggero, Onderwater [74] and Adamcová, Zloch [75] studies.

Table 2.4. Literature review on composting conditions for laboratorial assays.

Reactor capacity (L)	Sample size (cm)	Composting mixture	Sample/Composting mixture ratio	Time	Operational conditions (Temperature; Moisture; C/N ratio; pH)	Material(s)	Disintegration/Biodegradation** (%)	Method	Reference
6 30x20x10 cm	2.5x2.5	51% compost, 4% wood sawdust, 44% municipal biowaste, 1% glucose	1.2	12 weeks	58°C 30-65% <30 6-8.5	HDPE+TDPA Starch Starch + Polycaprolactone	0 99.6 100	weight loss	[76]
90	2x2	10% compost, 36% wood chips, 54% vegetable residues	6.7	31 weeks	25°C 55% - -	OXO black bags OXO white bags PLA Polyethylene white plates	not significant	weight loss	[77]
5	5x5	Compost from green and agricultural waste	2.9	20+40* days	58+37°C* 47% 15 7.5	Mater-Bi® PBAT PLA	45 8 3	weight loss	[74]
2	2x2	derived from compost of organic agriculture waste	8.3	90 days	58°C 50-55% 14.78 7.97	MCE PLA PE PE/starch	94.34 85.75 0.56 11.5	ultimate aerobic biodegradability	[78]
4	1x1	dairy manure and hardwood sawdust	22.9	16 weeks	55°C 60% 20 7.95	plastarch	51.3	carbon mineralisation to CO ₂	[22]
-	-	3% compost, 16% wood sawdust, 64% municipal biowaste, 2% glucose	-	12 weeks	58°C - - -	Mater-Bi®	93.5-98.7	weight loss	[75]

HDPE – High-Density Polyethylene | PLA – Polylactic acid | PBAT – Polybutylene Adipate Terephthalate | MCE – Microcrystalline Cellulose | PE – Polyethylene

*Active composting + maturation phase | **Only for Leejarkpai, Suwanmanee [78] and Gómez and Michel [22]

3. MATERIALS AND METHODS

3.1. Characterization of studied bioplastics

Two types of bioplastics were studied, both obtained commercially in the Portuguese market. Both bioplastics were purchased in the form of “trash” bags, and sold in rolls.

Bioplastic A (BA), is labeled as “100% biodegradable and compostable”, having the certification 'OK compost INDUSTRIAL', issued by the Belgian certifier TÜV Austria, indicating compliance with the EN 13432 standard (section 2.4). Regarding its composition, it is made with 'Bioplast', a potato starch polymer.

Bioplastic B (BB), is labelled “100% compostable” but displays no certification to support it. Regarding its composition, it is referred to be manufactured with polymers of vegetable origin - Mater-Bi®.

Given the above descriptions and accordingly to the three major groups of bioplastics presented in section 2.3.1, the two bioplastics mentioned (BA and BB) can thus be classified as bio-based and biodegradable. However, obtaining the specific final composition of these polymers proved impossible, even after contact with the suppliers.

Bioplastic A bags have the dimensions 55x55 cm, while Bioplastic B bags have 45x44 cm, as illustrated by Figure 3.1. It should be noted that the dimensions of the bags were not maintained in all studies, as will be explained later on.

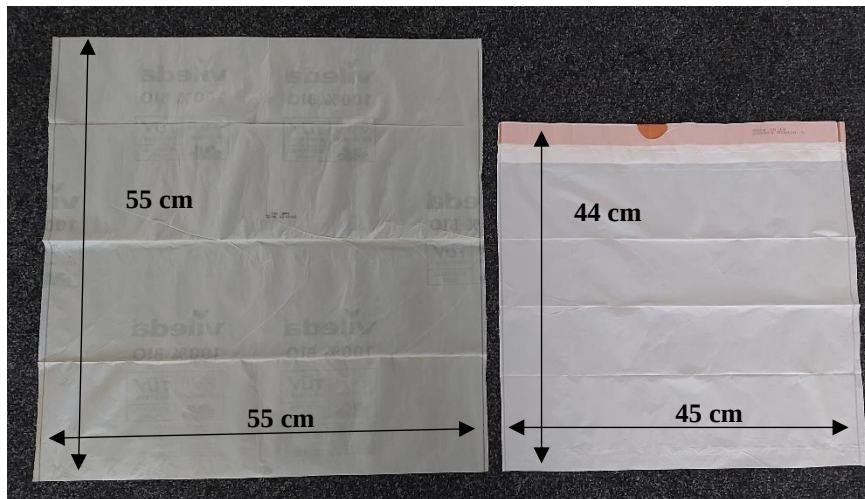


Figure 3.1. Photographic record of Bioplastic A (left) and B (right) bags used for trials.

3.2. Laboratory scale trials

Laboratory scale trials aimed at simulating industrial composting (sIC) and home composting (sHC) conditions. The trials were conducted during a continuous period of 12 weeks (84 days), in reactors adapted for the process, containing a composting mixture previously defined according to the literature review carried out.

3.2.1. Set up of the laboratory composting process

Under laboratory conditions, the biodegradable waste was composted in plastic boxes both during sHC and sIC trials, with a capacity of 6.5 L and dimensions of 29x20x18 cm, perforated on all sides with orifices of 5 mm in diameter to allow aeration, as well as the draining of possible leachates, as shown in Figure 3.2.



Figure 3.2. Photographic record of the plastic boxes used to contain the biodegradable material during composting in the laboratory trials.

3.2.2. Sample characterisation

The European standard EN 13432, refers to ISO 14855:1999 as the standard to be used for laboratory scale biodegradability trials to determine “the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions”. This standard refers that the maximum surface area of an individual sample should be 2x2 cm [79].

However, to allow characterization of the mechanical properties of the samples and considering the total surface area referred in the standard, 5x1 cm strips were used in the trials. These strips were obtained by precisely cutting the previously mentioned bioplastic bags.

Besides samples of BA and BB, a conventional HDPE plastic bag, readily available in Portuguese supermarkets to store/transport fruits and vegetables, was used in the home composting trials.

In both trials (sHC and IC), Whatman® Grade 1 cellulose filter paper strips with a nominal thickness of 180 µm were used as control.

Each sample strip was placed in a plastic mesh (2 mm openings), in order to easily take samples for analysis during the process. All the different sample strips used, as well as their appearance after wrapped in the mesh, is illustrated in Figure 3.3.

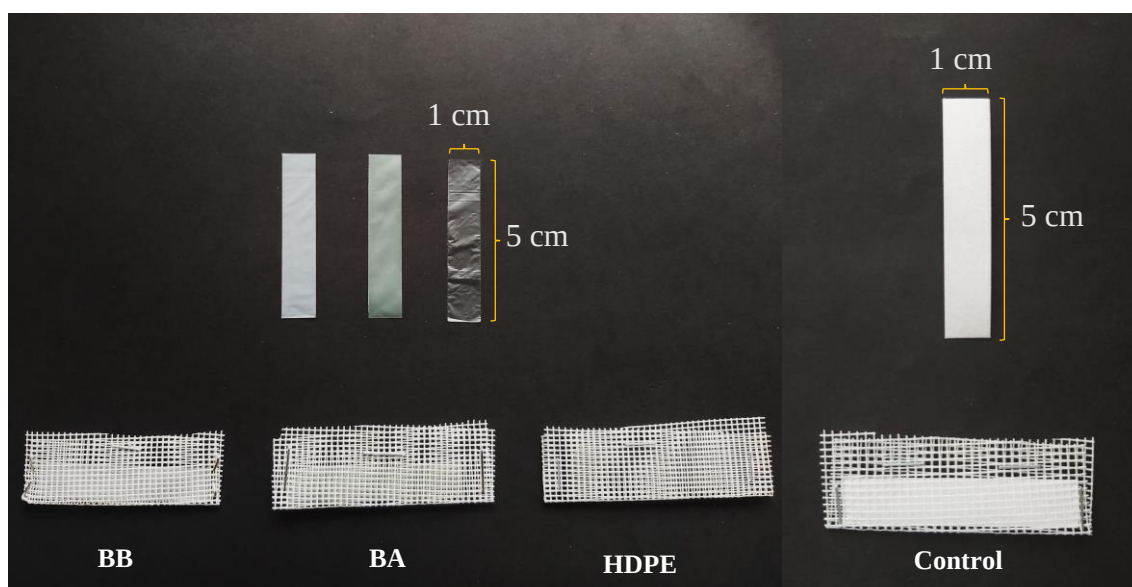


Figure 3.3. Strip samples of Bioplastic B (BB), Bioplastic A (BA), HPDE and control used in trials.

3.2.3. Composting mixture

The composting mixture used, with a total weight of 583 g per reactor, was based on the study of Vaverková, Toman [76], being detailed in Table 3.1.

Table 3.1. Composting mixture used in the laboratory trials [76].

Component	Ratio (wt. %)	weight per reactor (g)
Compost	10	58.3
Bark and wood chips	36	210
Biowaste	54	315

The compost used was obtained from the industrial composting plant where the industrial scale composting (IC) trials were carried out, namely LIPOR, and served as inoculum for the process. Bark and wood chips were obtained through green waste from the maintenance of a private garden.

For the proportion of the biowastes to be used in the mixture, the study by Ghinea, Apostol [80] was followed, in order to approximate the C/N ratio of the mixture to 35. This value was chosen, taking into consideration the subsequent addition of compost to the mixture. Although information on its composition or C/N ratio was unknown, as it was from an intermediate composting process, so it would in principle contribute to a decrease in the C/N ratio considering an initial optimum value. Thus, the value of 35 was chosen in order to bring the C/N ratio of the composting mixture closer to the upper range of optimum values for composting (Table 2.3).

The biowastes used consisted of 2 to 3 mm strips of peels from various fruits and vegetables typical of household waste, to better simulate a conventional biowaste mixture constitution. The mixture used is shown in Table 3.2.

Table 3.2. Biowastes mixture composition [80].

Biowaste	Weight per reactor (g)
Apple	50
Banana	38
Orange	25
Kiwi	25
Potato	63
Carrot	50
Cabbage	63

Each reactor used in IC or sHC trials consisted of 583 g of the already mentioned composting mixture (Table 3.1), together with 7 g of strips of the material to be studied, in order to obtain a sample/composting mixture ratio of 1.2 %, according to the study of Vaverková, Toman [76]. It should be noted that not all strips were removed over time for sampling. In fact, only 48 strips were taken in total from each reactor over the 12 weeks of trials, thus, only those strips were wrapped in the previously mentioned plastic mesh. The initial appearance of the reactors is presented in Figure 3.4.



Figure 3.4. Initial appearance of a full reactor (BB).

The composting mixture was characterized before sHC trials for C/N ratio determination and before and after the sHC trials in terms of moisture, volatile solids and pH. All parameters were determined in duplicate, and compost samples from the composting of control and BA strips were used for the characterization of the composting mixture after sHC.

The C/N ratio was determined by ultimate analysis (carbon (C), hydrogen (H), nitrogen (N) and Sulfur (S) percentual content) in a Vario micro cube analyzer (Elementar GmbH) by combustion of the sample at 1050 °C. Oxygen (O) content was determined in a Vario micro cube analyzer (Elementar GmbH). Moisture was determined by drying the samples at 105 °C for 24 hours in an oven (INDELAB Serie AI), and volatile solids by successive combustion in a muffle furnace at 550 °C for 2 hours. Finally, the pH was measured (Crison pH meter GLP 21) by analysis of the supernatant of a mix of 60 mL of composting mixture with 300 mL of distilled water after 1 hour in magnetic stirring [81].

3.2.4. Simulated Industrial Composting trials

Only BA was studied under sIC conditions due to space constrains, and also due to the fact that it was the only one presenting certification for industrial composting.

Thus, two reactors (duplicate), were introduced in an oven with natural convection (J.P. SELECTA - "Digitheat" Series) (Figure 3.5) at a temperature of 58 °C, as mentioned in EN 13432 via ISO 14855:1999 and in the literature review carried out (Table 2.4).



Figure 3.5. Experimental set-up for simulated industrial composting trials.

3.2.5. Simulated Home Composting trials

For the sHC trials, reactors containing strips of BA, BB, HDPE plastic and control paper strips were studied in duplicate, thus making a total of 8 reactors.

The reactors were inserted in a laboratory facility assembled specifically for that purpose (Figure 3.6), which consisted of a housing made of insulating material (Extruded Polystyrene XPS), in order to avoid excessive heat loss from the process, as also to guarantee no light exposure of the reactors, to better simulate the conditions in the interior of a composting pile.



Figure 3.6. Experimental set-up for simulated home composting trials.

3.2.6. Process Monitoring and sampling

During both laboratory trials (sHC and sIC), temperature, moisture, mixing and aeration of the reactors were periodically controlled as described by Vaverková, Toman [76] and in accordance with EN 14806 and EN ISO 20200 (Table 3.3) [82, 83].

Table 3.3. Composting procedure [76].

Composting day	Procedure
0	1. Reactors preparation 2. Reactors weighting
1, 2, 3, 4, 7, 9, 11, 14	1. Reactors weighing 2. Water addition to restore initial mass 3. Reactors mixing
8, 10, 16, 18, 21, 23, 25, 28	1. Reactors weighting 2. Water addition to restore initial mass
30, 45	1. Reactors weighting 2. Water addition to restore 80% of the initial mass 3. Reactors mixing
From 30 to 45 and from 45 to 60, twice a week	1. Reactors weighting 2. Water addition to restore 80% of the initial mass
From 60 to 84, twice a week	1. Reactors weighting 2. Water addition to restore 70% of the initial mass

The moisture control was performed, as mentioned in Table 3.3, by the difference in weight of the reactors, adding water until the desired value was reached (initial weight of the reactor, or a percentage of it). However, and as referred in EN 14806 and EN ISO 20200, the optimum water content is reached when the composting material is wetted but there is no free water, i.e., it has not yet reached saturation. This can be directly evaluated by manual squeezing of the composting matter. In the ideal conditions of moisture, no water should come out, but the composting material should stick to the palm of the hand [76]. In this way, the moisture control referred in Table 3.3 was also adjusted manually whenever it was considered necessary. Distilled water was used in order to adjust moisture.

The mixing and aeration of the mixture were carried out manually, by stirring by hand the composting material. Regarding the temperature, in the sIC it was kept constant automatically, and in sHC it was registered at the days referred in Table 3.3.

As previously mentioned, in the laboratory scale tests, 48 strips were removed from each reactor over time in order to assess their degree of disintegration and modification of their mechanical properties. Thus, fortnightly, 8 strips were removed from each reactor, washed carefully in order to avoid their disintegration and oven dried (INDELAB Serie AI), for 3 days at 40 °C. After drying, the strips were removed from the plastic mesh for characterisation [76, 82, 83].

3.3. Industrial scale trials

The industrial scale composting trials (IC), were carried out in a composting tunnel at LIPOR's composting plant. The composting process in tunnel (active composting phase), was performed during three weeks (23 days), followed by tree weeks of maturation in pile, accordongly to section 2.6. The materials analysed were the same of the laboratory assays, namely “trash” bags of BA, BB (Figure 3.1), and HDPE with an experimentally determined mass of 17.6, 14.2 and 1.9 g, respectively.

The composting process was not changed in any aspect from the usual pratice, and the samples were submitted to composting together with selectively collected biowaste. In this way, the samples experienced the usual conditions in which the industrial process unfolds, which is described in Appendice B.

In order to avoid the loss of the samples during the process, burlap bags were used. In each of these bags, a torn bag of the material to be studied was inserted, as well as 4 strips of 5x1 cm (wrapped in plastic mesh) of the respective material, together with a small amount of composting material (so as to ensure the total embedding of the samples in the compost mixture), as well as a strip of control paper (55x4 cm). All trials were carried out in duplicate, making a total of 8 burlap bags used.

As an example for BB, a torn bag was inserted into a burlap bag, together with 4 strips, as illustrated in Figure 3.7. The bags were torn in order to simulate their passage through a bag opener and in order to increase their surface area of contact.



Figure 3.7. Sample of torn bioplastic B bag (left) and bioplastic B bag and corresponding strips inside a burlap bag (right).

The samples inside the burlap bags were horizontally placed along the compost tunnel and then covered, as illustrated in Figure 3.8.



Figure 3.8. Arrangement of the samples in the composting tunnel before covering (left) and after covering (right).

3.4. Soil incubation trials

In order to simulate the uncontrolled disposal into nature of BA, BB and HDPE bags, these were buried in the soil at a depth of 20 cm, as mentioned by Vaverková, Adamcová [84], for the same period as the laboratory scale trials - 12 weeks. As illustrated in Figure 3.9, a strip of control filter paper was placed between each bag studied. The trials were conducted in duplicate on a private agricultural site.



Figure 3.9. Incubation trials on soil before cover (left) and after (right).

3.5. Determination of weight loss

As described in section 3.2.6, the 8 strips of each material were weighted (Sartorius M-Power Precision Balance AZ124) in duplicate, and their degree of disintegration (D) [%] calculated, according to the equation (2).

$$D = \frac{m_i - m_f}{m_i} \times 100 \quad (2)$$

where m_i [g] corresponds to the initial mass of 8 strips of a given studied material and m_f [g] to the mass of 8 strips of the same material after 2, 4, 6, 8, 10 and 12 weeks of composting (duplicates).

3.6. Tensile properties determination

The mechanical properties of the plastic strips over time were evaluated by characterising their tensile properties. The tests were performed on a Shimadzu EZ-LX Compact Table-Top Universal / Tensile Tester with a maximum capacity of 5 kN, equipped with wedge grips. Tensile strength and strain at break were determined for the strips (5x1 cm) taken after 2, 4, 6, 8, 10 and 12 weeks of composting. Tensile tests took place at room temperature (≈ 23 °C) and using a speed of 50 mm/min [85].

With respect to force and elongation values, the following properties were determined according to ISO 527-1:2012 [86].

Tensile strength:

$$\sigma_m = \frac{F_{max}}{A_0} \quad (3)$$

where σ_m [N/mm²] corresponds to tensile strength, F_{max} [N] to the maximum force applied and A_0 [mm²] to the strip's initial cross section.

Strain at break:

$$\varepsilon_b = \frac{\Delta l}{l_0} \times 100 \quad (4)$$

where ε_b [%] corresponds to strain at break, Δl [mm] to the increase of the strip's length and l_0 [mm] to its gauge length.

3.7. Scanning Electron Microscopy analysis

In order to evaluate the change in surface morphology of the strips after laboratory and industrial trials, a Scanning Electron Microscope (SEM) analysis was conducted. The SEM / EDS exam was performed using a High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: FEI Quanta 400 FEG ESEM / EDAX Genesis X4M. All samples were previously coated with Au/Pd thin film, by sputtering, for 100 seconds and with a 15 mA current through SPI Module Sputter Coater equipment.

All the experimental procedure related to the SEM analysis took place and was carried out by technicians from CEMUP - "Centro de Materiais da Universidade do Porto" (in english: Materials Centre of the University of Porto).

3.8. Fourier Transform Infrared analysis

Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed using a FTIR-6800 spectrometer equipped with a DLaTGS detector (JASCO, Japan) with a MIRacle single reflection horizontal ATR attachment (PIKE Technologies, USA), with a ZnSe crystal. The measurements were accomplished with a 4 cm⁻¹ resolution of the 4000 – 600 cm⁻¹ region, with 256 scans/sample. Background (empty and clean system) was performed for every two samples analysed, and the baseline correction was performed with the Spectra Manager software for every sample. In addition to the analysis of the plastics strips samples, a commercial virgin LDPE film sample (Goodfellow, UK) was also analysed as reference. All strips were analysed once.

4. RESULTS AND DISCUSSION

4.1. Composting mixture

As mentioned in section 3.2.3, the composting mixture was characterised before and after the sHC process and the results are shown in Table 4.1.

Table 4.1. Characterisation of the composting mixture before and after the composting process.

	Before sHC	After sHC
Ultimate analysis	39% C, 5% H, 2% N, 41% O	-
C/N ratio	22	-
pH	6.5	9.4
Moisture (%)	70	75
Volatile solids (VS) (%)	92	75

The C/N ratio of the mixture used is, as expected, lower than the value of 35 used as reference for the preparation of the biowaste mixture. This decrease could be explained by differences in the C/N of the vegetables and fruits used and also by the influence of the C/N ratio of the compost, which was unknown.

It was also verified an increase in the pH of the mixture, which may be due to the synthesis of organic acids by the various microbial populations, thus increasing the pH of the medium. The generation of ammonia as a result of the decomposition of urea and proteins can also contribute to a rise in the pH of the medium [58, 70]. Additionally, and as mentioned by Martinho and Gonçalves [71], the final compost usually presents a slightly alkaline pH, between 7.5-9.0. Finally, the decrease of about 18.5% in volatile solids is an indicator that the composting process has occurred, verifying the mineralization of organic matter.

4.2. Visual Analysis

4.2.1. Simulated Home Composting trials

Regarding the visual analysis of the strips throughout the 12 weeks of sHC (Figure 4.1), it is noteworthy that BA presented the greatest change in terms of fragmentation, loss of material and change in colour. The analysis of the BB strips also reveals a change in colour, however, not comparable in intensity to that visualized in the BA strips. However, BB samples also seems to present physical degradation. HDPE strips showed no visual alteration over time, as expected. Regarding the control, a complete degradation was verified after 12 weeks, being evidenced that after 10 weeks, only powder residues were present.

The average temperature at which the sHC trials occurred, is represented in Appendix A. It should be noted that the average temperature recorded over the 12 weeks of testing was 18.8 °C, which is within the typical values for this type of composting. However, it should be also noted that, although the tests have occurred during a period of mild temperatures (March to May), since the laboratory where they were performed has a considerable ceiling height, significant temperature ranges could be recorded, as can be seen in Appendix A.

4.2.2. Simulated Industrial Composting trials

The visual analysis of the sIC trials (Figure 4.2), shows that the degradation of the control strips over time was very limited, being only observed a relevant change after 8 weeks, putting into question whether composting conditions were adequate. In an opposite manner, the complete deterioration of the BA strips was observed after 8 weeks, with only 1 strip out of 8 having being found at that time, and at the end of 10 weeks no trace of them was found. At the end of 12 weeks, 1 strip was however still removed, being the fact attributed to the sampling procedure and the nature of the process (e.g., natural heterogeneity of the material and its exposure to temperature and humidity conditions).

4.2.3. Industrial Composting

It is clearly observed that the IC process was much harsher to the strips when compared to the laboratory tests (Figure 4.3), as expected. Effectively, only residues remained for

BB, and for BA, only one strip was found, together with the residues of another. The HPDE strips were unchanged.

When the degradation of whole bags (torn) of the same materials is analysed (Figure 4.4), despite a considerable change in their appearance and morphology, they are still perfectly identifiable, with the HDPE remaining unchanged, as expected. The maturation process seems to have contributed for a further alteration in both BA and BB bags, not being, however, of high proportions.

No trace of control filter paper strips was found after the industrial composting process in tunnel, indicating their complete biodegradation, thus validating the results obtained.

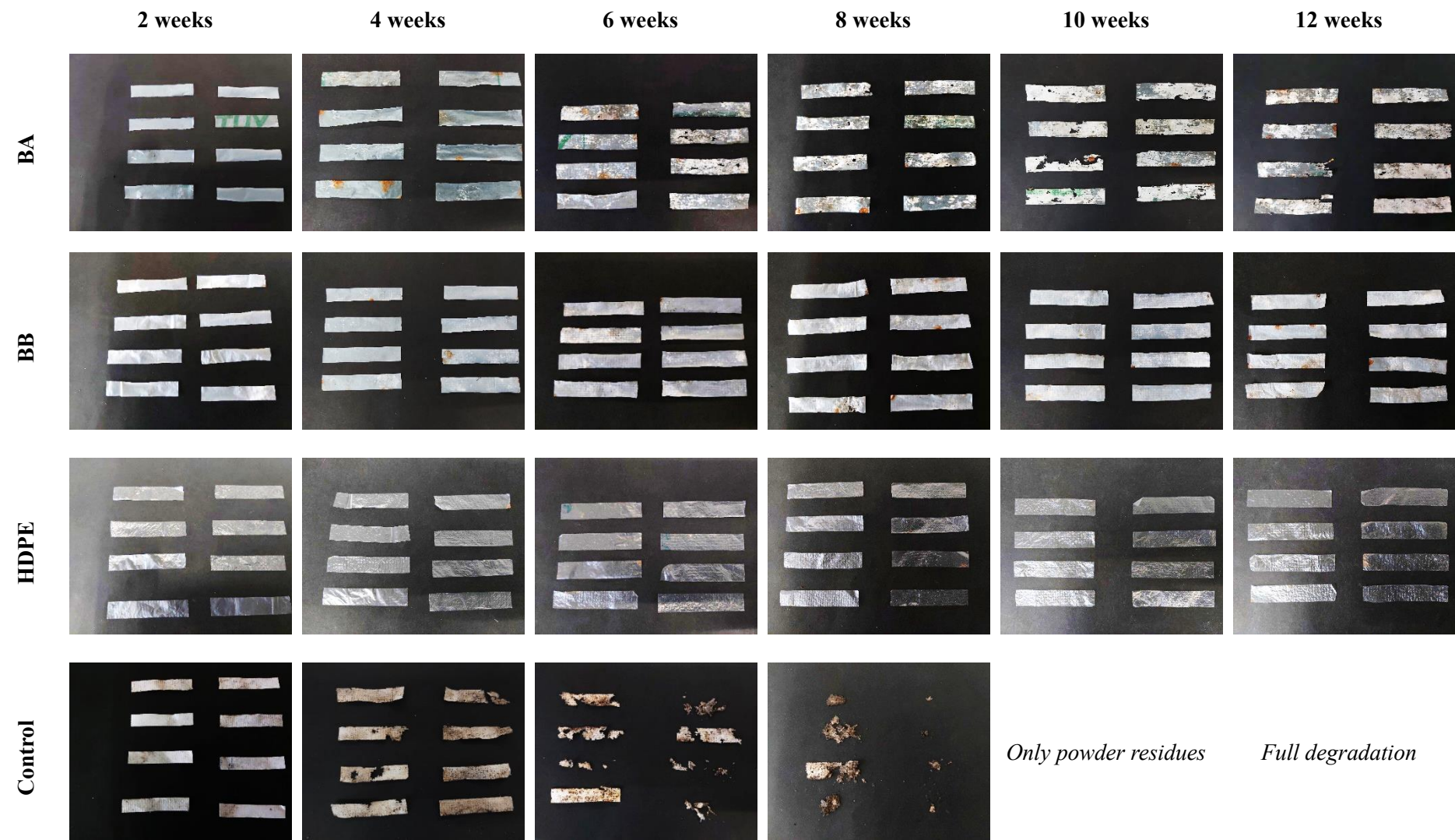


Figure 4.1. Visual appearance of strips of the materials under analysis, Bioplastic A (BA), Bioplastics B (BB) and High-Density Polyethylene (HDPE) throughout the 12 weeks of simulated home composting trials (sHC). Control refers to cellulose filter paper strips.

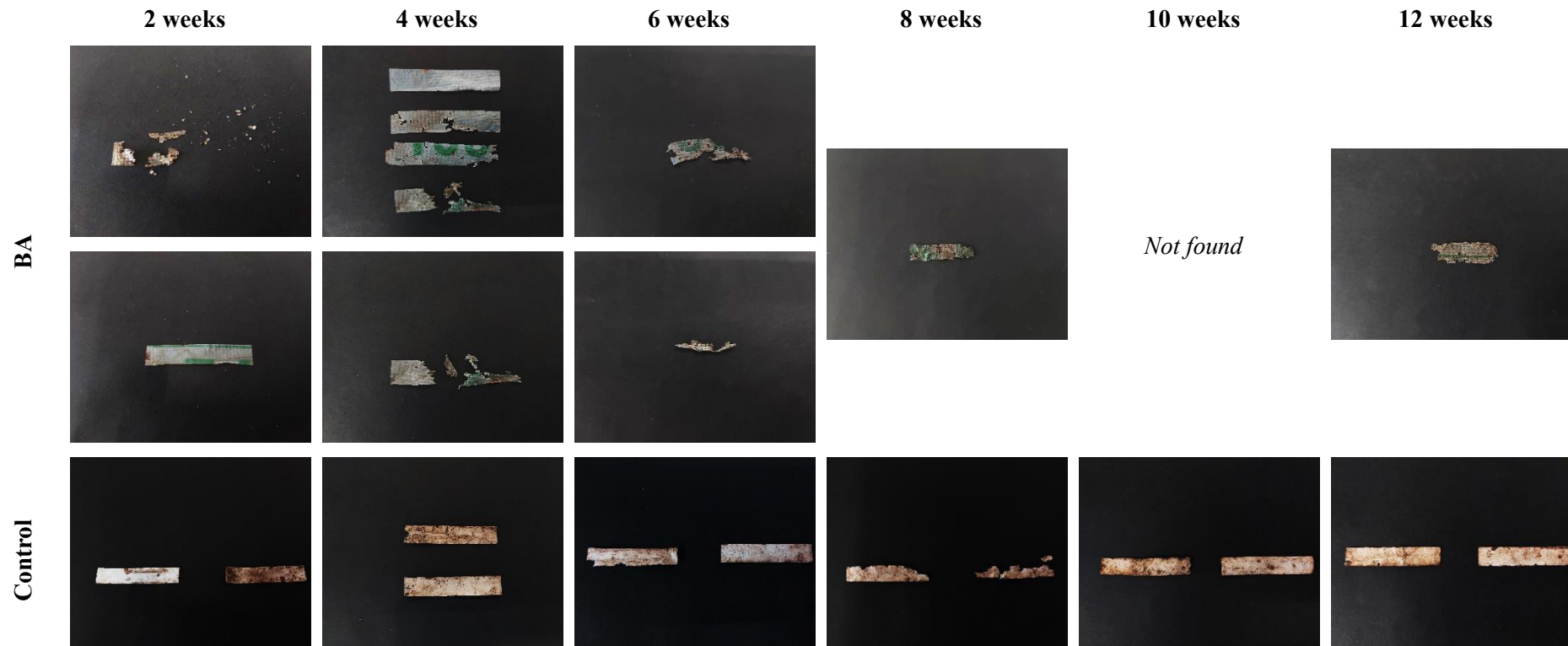


Figure 4.2. Visual appearance of strips of Bioplastic A (BA), throughout the 12 weeks of simulated industrial composting trials (sIC). Control refers to cellulose filter paper strips.

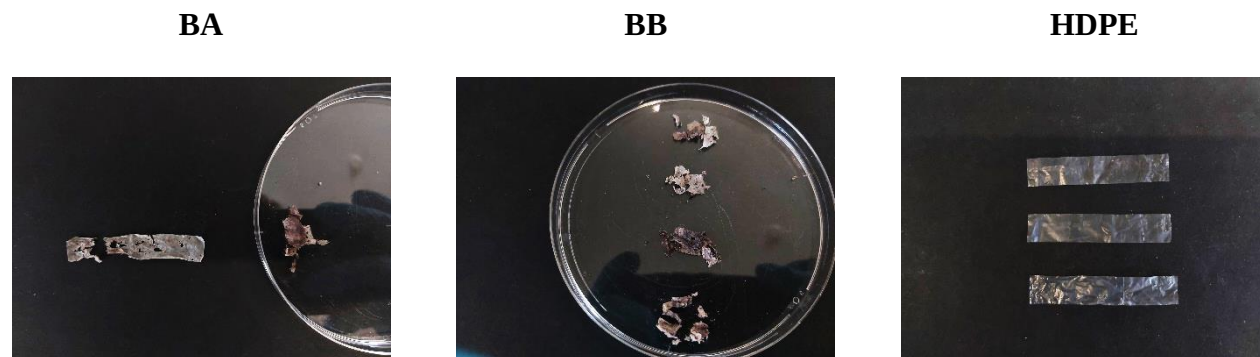


Figure 4.3. Visual appearance of strips of the materials under analysis, Bioplastic A (BA), Bioplastic B (BB) and High-Density Polyethylene (HPDE) after 3 weeks of active industrial composting process (IC).

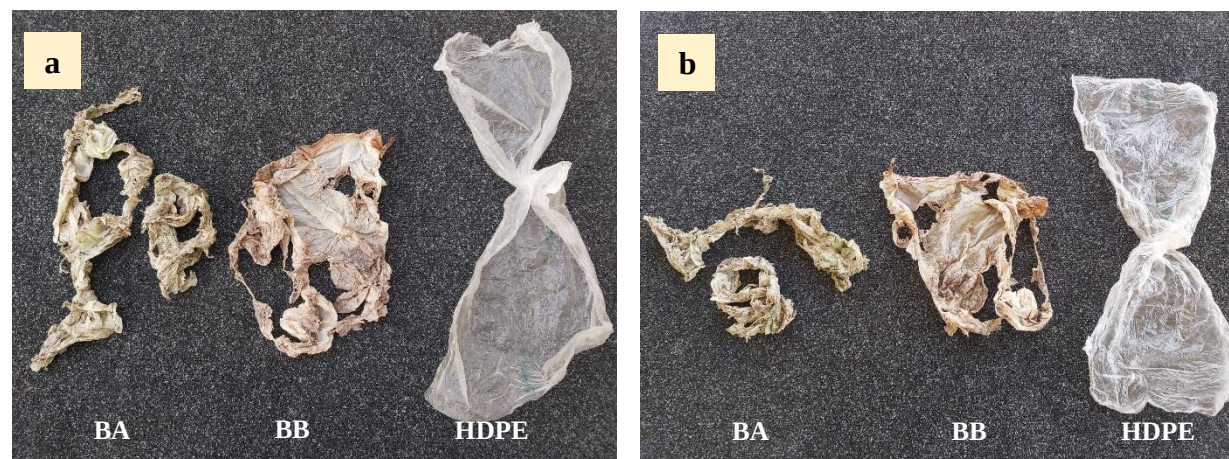


Figure 4.4. Visual appearance of the bags of the materials under analysis, Bioplastic A (BA), Bioplastic B (BB) and High-Density Polyethylene (HPDE) after the (a) active phase (3 weeks) and (b) maturation phase (3 weeks) of the industrial composting process (IC).

4.3. Weight loss

In order to evaluate the weight loss of the strips and bags over time, their initial and final weight were determined, being the initial results shown in Table 4.2.

Table 4.2. Initial weight of the strips and bags of the materials under study.

Material	Strips ^a weight (g)	Bag weight ^b (g)
Bioplastic A	0.015 ± 0.002	17.5665 ± 0.0007
Bioplastic B	0.0140 ± 0.0002	14.199 ± 0.003
Plastic – HDPE	0.003 ± 0.001	1.920 ± 0.001
Control – cellulose paper	0.0433 ± 0.0007	-

^aEach value corresponds to the average of weighing 8 strips in duplicate for bioplastic A and B, and in triplicate for HDPE. For bioplastic strips A and B, the absolute error is presented, and for HDPE strips, the standard deviation. ^bEach value corresponds to weighing of one bag in triplicate. The respective standard deviation is presented.

4.3.1. Simulated Home Composting trials

Using equation (2) and according to the previously mentioned sampling method, the weight loss was calculated for the strips of each material over time subjected to the sHC process (Figure 4.5).

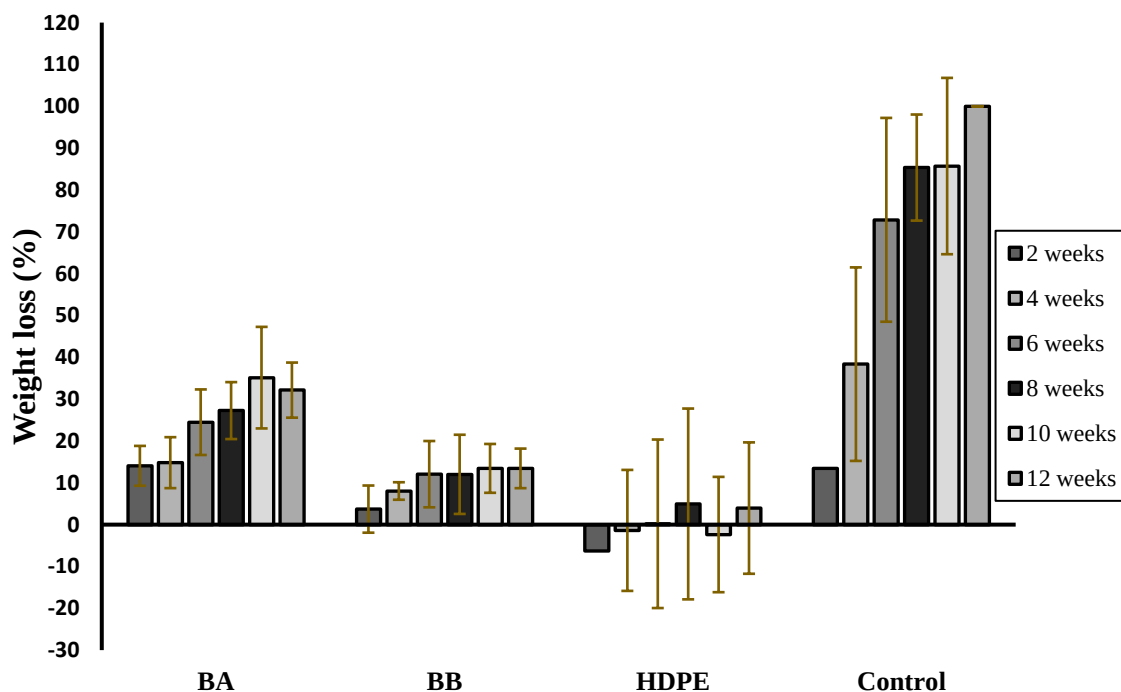


Figure 4.5. Weight loss of sample strips of Bioplastic A (BA), Bioplastic B (BB), and High-Density Polyethylene (HDPE), subjected to simulated home composting (sHC) over 12 weeks. Each column corresponds to the duplicates average considering 8 strips each. Error bars correspond to the standard deviation. Control refers to cellulose filter paper strips.

By the analysis of the Figure 4.5 it is verified the total weight loss of the control strips, reaching a value of 100% after 12 weeks. This fact indicates that the necessary conditions for the composting process have been reached, leading to the composting of the control strips. Regarding BA and BB strips, their weight loss increased over time, although never exceeding 35% for BA and 15% for BB, with BA strips consequently showing a better performance. The verified weight loss could have been due to the combined effect of their decomposition by biological processes, as well as to their physical fragmentation into small pieces. Regarding the plastic strips (HDPE), their weight loss was not significant, having occurred in most cases a weight increase, most probably due to some contaminations that have subsisted to the strip washing and cleaning process. Thus, it should be noted that the weight loss values obtained in all the materials studied, may actually be higher in reality, due to the extreme difficulty in removing the contaminations remaining in the strips.

The weight loss results reinforce therefore the visual analysis already presented (section 4.2), leading to the conclusion that BA underwent the greatest biological degradation, while BB presented only slight degradation.

Finally, reference should be made to the standard deviations obtained, which are sometimes considerably high. In fact, factors such as the position of the strip in the reactor or its grouping with other strips can affect the exposure of the strip to the degradation conditions, meaning that the strips removed from the same reactor on the same day can present variability in terms of weight. This is expected considering the nature of the process and the heterogeneity of the biodegradable materials in the composting reactor.

4.3.2. Simulated Industrial Composting trials

The results concerning the weight loss of the samples subjected to sIC are presented in Figure 4.6.

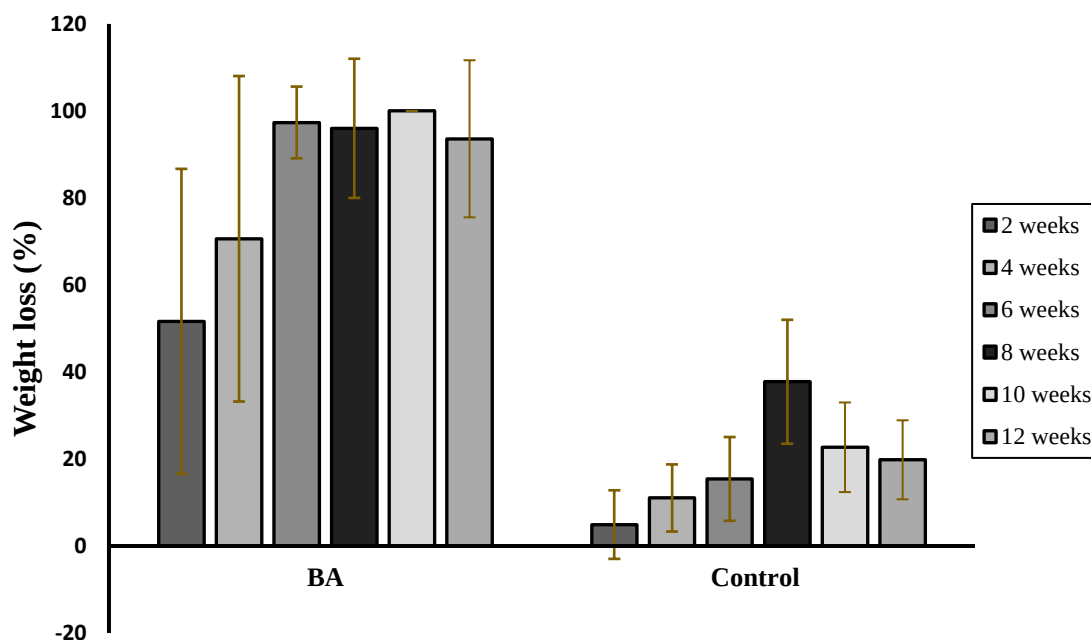


Figure 4.6. Weight loss of sample strips of Bioplastic A (BA), subjected to simulated industrial composting (sIC) over 12 weeks. Each column corresponds to the duplicates average considering 8 strips each. Error bars correspond to the standard deviation. Control refers to cellulose filter paper strips.

The results show that even at the end of 12 weeks, the maximum weight loss of the control strips was only 40% (achieved after 8 weeks). In fact, the analysis of the control suggests that appropriate composting conditions were not reached, given the reduced weight loss obtained over time and the results of sHC previously presented. However, it can be observed that BA strips have almost reached a total weight loss (95%) at the end of the process (12 weeks). This fact leads to conclude that a thermal degradation of the bioplastic strips has occurred, thus resulting in a fragmentation/disintegration process, but not necessarily biological decomposition, since the control did not follow this evolution. This raises serious questions about the potential of these materials to release meso- and microplastics into the environment, since even though they did not compost, they physically degraded. The emission of meso- and microplastics, as mentioned in section 2.3.2 above, is highly harmful to living beings, becoming a source of pollution and contamination.

The absence of appropriate composting conditions in these trials, may have been caused by a low moisture content of the mixture (although being controlled as referred in section 3.2.6), since the reactors were permanently exposed to a constant temperature of

58 °C. Besides the moisture corrections performed, the mixture in sIC process was possibly dry after a short time of the adjustment, not guaranteeing the required composting conditions.

The high values of standard deviations are related to the high variability between conditions of each 8 strips taken from the same reactor at the same moment, as previously highlighted.

4.3.3. Industrial Composting

As mentioned in section 3.3, BA, BB and HDPE bags and their respective strips were submitted to an IC process in tunnel (active phase of composting). Afterwards, and due to the already high degree of deterioration of the strips, only the bags of the different materials under study were subjected to the subsequent maturation phase in composting piles. The weight loss results obtained are presented in Figure 4.7.

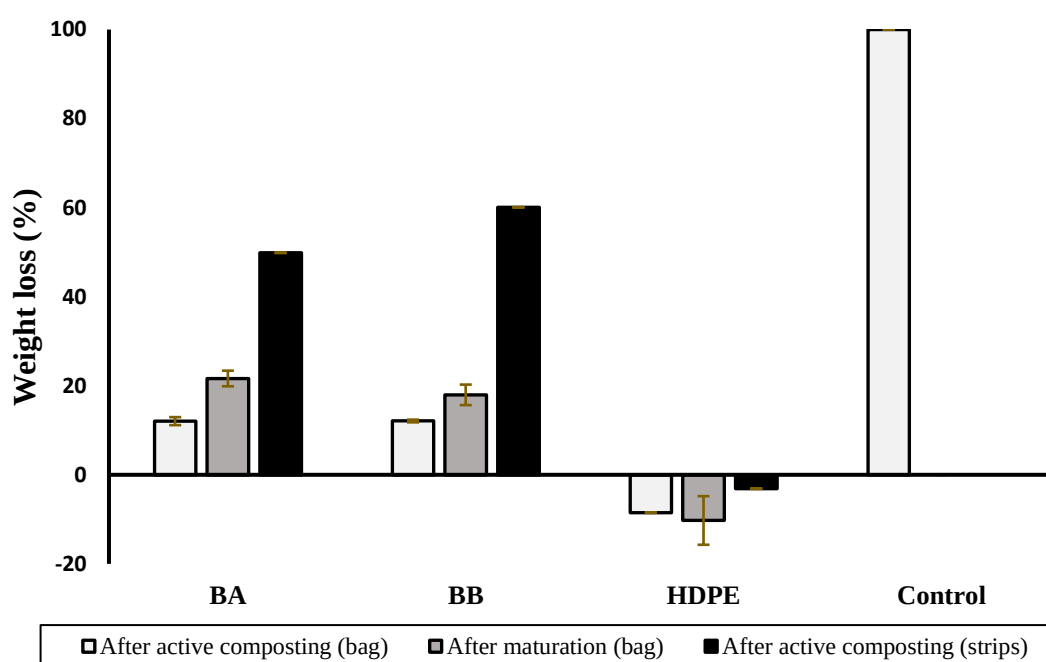


Figure 4.7. Weight loss of sample strips and bags of Bioplastic A (BA), Bioplastic B (BB) and High-Density Polyethylene (HDPE), subjected to industrial composting (IC) over 3 weeks of active phase and 3 weeks of maturation. Each column corresponds to the duplicates average considering 4 strips each or 2 bags. Error bars correspond to the standard deviation. Control refers to cellulose filter paper strips of 55x4 cm, placed together with each material to be studied.

As expected, the highest weight loss values for both bioplastics were obtained for the strips, with a maximum of 50% for BA and 60% for BB. This is certainly related to the very small size of the strips and consequently a significantly higher surface area when

compared to the bags. It is also important to note that the maturation phase contributed to the increase of around 10% in the weight loss of the bags, comparatively to the values achieved at the end of the active composting phase, attaining a final weight loss of 22% for BA and 18% for BB. Regarding the control strips, it was verified a total degradation after the active composting phase, proving that the composting conditions were achieved.

The increase in weight in both HPDE strips and plastic bags highlights once more the difficulty in removing contamination adhered to the surface of the materials after the composting process and emphasises further that it is non-biodegradable.

The weight loss (and visual analysis) of BA and BB for the IC conditions are particularly relevant, since they allow to objectively analyse the behaviour of these bioplastic bags when submitted to the organic recovery processes currently in use, in the conditions in which they are most likely to arrive (whole bags). Even if further analyses (as presented later on), may allow to conclude that effectively these bioplastics have started their biodegradation process, the values of weight loss and visual analysis carried out already indicate that they constitute contaminations for the current processes of industrial composting. In fact, these bags were not only easily identified visually, but also showed only a slight loss of mass. In this way, questions of disruptions in the industrial composting processes and quality of the compost obtained are raised.

The use of strips, apart from the aforementioned reasons of suitability for mechanical properties testing, should not be neglected. These effectively indicated that the biodegradation process occurred when these materials were subjected to IC, as evidenced by their weight loss.

4.4. Tensile Properties

Given the characteristics of the plastic strips, it proved impossible to follow specifically any existing standard for the tests performed, as the use of an extensometer, as well as the marking of the gauge marks was not possible. Furthermore, the fragility and lightness of the strip made it very difficult to guarantee that it was straight and aligned with the clamps. Finally, the occasional slipping and deviation of the strips in the positions of the tethers/clamps stands out. However, the tests were carried out as rigorously as possible (Figure 4.8).



Figure 4.8. Example of a tensile test for a strip of BA (Bioplastic A).

In order to make use of equations (3) and (4), and therefore to calculate the cross section of each strip, the thickness of the BA, BB and HPDE bags was measured (MITUTOYO 293-101 Digital Micrometer), obtaining the average thickness values of 0.023 mm for BA, 0.019 mm for BB and 0.010 mm for HPDE.

4.4.1. Tensile Strength

The results obtained related to the tensile strength of the strips over the 12-week period for both sIC and sHC trials are shown in Figure 4.9.

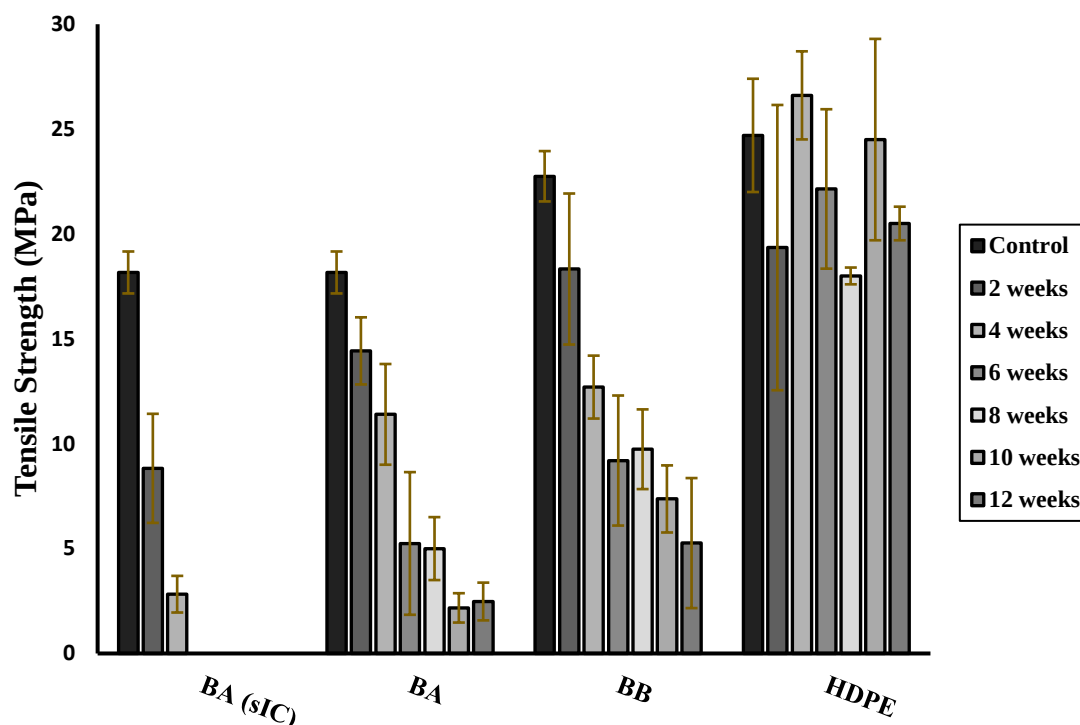


Figure 4.9. Evolution of the tensile strength of Bioplastic A (BA), Bioplastic B (BB) and High-Density polyethylene (HDPE) sample strips over 12 weeks. BA (sIC) represents the evolution of the tensile strength of BA strips under simulated industrial composting conditions (12 weeks), whereas the remaining results are referred to simulated home composting conditions (12 weeks). In this case, the control corresponds to a virgin strip of the respective material.

From the analysis of the Figure 4.9, it is observed an expressive loss of tensile strength for both bioplastics, in both conditions presented. In fact, at the end of the 12-week period, BA and BB experienced 86% and 87% loss in their tensile strength, respectively. It should be noted that in sIC, BA only shows results up to 4 weeks (85% loss), because after that period no strip with conditions to be tested was found, which indicates a complete loss of physical integrity. The results also show that, globally, BB has a higher tensile strength when compared with BA.

Regarding the HDPE strips, there is some inconsistency in the results. However, by analysing the respective standard deviations, the values obtained do not seem to indicate any trend towards a change in the tensile strength, being this also observed in the literature [87]. The value obtained for the control is also within the ranges indicated in the literature for HDPE (23.0-29.5 MPa) [88].

In short, it can be inferred from the data analysis that there was a clear loss of tensile strength in both conditions (sIC and sHC), for the analysed bioplastics, which may be due to biological degradation in the case of the sHC process and due to fragmentation in the case of the sIC, in consistency with previous discussions (weight loss and visual appearance).

4.4.2. Strain at break

The strain at break results are shown in Figure 4.10.

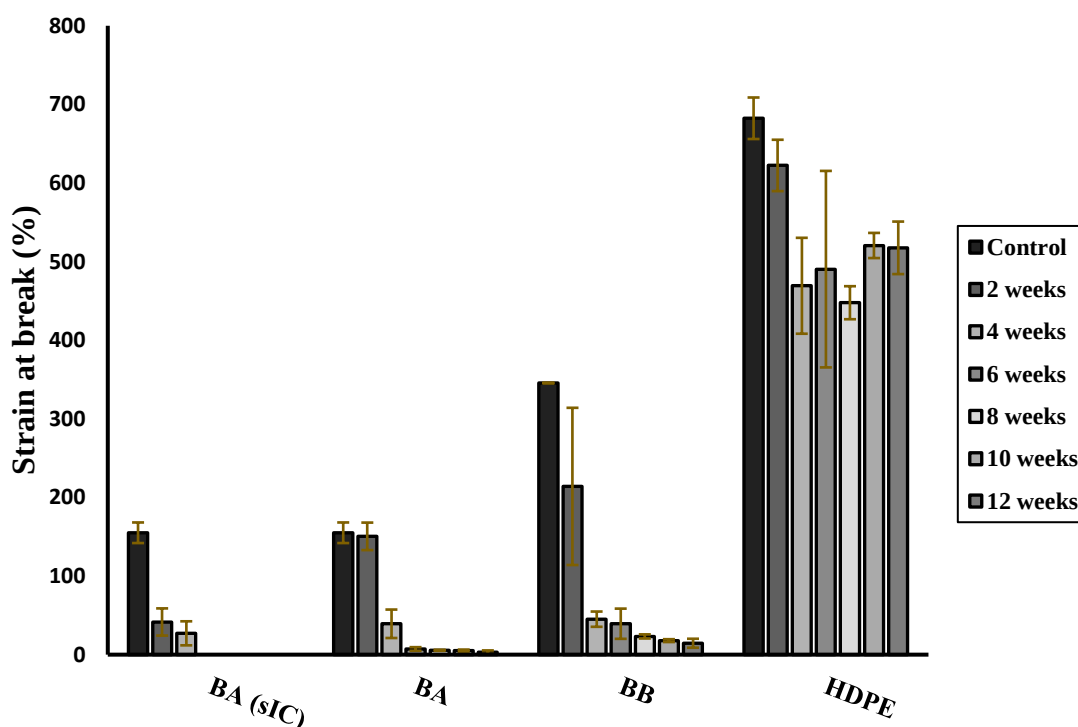


Figure 4.10. Evolution in strain at break of Bioplastic A (BA), Bioplastic B (BB) and High-Density polyethylene (HDPE) sample strips over 12 weeks. BA (sIC) represents the evolution of the strain at break of BA strips under simulated industrial composting conditions, whereas the remaining results are referred to simulated home composting conditions. The control corresponds to a virgin strip of the respective material.

As observed for tensile strength, there was an expressive decrease of around 98% in strain at break for both bioplastics in the two conditions studied, thus indicating that the respective bioplastic strips progressively elongated less until reaching rupture, as expected, therefore indicating a marked loss in their mechanical properties. A strong decrease of this parameter is seen both for BA and BB after 4 weeks. Again, for BA under sIC, after 4 weeks, no strip suitable for analysis was found.

For HDPE strips, the value obtained for the control is within the range reported in the literature (600-1350%), thus validating the results obtained [88]. In addition, the loss from about 700% to about 500% at the end of 12 weeks, although not highly expected (given

the non-biodegradability characteristics of the polymer), is described in the literature [89, 90]. The presence of inorganic contaminants in the composting mixture may be at the origin of the mentioned elongation loss, as well as an increase in the fragility of the material itself. [91].

4.5. Scanning Electron Microscopy analysis

The results of the SEM analysis for BA, BB and HPDE are shown in Figure 4.11.

In relation to the analysed HPDE strip, it is remarkable how minor its morphological change was, according to the different processes to which it was submitted; however, a change in its morphology seems to have occurred. The IC process appears to be the most abrasive, causing small bumps to appear on the polymer surface, while also causing an orientation of the polymer fibres. The morphology after sHC is quite similar to that of the virgin polymer, with small bumps on the polymer surface observed, but with lower intensity than those observed under IC conditions. Thus, and as expected, only a small modification in the surface morphology of the polymer was visualised, corroborating the visual and weight loss analysis performed, as observed in reported studies [74].

When analysing BA, the high difference between its polymeric structure is easily denoted. In fact, unlike a smooth surface, the polymer presents a composite structure, with embedded granules, possibly of starch, as identified by other authors [74, 92]. After IC, the morphology greatly changes, and it is visible that the polymer surface was colonised by several microbial consortia, and also the appearance of long fibres is observed, which may correspond to less degradable parts of the material, which emerged as a consequence of the biodegradation process as previously reported [74, 93]. It should be noted how the granular structure has disappeared leading to the appearance of pores. The sHC conditions also showed a total loss of the initial polymer appearance, resulting in a porous surface with lumps of polymer material, as seen by other authors [74].

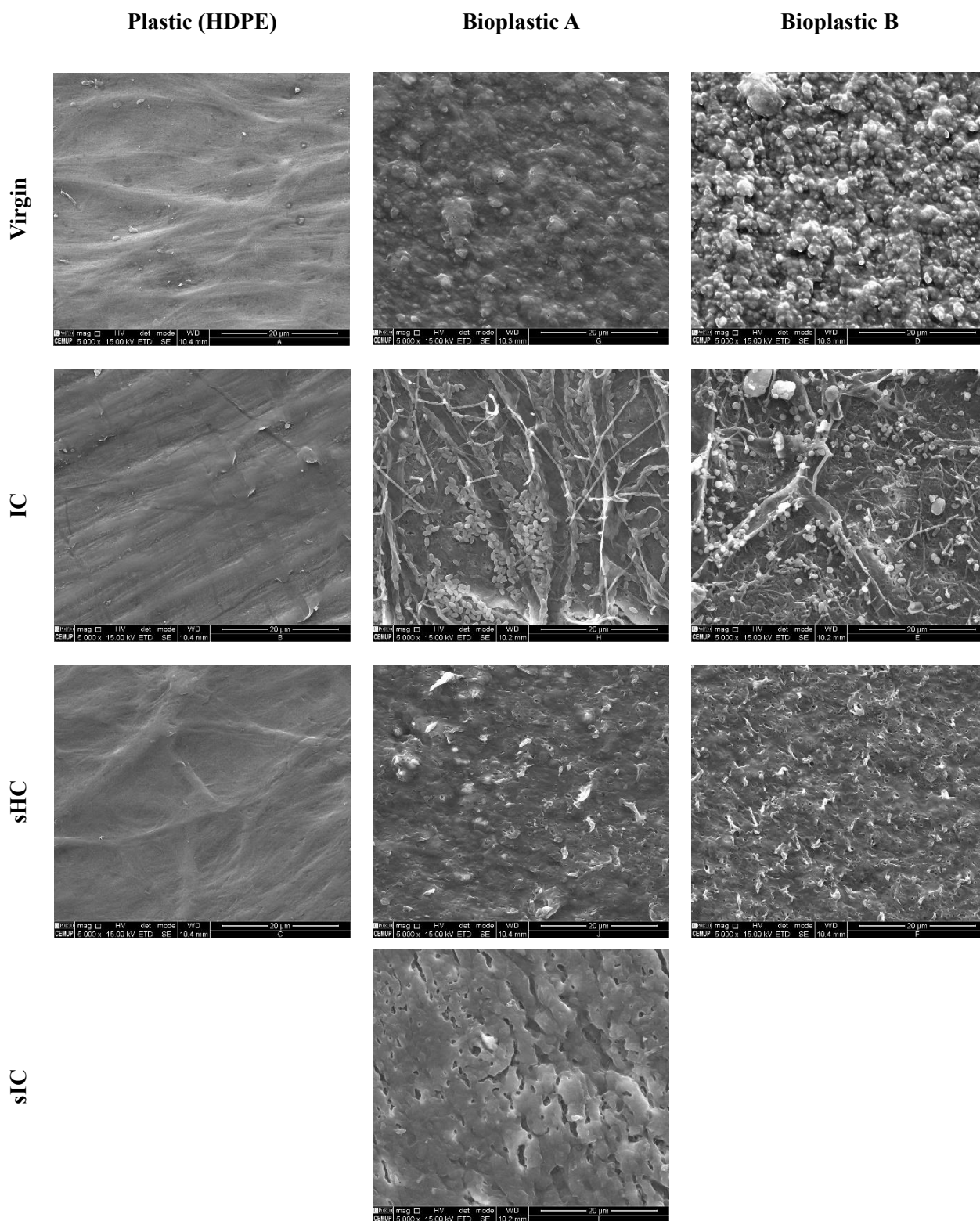


Figure 4.11. Scanning Electron Microscopy micrographs for Bioplastic A (BA), Bioplastic B (BB) and High-Density Polyethylene (HDPE) before undergoing composting process (virgin), and after 3 weeks of industrial composting (IC), 12 weeks of simulated home composting (sHC) and 12 weeks of simulated industrial composting (sIC). Magnification is 5000x.

In this case, no microbial colonisation was observed, thus indicating that the sHC process was less intense when compared to IC, as also previously discussed. Finally, after sIC, the porous structure is again denoted, with high cracks and breaks, with no microbial colonisation being observed, corroborating the visual inspection and weight loss already presented, indicating that only material fragmentation should have occurred.

The analysis of BB is very similar to that of BA. A similar composite structure is seen but appears more prominent and with a greater amount of granules. After IC the same appearance due to microbial colonisation is observed, as well as a porous structure, as for BA. The sHC process also seems to have been the least intense, visualizing only a non-colonized porous structure.

The SEM analysis has thus proven to be very important, allowing to consolidate previous observations/findings concerning the actual biodegradation of the polymers of BA and BB, denoting that they suffer morphological changes by the composting process to which they were subjected.

4.6. Fourier Transformed Infrared analysis

To ensure a complete analysis in order to evaluate the effective biodegradation of the bioplastics under study, the characteristic chemical bonds of each material were analysed by FTIR. The results obtained are shown in Figure 4.12.

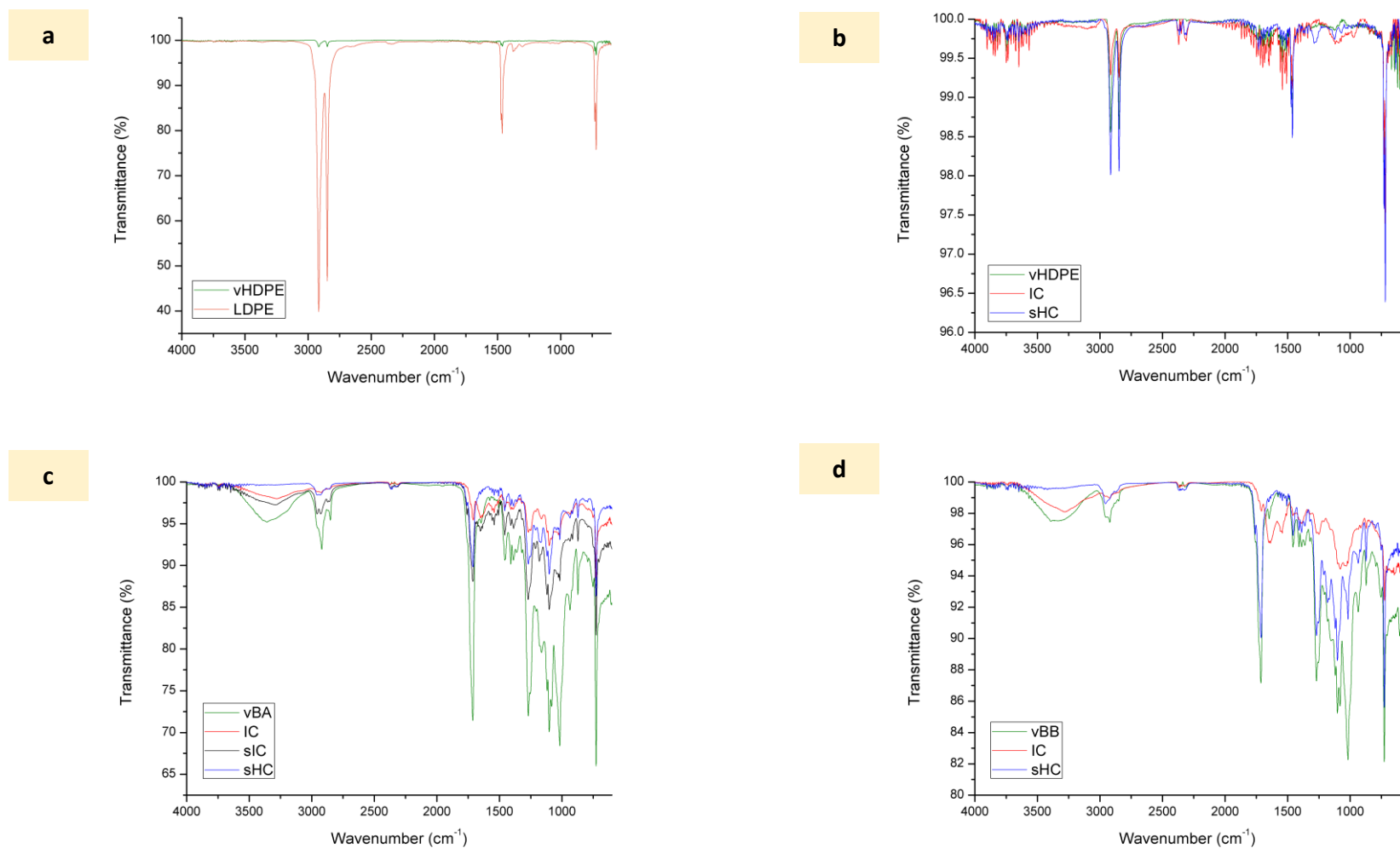


Figure 4.12. FTIR spectra for (a) virgin HPDE polymer (vHDPE) and reference LDPE polymer (LDPE) and effect of the various composting processes: industrial composting (IC), simulated industrial composting (sIC) and simulated home composting (sHC) for (b) virgin High Density Polyethylene (vHDPE), (c) virgin Bioplastic A (vBA) and (d) virgin Bioplastic B (vBB) polymers. Results are after 12 weeks of sIC and sHC and 3 weeks of IC. Each sample was analysed once.

Figure 4.12a shows the comparison of the virgin plastic film under study - vHDPE, with a commercial virgin LDPE film sample, whose spectrum is known. Since both films are made of polyethylene, their characteristic peaks are the same, which is observed, thus proving that the plastic film used in the study is polyethylene. At around 2900 and 2800 cm^{-1} is observed the peak corresponding to the asymmetric and symmetric stretching of the aliphatic C-H groups, respectively, and at around 1500 cm^{-1} a peak due to the aliphatic C-H deformation is identified. Lastly, at around 720 cm^{-1} a peak related to methylene rocking is observed, as observed in reported studies [74, 85, 94, 95]. Lastly, it is also clearly seen how the HDPE film has peaks with much lower intensity when compared to those of LDPE, which could be due to possible additives that the HDPE bag contains.

Figure 4.12b allows the assessment of the evolution of HDPE peaks according to the different conditions to which the samples were subjected. In general, there is no great variability between the results for the different studied conditions (IC and sHC). However, around 1615 cm^{-1} , a new peak may have appeared for the IC conditions, related to a C-O bond, which may indicate a small degradation trace, as stated by Ruggero, Onderwater [74]. It is also possible to identify 2 background noises, concerning water vapour, between 4000 and 3400 cm^{-1} and concerning carbon dioxide, around 2350 cm^{-1} and 670 cm^{-1} [74, 94].

As expected, the characteristic peaks for BA vary from those for HDPE (Figure 4.12c), indicating the presence of a different polymer. When analysing the impact that the different composting conditions had on the intensity of the recorded peaks, it is easily seen how the IC process was the most intense and harsh, leading to an extreme reduction in the intensity of the characteristic peaks. Afterwards, the sHC conditions seem to have had the most effect, followed at the end by the sIC conditions. It should be noted, however, that no new peaks seem to have appeared besides the one's characteristic of the virgin polymer of BA. The peaks identified are thus, at around 2900 and 2800 cm^{-1} , corresponding to the asymmetric and symmetric stretching of the aliphatic C-H groups, respectively; by 1700 and by 727 cm^{-1} due to C=O stretching vibration of the ester group and the out-of-plane C-H deformation of the aromatic ring, respectively; around 1270 and 1100 cm^{-1} to C-O and C-O-C stretching vibrations, respectively; by 1017 cm^{-1} as a result of characteristic group stretching of the phenylene group, as mentioned in the consulted literature [74, 85, 94, 96, 97]. It is possible to identify two background noises

possibly related to water vapour and carbon dioxide in the same intervals as previously reported.

Finally, Figure 4.12d shows the characteristic peaks for the BB polymer, as well as their changes after different composting processes. When analysed, it can be seen that these are in the same range as those referred to for BA, which leads to the conclusion that the polymers constituting BA and BB are very similar, and may even be identical, with only a few potential additive changes, given that the intensity of their characteristic peaks differ in some cases, as for example at 1700 cm^{-1} . In fact, and according to the literature consulted, BA and BB are likely to consist in polymer blends of poly(butylene adipate-co-butylene terephthalate) (PBAT) and thermoplastic starch (TPS), both presenting a broad peak at around 3340 cm^{-1} , related to OH groups [85]. With respect to their intensity, the IC process appears to be the strongest, leading to a decrease in peak intensity, followed by the sHC process. Similarly, there seems to have been no formation of new peaks when compared to the virgin polymer - vBB.

It is extremely important to emphasise that the two bioplastics under study lost weight in all the conditions studied, as already mentioned. This may lead to a reduction in the amount of material analysed by FTIR, and naturally, to a reduction in the intensity of the characteristic peaks. Hence, the mentioned weight loss may be in the explanation that, in Figure 4.12c, a reduction in peak intensity is evidenced for sIC; however, as described before, no composting conditions have occurred in this test, but only a disintegration, and therefore weight loss in the samples. The interpretation of the remaining composting conditions by FTIR, when crossed with the visual results, mass loss and mechanical properties, lead however to conclude about the effective beginning of biodegradation of the samples. Nonetheless, as mentioned, the loss of weight will always contribute to a decrease in the intensity of the bonds, and therefore, in the characteristic peaks.

In summary, the FTIR results were highly relevant to confirm what was analysed by SEM, and indicated by visual, mechanical and weight loss analysis, that effectively, bioplastics BA and BB started a biodegradation process when subjected to composting conditions.

4.7. Soil incubation trials

The soil incubation assays aimed to better understand the degradation state that BA, BB and HDPE bags would suffer if they were freely discarded to nature, eventually getting overground in the soil. Given the high degree of contamination of the samples with soil after 12 weeks, the analysis of the weight loss was considered to be inadequate and a visual analysis was therefore performed (Figure 4.13 and Figure 4.14). The maximum and minimum temperature and precipitation values recorded in the environment where the tests took place are presented in Appendix C.

By the analysis of Figure 4.13, it is observed how the behaviour of the bioplastic bags was significantly different when compared to the HDPE one. In fact, the latter was totally unchanged, while the ones made of BA and BB show clear signs of degradation, such as change in appearance and loss of material; however, not expressive. It should also be highlighted that initially, between each bag, control strips of paper had been placed (Figure 3.9) and these had now completely disappeared. Thus, it can be inferred that an effective biodegradation process has occurred for the BA and BB bags.

From the analysis of Figure 4.14, which show details of the BA and BB bags, respectively, it is noteworthy that these bags allowed the passage of root tissues through them and that, at the time of opening for their withdrawal, vegetation could be found on the soil surface. This is an important aspect, as for the HDPE bag no trace of root tissues was found, but it is clearly shown for the two bioplastic bags under study.

In general, despite the signs of degradation mentioned above, it is difficult only by visual analysis to infer about the biodegradation of the bags or their simple disintegration/fragmentation. However, several authors have stated that despite the fact that biodegradable bioplastic bags effectively start degradation processes when buried in the soil, there is a high variability in the results obtained [98-100]. In fact, the biodegradation of these is strongly dependent on various conditions such as temperature, humidity (intrinsically linked to precipitation), pH and, naturally, the bacterial and fungal biomass of the soil. Thus, times for complete biodegradation vary in the literature between values from around 170 days up to 3000 days (based on kinetic predictions) [101].

Furthermore, the biodegradation of bioplastics in soil appears to be relevantly slower (as expected) when compared to composting or anaerobic digestion processes, much due

to the lower concentration of microorganisms in soil compared to composting or anaerobic digestion conditions [101].

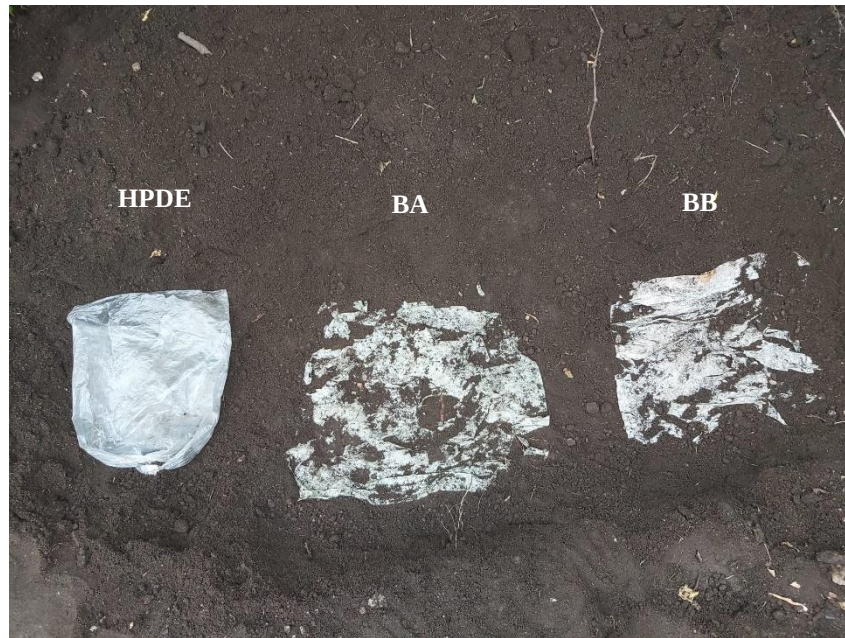


Figure 4.13. Appearance of High-Density Polyethylene (HDPE), Bioplastic A (BA) and Bioplastic B (BB) bags after incubation trials in soil for 12 weeks.

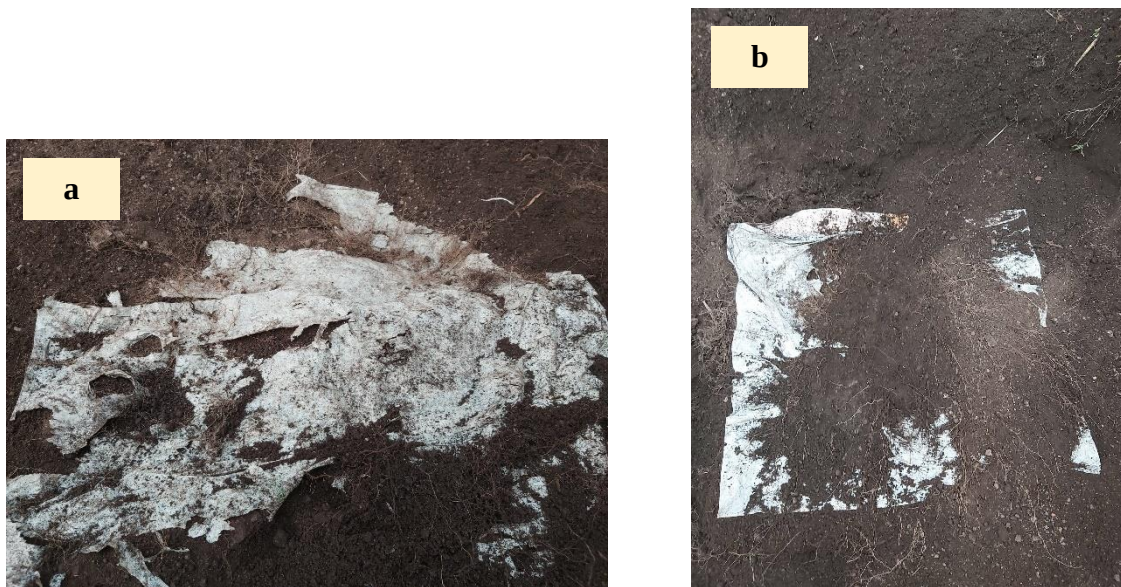


Figure 4.14. Detail of (a) Bioplastic A (BA) and (b) Bioplastic B (BB) bags after soil incubation trials.

4.8. Inspection of an organic waste collection route served by LIPOR

Finally, and as outlined in the objectives, a better understanding of the current impact of the increasing dissemination of bioplastic bags on organic waste collection routes was sought.

Therefore, a recently implemented door-to-door collection route for organic waste from a municipality with 94672 inhabitants served by LIPOR was roughly inspected. The total weight of the load of the mentioned circuit was 1920 kg. However, only about 200 kg were in fact analysed (Figure 4.15), corresponding to the quartering of the entire load received. In the 200 kg inspected, 1 BB bag and 3 other bags classified as compostable were visually identified.

It is important to highlight once again, the already mentioned practical difficulty in visually identifying a compostable bioplastic bag from another common plastic bag, which naturally results in a limitation and possible problem of waste contamination. The identified bioplastic bags were only identified due to the touch and experience of the operator, who was already familiar with these products. Thus, the real value present in the analysed load could be considerably higher.

By analysing Figure 4.15, it is also visible a high quantity of conventional plastic bags that go along with the biowaste, which may translate into potential contaminations. This fact, together with the observation that, although bioplastic bags are already present in the organic waste collection routes, they are still not significant (4 bags identified in 50 kg), especially when compared to the presence of conventional plastic bags, leads to the conclusion that they are not yet a significant contamination for the processes. However, with the increasing pressure on SUP, such as that exerted by the EU, and the higher offering of these materials, it may be possible to foresee a change of this reality to one in which the bioplastic bags take on the representativeness of conventional bags. However, an enormous contamination for these, causing disruptions in the composting of biowaste and compost quality, if not removed previously. In case they are removed previously to the process, they will constitute a refuge, as the conventional plastics currently do, thus contributing nothing to a better effectiveness and efficiency of the organic collection and valorisation processes. Finally, when mechanically recyclable, their mixture will also greatly impair further recovery of these materials.

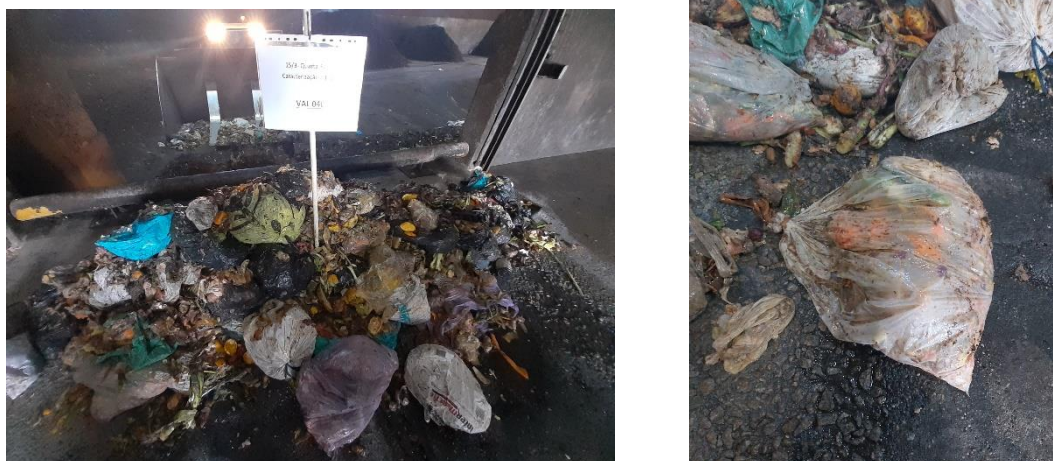


Figure 4.15. Analysed load from a door-to-door organic waste collection route (left) and detail of a Bioplastic B (BB) bag found on it (right).

5. CONCLUSIONS

Through this dissertation, a better understanding of the emerging reality of bioplastics, emphasising the ones labelled as compostable, was possible, by evaluating their compostability in simulated conditions both at a laboratory and industrial scale.

In general, all the results obtained after industrial composting (IC) and simulated home composting (sHC), allow for the conclusion that effectively, the two "so-called" compostable bioplastics under study, one certified as compostable made from 'Bioplast' (BA) and another presenting only an indication of compostability, made from Mater-Bi® (BB), started their biodegradation process by composting, yet not sufficiently enough to be disregarded as contaminations in the end of both processes.

Visually, a change in colour, structure and integrity was observed in both strips, this being more prominent for the BA strips. However, both strips were still identifiable at the end of the trials after 12 weeks of sHC and 3 weeks of IC. In terms of weight loss, only 35% and 15% losses were recorded for BA and BB strips after sHC, respectively. For BA and BB strips after IC, losses of 50% and 60% were recorded respectively. Regarding the mechanical properties, a maximum loss in tensile strength of 85% for BA and 86% for BB and a maximum loss in strain at break of 98% for both bioplastics were observed.

The IC studies using samples of whole BA and BB bags allowed concluding that, despite a significant alteration resulting from the process, at the end of the process, these bags constitute a strong contamination as they clearly haven't completely biodegraded, only showing signs of it, with a maximum weight loss of 22% for BA bags and 18% for BB bags. This fact could lead to serious disruptions in the subsequent processes as well as strongly affect the quality of the compost obtained.

An issue raised by this type of material is its easy disintegration. In fact, and as mentioned in the standards analysed, these products should effectively disintegrate, however, it was verified that this occurs even if the composting conditions were not the most appropriate (as occurred in the simulated industrial composting process (sIC)). This

fact may result in a false perception of biodegradation by the public perception, since their "disappearance" is interpreted as a clear sign of their biodegradation/compostability; however, this is not necessarily true. The question thus arises of the generation of meso- and microplastics and their potential negative impacts on the environment and living beings resulting from such physical disintegration.

The High-Density polyethylene (HPDE) samples remained unchanged throughout all the studies undertaken, showing only slight changes in their morphology evidenced by SEM analysis (small bumps) after the IC process. However, it is worth mentioning the significant loss in their strain at break, of about 200%.

The incubation of whole bags samples of BA and BB on soil suggests that the polymers under study (BA and BB), do not seem to have a negative effect on vegetation, not preventing its proliferation, which was an aspect that had never been considered before. A slight change in bag integrity and consequent disintegration was similarly observed after the 12-week trials.

Finally, it became clear how the presence of this type of materials and their increasing publicity and dissemination by large brands and supermarket chains, leads to their presence in the selective collection routes of organic waste, which might constitute a serious problem, given their non-biodegradability in industrial composting plants, emphasizing once again the urgency and relevance of this topic.

Overall, the present study allows to conclude that the topic of bioplastics, which has been increasingly presented as *the revolutionary solution* to the plastics problem, is not close to present itself as such, considering the existing composting facilities at national level, which are using the best available techniques at a European Level.

6. LIMITATIONS AND FUTURE WORK

One of the major limitations identified throughout the developed work was the difficulty in adjusting the moisture in the simulated industrial composting process, which resulted in a deficient composting process. Also, the temperature and humidity sensors used in the sHC and sIC trials revealed to be unreliable as the trials progressed, even failing to function or giving incorrect values. This fact compromised the monitoring of the composting process and related adjustments.

In the same way, the determination of the biodegradability of the samples by the continuous monitoring of the CO₂ production during composting was not conducted (as referred in ISO 14855:1999 via EN 13432), due to the absence of technical means, being identified as relevant to develop in the future.

The difficulty in the washing of the strips and bags, to remove contaminations adhered to the surface, influenced their final weight and consequently the weight loss determination, and thus the real values are expected to be higher than those calculated.

Finally, it is also worth mentioning the challenge in performing the mechanical studies, since the size and transparency of the strips prevented the use of more accurate equipment (such as an extensometer), being also very difficult to maintain the same experimental conditions in all tests, such as the area of the strip under effective traction, as well as its verticality.

Accordingly, as suggestions for future work, the following may be considered:

- Determination of the aerobic biodegradability of plastic materials under controlled composting conditions according to ISO 14855:1999;
- Use of whole bags instead of strips in home composting trials;
- Extend the duration of the tests until more expressive changes are observed, including the full compliance with the duration mentioned in standards (EN 13432);

- Evaluate the possibility of returning the composting material to the beginning of the industrial process of the bags subjected to industrial composting trials (recirculation);
- Analysis of the sample's disintegration in meso- and microplastics at the end of the composting trials;
- Analysis on how the various parameters associated with the composting process (temperature, moisture, C/N ratio) affect the sample's biodegradation;
- Analysis of biodegradation of bioplastic bags with home composting labelling;
- Quality analysis of the compost obtained, including physical-chemical parameters, microbiological parameters and toxicity and ecotoxicity tests.

REFERENCES

1. Halden, R.U., *Plastics and health risks*. Annu Rev Public Health, 2010. **31**: p. 179-94.
2. Thompson, R.C., et al., *Introduction: Our Plastic Age*. Philosophical Transactions: Biological Sciences, 2009. **364**(1526): p. 1973-1976.
3. Ritchie, H. and M. Roser, *Plastic pollution*. Our World in Data, 2018.
4. Millet, H., et al., *The nature of plastics and their societal usage*. 2018.
5. Walker, T.R. and L. Fequet, *Current trends of unsustainable plastic production and micro(nano)plastic pollution*. TrAC Trends in Analytical Chemistry, 2023. **160**: p. 116984.
6. Andrady, A., et al., *Plastics in a sustainable society*. Background paper, Stockholm, 2015.
7. European Parliament & Council, *Directive (EU) 2019/904 on the reduction of the impact of certain plastic products on the environment*, in L 155, E.P.a. Council, Editor. 2019, Official Journal of the European Union: Brussels. p. 19.
8. Geyer, R., J.R. Jambeck, and K.L. Law, *Production, use, and fate of all plastics ever made*. Science Advances, 2017. **3**(7): p. e1700782.
9. North, E.J. and R.U. Halden, *Plastics and environmental health: the road ahead*. Rev Environ Health, 2013. **28**(1): p. 1-8.
10. Allsopp, M., P. Costner, and P. Johnston, *Incineration and human health*. Environmental Science and Pollution Research, 2001. **8**(2): p. 141-145.
11. Hopewell, J., R. Dvorak, and E. Kosior, *Plastics recycling: challenges and opportunities*. Philos Trans R Soc Lond B Biol Sci, 2009. **364**(1526): p. 2115-26.
12. Shen, L. and E. Worrell, *Chapter 13 - Plastic Recycling*, in *Handbook of Recycling*, E. Worrell and M.A. Reuter, Editors. 2014, Elsevier: Boston. p. 179-190.
13. Alassali, A., et al., *Towards Higher Quality of Recycled Plastics: Limitations from the Material's Perspective*. Sustainability, 2021. **13**(23): p. 13266.
14. Borg, K., et al., *Curbing plastic consumption: A review of single-use plastic behaviour change interventions*. Journal of Cleaner Production, 2022. **344**: p. 131077.
15. Zalasiewicz, J., et al., *The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene*. Anthropocene, 2016. **13**: p. 4-17.
16. Cambridge University Press, *Anthropocene*, in *Cambridge dictionary*.

17. MacLeod, M., et al., *The global threat from plastic pollution*. Science, 2021. **373**(6550): p. 61-65.
18. Iroegbu, A.O.C., et al., *Plastic Pollution: A Perspective on Matters Arising: Challenges and Opportunities*. ACS Omega, 2021. **6**(30): p. 19343-19355.
19. Moshood, T.D., et al., *Sustainability of biodegradable plastics: New problem or solution to solve the global plastic pollution?* Current Research in Green and Sustainable Chemistry, 2022. **5**: p. 100273.
20. LIPOR. *A LIPOR*. 2023 [cited 2023 March 16, 2023]; Available from: <https://www.lipor.pt/pt/sobre-nos/a-lipor/>.
21. Porto Ambiente. *Quem Somos*. 2023 [cited 2023 March 16, 2023]; Available from: https://www.portoambiente.pt/quem-somos/Quem_somos.
22. Gómez, E.F. and F.C. Michel, *Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation*. Polymer Degradation and Stability, 2013. **98**(12): p. 2583-2591.
23. Emadian, S.M., T.T. Onay, and B. Demirel, *Biodegradation of bioplastics in natural environments*. Waste Management, 2017. **59**: p. 526-536.
24. Plastics Europe, *Plastics - the Facts 2022*. 2022, Plastics Europe.
25. Chen, Y., et al., *Single-use plastics: Production, usage, disposal, and adverse impacts*. Science of The Total Environment, 2021. **752**: p. 141772.
Reprinted from Science of The Total Environment, Vol. 752, Yuan Chen, Abhishek Kumar Awasthi, Fan Wei, Quanyin Tan, Jinhui Li, Single-use plastics: Production, usage, disposal, and adverse impacts, Page No. 141772, Copyright (2021), with permission from Elsevier.
26. Gibb, B.C., *Plastics are forever*. Nature Chemistry, 2019. **11**(5): p. 394-395.
27. UNEP, *Single-Use Plastics: A Roadmap for Sustainability*, Rev., Editor. 2018.
28. European Commission, *Assessment of options for reinforcing the Packaging and Packaging Waste Directive's essential requirements and other measures to reduce the generation of packaging waste*, P.O.o.t.E. Union, Editor. 2023: Luxembourg.
29. Kwon, G., et al., *A review of plastic pollution and their treatment technology: A circular economy platform by thermochemical pathway*. Chemical Engineering Journal, 2023. **464**: p. 142771.
30. IUCN, *Marine Plastic Pollution*. 2021, International Union for Conservation of Nature.
31. Thushari, G.G.N. and J.D.M. Senevirathna, *Plastic pollution in the marine environment*. Heliyon, 2020. **6**(8): p. e04709.
32. UNDRR. *Sendai Framework Terminology on Disaster Risk Reduction*. 2023 17/04/2023]; Available from: <https://www.undrr.org/terminology/disaster>.
33. Senathirajah, K., et al., *A disaster risk reduction framework for the new global instrument to end plastic pollution*. Journal of Hazardous Materials, 2023. **449**: p. 131020.

34. Briassoulis, D., A. Pikasi, and M. Hiskakis, *Organic recycling of post-consumer /industrial bio-based plastics through industrial aerobic composting and anaerobic digestion - Techno-economic sustainability criteria and indicators*. Polymer Degradation and Stability, 2021. **190**: p. 109642.
35. European Commission, *EU policy framework on biobased, biodegradable and compostable plastics*. 2022, European Comission: Brussels.
36. European Bioplastics, *What are bioplastics?*, in *Fact Sheet*, E. Bioplastics, Editor. 2022a, European Bioplastics: Berlin.
37. Group of Chief Scientific Advisors, *Biodegradability of Plastics in the Open Environment*, E. Commission, Editor. 2020, European Commission: Luxembourg.
38. European Bioplastics, *Frequently Asked Questions on Bioplastics*, E.B. e.V., Editor. 2023, European Bioplastics: Berlin.
39. EEA, *Biodegradable and compostable plastics - challenges and opportunities*, E.E. Agency, Editor. 2020, European Environment Agency.
40. Srikanth, M., et al., *Biodegradation of plastic polymers by fungi: a brief review*. Bioresources and Bioprocessing, 2022. **9**(1): p. 42.
41. UNEP, *Plastics and Microplastics - Fact Sheet*, U.N.E. Program, Editor. 2015.
42. European Bioplastics, *Environmental Communication Guide for Bioplastics*, E. Bioplastics, Editor. 2017, European Bioplastics e.V.: Berlin.
43. Slovenski inštitut za standardizacijo, *Plastics - Evaluation of compostability - Test scheme and specifications*. 2007.
44. AFNOR, *Requirements for packaging recoverable through composting and biodegradation*. 2000, AFNOR - Association Française de Normalisation: 11, avenue Francis de Pressensé, 93571 Saint-Denis La Plaine Cedex
45. European Bioplastics. *What are the required circumstances for a compostable product to compost?* 2016a [cited 2023 April 24, 2023]; Available from: <https://www.european-bioplastics.org/faq-items/what-are-the-required-circumstances-for-a-compostable-product-to-compost/>.
46. European Parliament & Council, *Directive (EU) 2015/720 amending Directive 94/62/EC on packaging and packaging waste to reduce the consumption of lightweight plastic carrier bags.*, in *L 115*, E.P.a. Council, Editor. 2015, Official Journal of the European Union: Strasbourg.
47. European Bioplastics, *Home Composting of Compostable Bioplastics*, E.B. e.V, Editor. 2018.
48. European Bioplastics, *Bioplastics – Industry standards & labels*, E. Bioplastics, Editor. 2016b, European Bioplastics: Berlin.
49. European Bioplastics, *Bioplastics Market Development Update*, E. Bioplastics, Editor. 2022b, European Bioplastics: Berlin.
50. European Comission. *Waste Framework Directive*. 2023 [cited 2023 April 25th, 2023]; Available from: https://environment.ec.europa.eu/topics/waste-and-recycling/waste-framework-directive_en.

51. Ren, X., *Biodegradable plastics: a solution or a challenge?* Journal of Cleaner Production, 2003. **11**(1): p. 27-40.
52. Wojnowska-Baryła, I., D. Kulikowska, and K. Bernat, *Effect of Bio-Based Products on Waste Management*. Sustainability, 2020. **12**(5): p. 2088.
53. Chen, X., et al., *Influences of bioplastic polylactic acid on near-infrared-based sorting of conventional plastic*. Waste Management & Research, 2021. **39**(9): p. 1210-1213.
54. Fredi, G. and A. Dorigato, *Recycling of bioplastic waste: A review*. Advanced Industrial and Engineering Polymer Research, 2021. **4**(3): p. 159-177.
55. Calabrò, P.S. and M. Grosso, *Bioplastics and waste management*. Waste Management, 2018. **78**: p. 800-801.
56. Rynk, R., et al., *Chapter 1 - Why compost?*, in *The Composting Handbook*, R. Rynk, Editor. 2022, Academic Press. p. 1-26.
57. Pottipati, S., et al., *3 - Composting and vermicomposting: Process optimization for the management of organic waste*, in *Advanced Organic Waste Management*, C. Hussain and S. Hait, Editors. 2022, Elsevier. p. 33-43.
58. Oshins, C., et al., *Chapter 3 - The composting process*, in *The Composting Handbook*, R. Rynk, Editor. 2022, Academic Press. p. 51-101.
59. Bandini, F., et al., *The treatment of the organic fraction of municipal solid waste (OFMSW) as a possible source of micro- and nano-plastics and bioplastics in agroecosystems: a review*. Chemical and Biological Technologies in Agriculture, 2022. **9**(1): p. 4.
60. Mahapatra, S., M.H. Ali, and K. Samal, *Assessment of compost maturity-stability indices and recent development of composting bin*. Energy Nexus, 2022. **6**: p. 100062.
61. European Bioplastics, *Industrial Composting*. 2009, European Bioplastics e.V.: Berlin.
62. Rynk, R., et al., *On-farm composting handbook (NRAES 54)*. 1992: Northeast Regional Agricultural Engineering Service (NRAES).
63. Colón, J., et al., *Environmental assessment of home composting*. Resources, Conservation and Recycling, 2010. **54**(11): p. 893-904.
64. Finstein, M.S., F.C. Miller, and P.F. Strom, *Monitoring and Evaluating Composting Process Performance*. Journal (Water Pollution Control Federation), 1986. **58**(4): p. 272-278.
65. Ayilara, M.S., et al., *Waste Management through Composting: Challenges and Potentials*. Sustainability, 2020. **12**(11): p. 4456.
66. Michel, F., et al., *Chapter 5 - Passively aerated composting methods, including turned windrows*, in *The Composting Handbook*, R. Rynk, Editor. 2022, Academic Press. p. 159-196.
67. Yadav, K.D., D. Sharma, and R. Prasad, *5 - Challenges and opportunities for disposal of floral waste in developing countries by using composting method*, in *Advanced Organic Waste Management*, C. Hussain and S. Hait, Editors. 2022, Elsevier. p. 55-77.

68. Michel, F., et al., *Chapter 6 - Forced aeration composting, aerated static pile, and similar methods*, in *The Composting Handbook*, R. Rynk, Editor. 2022, Academic Press. p. 197-269.
69. Michel, F., et al., *Chapter 7 - Contained and in-vessel composting methods and methods summary*, in *The Composting Handbook*, R. Rynk, Editor. 2022, Academic Press. p. 271-305.
70. Tchobanoglous, G. and F. Kreith, *Handbook of Solid Waste Management*. 2nd Edition ed. 2002, New York: McGraw-Hill Education.
71. Martinho, M.d.G.M. and M.d.G.P. Gonçalves, *Gestão de resíduos*. 2000: Universidade Aberta.
72. Chen, L., et al., *The composting process*. Dairy Manure Compost Production and Use in Idaho, 2011. **2**: p. 513-532.
73. Sarasa, J., J.M. Gracia, and C. Javierre, *Study of the biodegradation of a bioplastic material waste*. Bioresource Technology, 2009. **100**(15): p. 3764-3768.
74. Ruggero, F., et al., *Degradation of Film and Rigid Bioplastics During the Thermophilic Phase and the Maturation Phase of Simulated Composting*. Journal of Polymers and the Environment, 2021. **29**(9): p. 3015-3028.
75. Adamcová, D., et al., *Biodegradation/Disintegration of Selected Range of Polymers: Impact on the Compost Quality*. Journal of Polymers and the Environment, 2019. **27**(4): p. 892-899.
76. Vavrková, M., et al., *Study of the Biodegradability of Degradable/Biodegradable Plastic Material in a Controlled Composting Environment*. Ecological Chemistry and Engineering S, 2012. **19**(3): p. 347-358.
77. Solano, G., et al., *Biodegradation of plastics at home composting conditions*. Environmental Challenges, 2022. **7**: p. 100500.
78. Leejarkpai, T., et al., *Biodegradable kinetics of plastics under controlled composting conditions*. Waste Management, 2011. **31**(6): p. 1153-1161.
79. International Organization for Standardization, *Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide*. 1999: Switzerland.
80. Ghinea, C., et al., *Development of a model for food waste composting*. Environ Sci Pollut Res Int, 2019. **26**(4): p. 4056-4069.
81. APHA, *Standard Methods for the Examination of Water and Wastewater*. 1998: EUA, Washington, D.C.
82. Slovenski inštitut za standardizacijo, *Packaging - Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test*. 2005: rue de Stassart, 36 B-1050 Brussels.
83. British Standards Institution, *Plastics — Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test*. 2015: Avenue Marnix 17, B-1000 Brussels

84. Vaverková, M., D. Adamcová, and J. Zloch, *How do degradable/biodegradable plastic materials decompose in home composting environment?* Journal of Ecological Engineering, 2014. **15**(4): p. 82-89.
85. Rujnić Havstad, M., et al., *Influence of Home Composting on Tensile Properties of Commercial Biodegradable Plastic Films*. Polymers (Basel), 2021. **13**(16).
86. International Organization for Standardization, *Plastics — Determination of tensile properties — Part 1: General principles*. 2012, International Organization for Standardization Switzerland.
87. Orhan, Y., J. Hrenović, and H. Büyükgüngör, *Biodegradation of plastic compost bags under controlled soil conditions*. Acta Chimica Slovenica, 2004. **51**: p. 579-588.
88. Polymer Database. *High-Density Polyethylene (HDPE)*. Available from: <https://polymerdatabase.com/Commercial%20Polymers/HDPE.html#top>.
89. Singh, G., et al., *Degradation behaviors of linear low-density polyethylene and poly(L-lactic acid) blends*. Journal of Applied Polymer Science, 2012. **124**(3): p. 1993-1998.
90. Quecholac-Piña, X., et al., *Biodegradation of compostable and oxodegradable plastic films by backyard composting and bioaugmentation*. Environ Sci Pollut Res Int, 2017. **24**(33): p. 25725-25730.
91. Badini, C., et al., *Composition and Workability of Plastic Fractions Recovered from Commingled Waste Discarded by a Composting Plant*. Polymers, 2023. **15**(7): p. 1690.
92. Cucina, M., et al., *Degradation of bioplastics in organic waste by mesophilic anaerobic digestion, composting and soil incubation*. Waste Management, 2021. **134**: p. 67-77.
93. Adamcová, D., et al., *SEM Analysis and Degradation Behavior of Conventional and Bio-Based Plastics During Composting*. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis, 2018. **66**: p. 349-356.
94. ThermoFisher Scientific. *Basic organic functional group*. 2015; Available from: <http://www.thermoscientific.com/content/dam/tfs/ATG/CAD/CAD%20Documents/Application%20%26%20Technical%20Notes/Molecular%20Spectroscopy/FIR/FTIR%20Spectrometers/XX51346-E-0215M-OrganicFunctionalChart.pdf>.
95. Wu, W.-L. and Y.-W. Wang, *Modified high-density polyethylene films: preparation, composition and their physical properties*. Bulletin of Materials Science, 2020. **43**(1): p. 143.
96. Alassali, A., et al., *Assessment of polyethylene degradation after aging through anaerobic digestion and composting*. Polymer Degradation and Stability, 2018. **158**: p. 14-25.
97. Campitelli, P. and S. Ceppi, *Effects of composting technologies on the chemical and physicochemical properties of humic acids*. Geoderma, 2008. **144**(1): p. 325-333.
98. Adhikari, D., et al., *Degradation of bioplastics in soil and their degradation effects on environmental microorganisms*. Journal of Agricultural Chemistry and Environment, 2016. **5**(01): p. 23.

99. Napper, I.E. and R.C. Thompson, *Environmental Deterioration of Biodegradable, Oxo-biodegradable, Compostable, and Conventional Plastic Carrier Bags in the Sea, Soil, and Open-Air Over a 3-Year Period*. Environmental Science & Technology, 2019. **53**(9): p. 4775-4783.
100. Slezak, R., et al., *Degradation of bio-based film plastics in soil under natural conditions*. Science of The Total Environment, 2023. **866**: p. 161401.
101. Cucina, M., et al., *The role of waste management in reducing bioplastics' leakage into the environment: A review*. Bioresource Technology, 2021. **337**: p. 125459.

APPENDICES

APPENDIX A – RECORDED TEMPERATURES DURING SIMULATED HOME COMPOSTING

In the present appendix, the average temperature value during the simulated home composting (sHC) process is presented by Figure A.1.

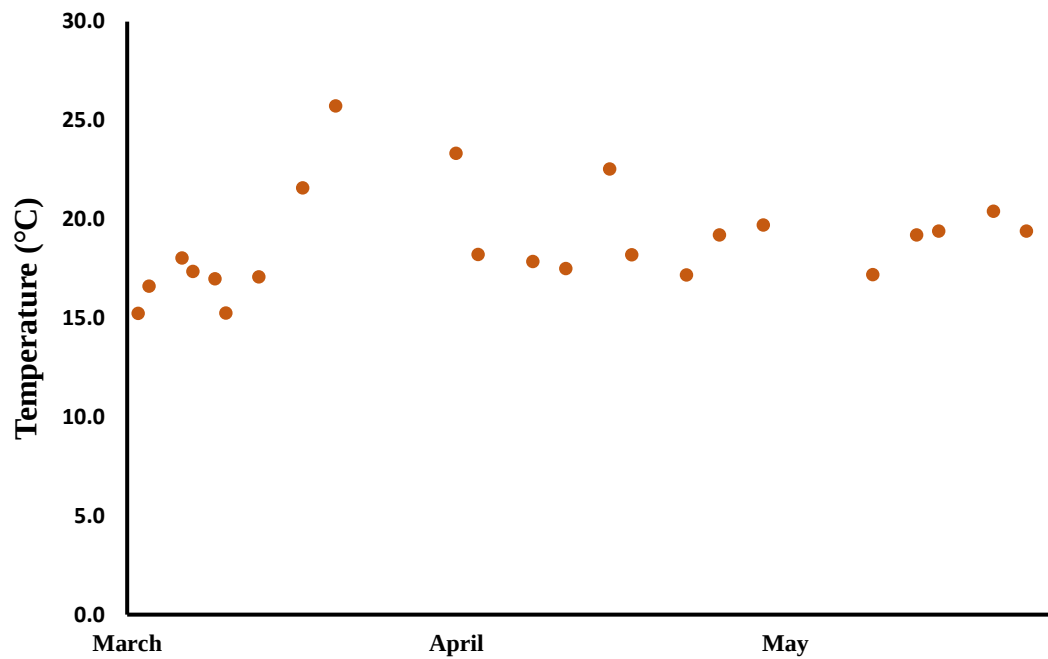


Figure A.1. Average temperatures recorded during the simulated home composting process (sHC, March-May). Each point corresponds to the average of 8 values (8 boxes).

APPENDIX B – BRIEF DESCRIPTION OF LIPOR COMPOSTING PROCESS

The composting process carried out in the industrial composting facility where the industrial composting (IC) trials were performed, receives four major selective collection waste streams as feedstock:

1. Green Waste (branches, gardening waste);
2. Catering/restaurants waste (food waste);
3. Markets' waste (horticultural products);
4. Waste from cemeteries (flowers and other green wastes).

The industrial composting process briefly comprises the following steps:

1. **Primary mechanical treatment:** Combining of the different wastes to be composted and screening of the mixture through a 150 mm sieve and magnetic separator;
2. **1st composting phase:** Controlled composting in tunnel over a period of 12 to 15 days;
3. **Secondary mechanical treatment:** The tunnel is emptied and the content is passed through a 60 mm sieve and magnetic separator;
4. **2nd composting phase:** A new composting phase in tunnel occurs over a period of 12 to 15 days;
5. **Compost adjustment:** The tunnel is emptied and its content is subjected to a 10 mm sieve and magnetic separation.
6. **Maturation:** The compost undergoes a maturation process in piles under aired flooring for 4 to 6 weeks.

At the end of each phase, samples are taken in order to analyse the following parameters:

- organic matter content;
- moisture content;
- pH and conductivity;
- carbon and nitrogen percentage and respective C/N ratio
- density;
- stones and inert content.

The operational parameters (during composting phase) are continuously monitored and controlled through an appropriate software. The results from the monitoring performed for the 1st and 2nd composting phase of the IC trials conducted in the present work, are shown in Figure B.1 and Figure B.2.

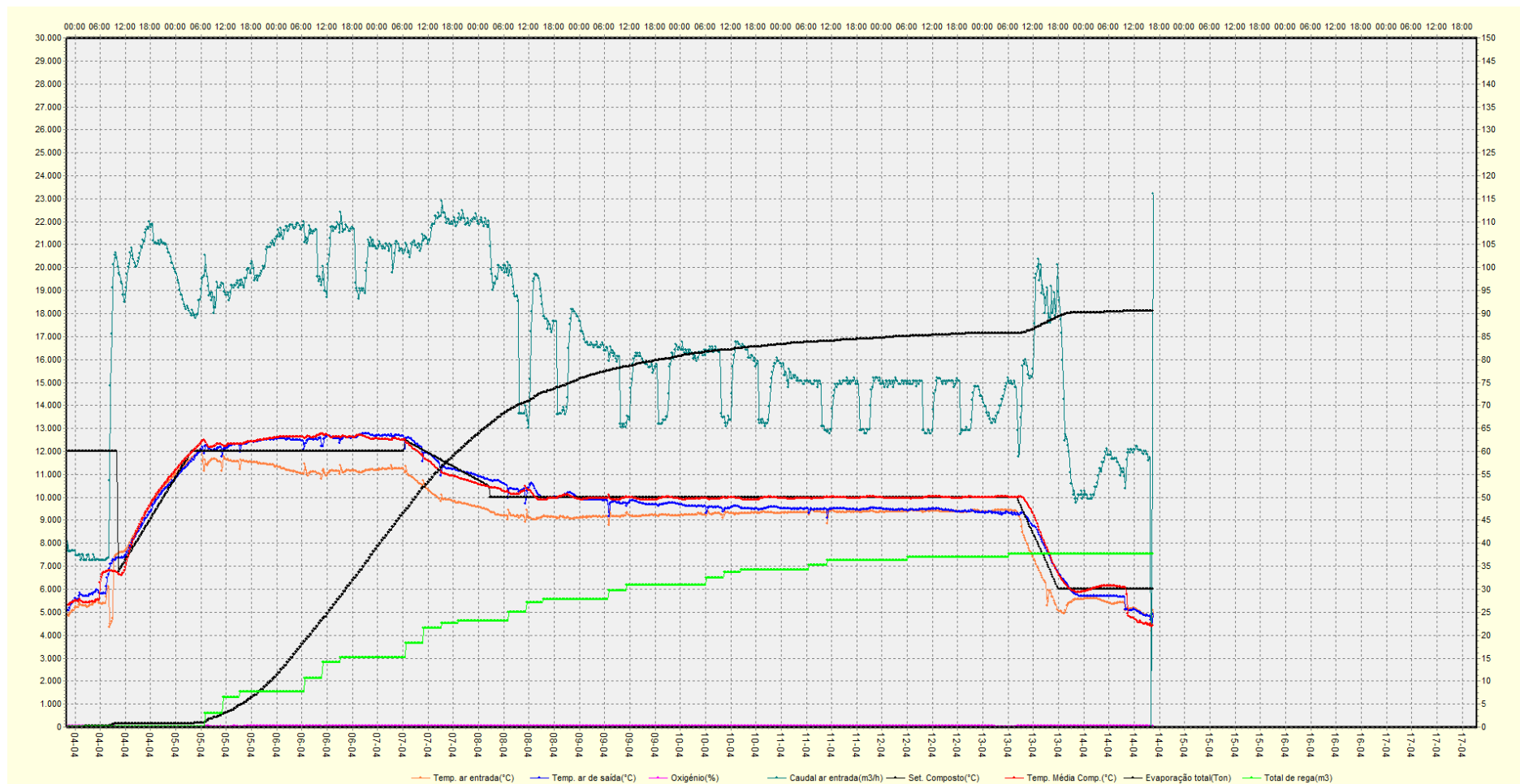


Figure B.1. Operational conditions of the 1st composting phase for the studies performed in Industrial Composting (IC). Orange: inlet air temperature (°C), Blue: outlet air temperature (°C); Purple: oxygen (%); Navy blue: inlet flow rate (m³/h); Black: Set. Compost (°C); Red: average compost temperature (°C); Black2: total evaporation (t); Green: total irrigation (m³). Upper axis: hours; lower axis: days; right axis: temperature and irrigation; left axis: evaporation and inlet flow rate.



Figure B.2. Operational conditions of the 2nd composting phase for the studies performed in Industrial Composting (IC). Orange: inlet air temperature (°C), Blue: outlet air temperature (°C); Purple: oxygen (%); Navy blue: inlet flow rate (m³/h); Black: Set. Compost (°C); Red: average compost temperature (°C); Black₂: total evaporation (t); Green: total irrigation (m³). Upper axis: hours; lower axis: days; right axis: temperature and irrigation; left axis: evaporation and inlet flow rate.

APPENDIX C – RECORDED TEMPERATURE AND PRECIPITATION FOR SOIL INCUBATION TRIALS

In this appendix, the values of temperature (Figure C.1) and precipitation (Figure C.2) recorded in the surrounding environment where the soil incubation tests took place are presented.

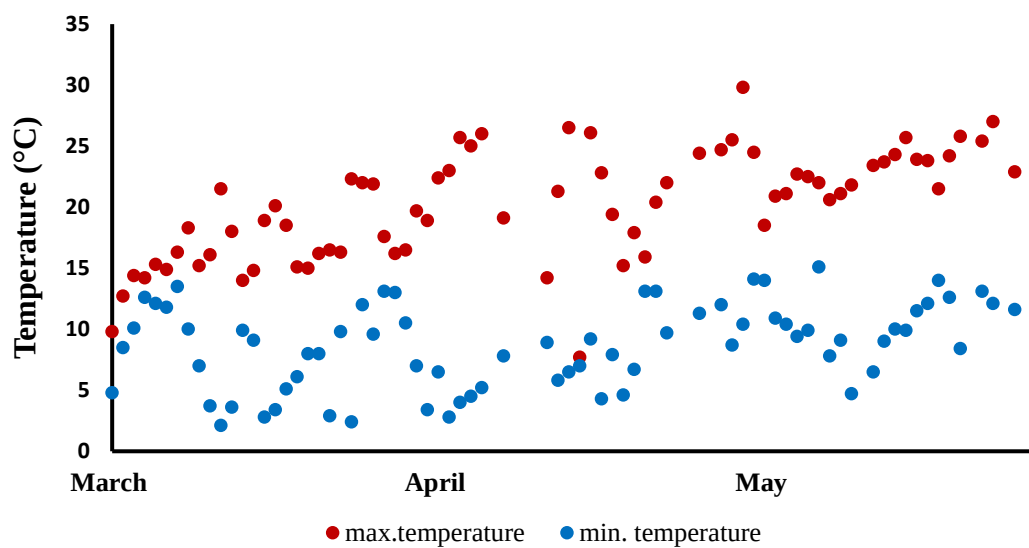


Figure C.1. Minimum and maximum temperatures (recorded daily) in the surrounding environment where the soil incubation tests took place (12 weeks, March-May).

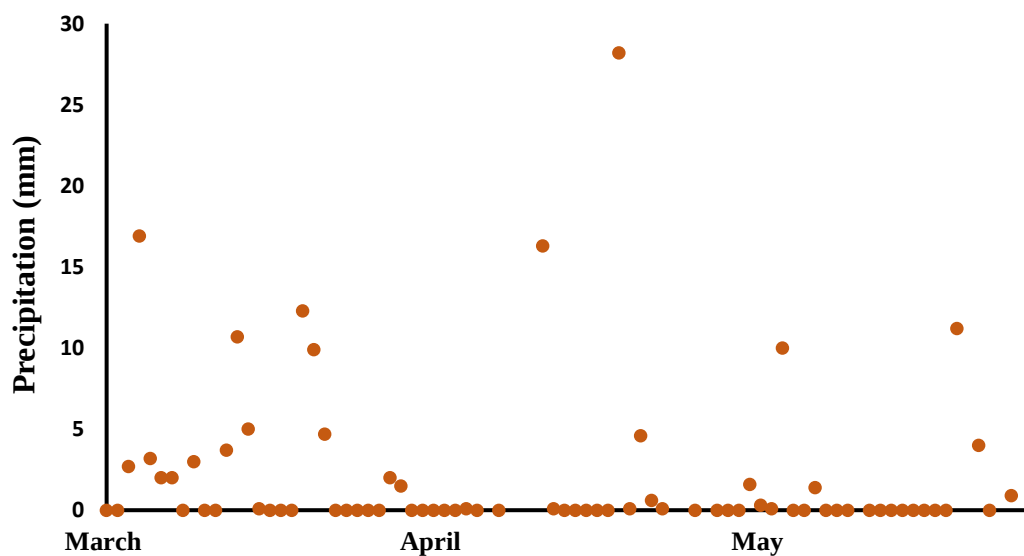


Figure C.2. Record of (daily) precipitation in the environment where the soil incubation tests took place (12 weeks, March-May).