Tomas Bata University in Zlín
Faculty of Technology

Doctoral Thesis

Investigating the influence of different additives on the mechanical properties and biodegradation of PHB and PBS

Zkoumání vlivu různých přísad na mechanické vlastnosti a biodegradaci PHB a PBS

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Abstract

In the current doctoral thesis, two well-known biodegradable polymers, polybutylene succinate (PBS) and polyhydroxybutyrate (PHB), are examined for their complex interactions with diverse additives. The study focuses on the effects of two different kinds of lignin antioxidants and essential oils on the biodegradability and mechanical characteristics of these polymers.

The first step in the research is to examine how antioxidants from lignin and essential oils may be added to the PBS and PHB matrices. This meant carefully examining how well these additives worked with the polymers and adjusting their concentrations to provide improved qualities. Advanced characterisation techniques were used to evaluate the thermal stability, morphology, and chemical interactions of the composite materials.

The modified PBS and PHB specimens exposed to simulated environmental conditions in order to assess the effect on biodegradability. The study also thoroughly studies the mechanical characteristics of the modified PBS and PHB materials. A thorough knowledge of the additive impacts on the overall performance and structural integrity of the polymers was possible after the determination of storage modulus, loss modulus, and other critical mechanical characteristics.

The results of this study showed that alkali lignin, organosolv lignin, and the chosen essential oils (eucalyptol, thymol, and limonene) could significantly retard biodegradation. However, the influence of neutralized alkali lignin was greater than that of the others in reducing PHB biodegradation (by around 50-60% with a 12% addition). Another outcome was that the influence of lignin was evident even with the addition of 1%, while essential oils had a completely different effect. Adding a high percentage of essential oils made the polymer more flexible than required by reducing the Tg. For PBS, the influence of both neutralized alkali lignin and organosolv lignin was almost the same, retarding biodegradation from 10 to almost 55% with an addition of 1 to 12%, respectively. Mechanical and thermal analyses were performed using DSC and DMA. The results showed that the two types of lignin used had a positive influence on the mechanical and thermal properties of the matrix. Moreover, by adding the optimum amount of essential oil, these properties can be controlled while also having a significant influence on biodegradation as antimicrobial agents.

Abstrakt

V současné doktorské práci jsou zkoumány dva známé biodegradovatelné polymery, polybutylensukcinát (PBS) a polyhydroxybutyrát (PHB), a jejich složité interakce s různými přísadami. Studie se zaměřuje na vliv dvou různých druhů antioxidantů z ligninu a esenciálních olejů na biodegradovatelnost a mechanické vlastnosti těchto polymerů.

Prvním krokem ve výzkumu je zkoumání, jak mohou být antioxidanty z ligninu a esenciální oleje přidány do matric PBS a PHB. To znamenalo pečlivé zkoumání toho, jak dobře tyto přísady pracují s polymery a upravování jejich koncentrací pro dosažení zlepšených vlastností. Pro hodnocení tepelné stability, morfologie a chemických interakcí kompozitních materiálů byly použity pokročilé charakterizační techniky.

Modifikované vzorky PBS a PHB byly vystaveny simulovaným environmentálním podmínkám, aby byl posouzen vliv na biodegradovatelnost. Studie také důkladně prozkoumala mechanické vlastnosti modifikovaných materiálů PBS a PHB. Po stanovení elastického modulu, ztrátového modulu a dalších kritických mechanických vlastností bylo možné získat hlubší znalosti o vlivu přísad na celkovou výkonnost a strukturální integritu polymerů.

Výsledky této studie ukázaly, že alkalický lignin, organosolv lignin a vybrané esenciální oleje (eukalyptol, thymol a limonen) mohou výrazně zpomalit biodegradaci. Nicméně, vliv neutralizovaného alkalického ligninu byl větší než u ostatních při snižování biodegradace PHB (o přibližně 50-60% při přidání 12%). Další zjištění bylo, že vliv ligninu byl patrný i při přidání 1%, zatímco esenciální oleje měly zcela odlišný účinek. Přidání vysokého procenta esenciálních olejů způsobilo, že polymer byl flexibilnější než požadováno, což snížilo Tg. U PBS byl vliv neutralizovaného alkalického ligninu a organosolv ligninu téměř stejný, zpomaloval biodegradaci od 10 do téměř 55% při přidání 1 až 12%. Mechanické a tepelné analýzy byly provedeny pomocí DSC a DMA. Výsledky ukázaly, že oba typy ligninu měly pozitivní vliv na mechanické a tepelné vlastnosti matrice. Navíc, přidáním optimálního množství esenciálního oleje mohou být tyto vlastnosti kontrolovány, přičemž mají významný vliv na biodegradaci jako antimikrobiální látky.

CONTENT

1. INTRODUCTION

1.1 Background and Motivation

The widespread production of commodity plastics has led to unprecedented pollution of both land and oceans, posing a significant challenge, particularly in developing nations with inadequate waste management systems [1,2]. Over recent years, plastic production has notably surged due to its cost-effectiveness, versatility, and favourable physical attributes, resulting in its expanded application across various industries. However, the linear consumption and slow degradation rate have led to the accumulation of plastic in the environment, recognized as a significant drawback [3]. The annual plastic production has seen a staggering increase from 2.3 million tons in 1950 to 448 million tons in 2015 [4], and almost 400 million in 2021. Approximately half of plastic waste still finds its way to landfills, with additional plastic leakage into the environment throughout different stages of its lifecycle. Nonetheless, certain countries, including Austria, Germany, and the Netherlands, have managed to achieve a remarkable 80-100% recovery of both energy and materials from plastic waste. In line with environmental concerns, as of July 3, 2021, EU Member States have prohibited the sale of single-use plastic items such as plates, cutlery, straws, balloon sticks, and cotton buds [5].

The development of biobased and biodegradable plastics is a direct result of the growing environmental concerns around the widespread usage of polymers made from petroleum [6–8]. Due to their potential to solve environmental challenges and their capacity to degrade under both aerobic and anaerobic circumstances, biodegradable polymers made from renewable resources have attracted a lot of interest [9,10].

Biodegradation refers to the complete breakdown of a substance into simpler molecules like water, nitrate, and ammonium, achieved through reduction or oxidation. The pursuit of a naturally biodegradable alternative to conventional plastics has captivated researchers across various fields [7]. However, biodegradable plastics necessitate specific environmental conditions for effective degradation to take place [11]. Successful biodegradation demands suitable factors like temperature, moisture, and oxygen, fostering the growth of microorganisms that break down the plastic. When used appropriately, biodegradable materials can help mitigate waste buildup, but effective waste management practices remain crucial. Notably, the by-products resulting from biodegradation may be more harmful than the original decomposed chemical [12].

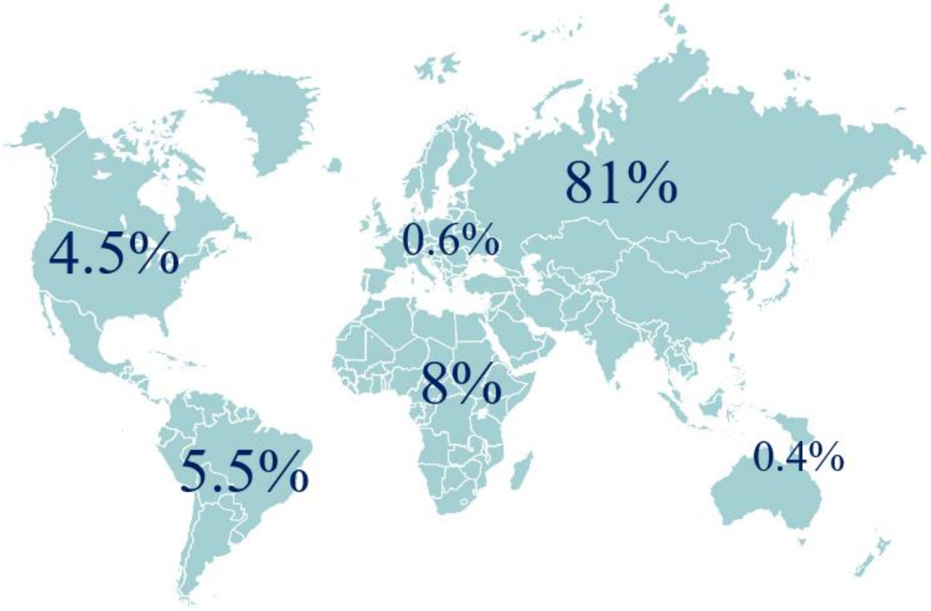


Fig 1. Continents that emit most ocean plastics in 2021.

In contemporary times, numerous analogous materials have been explored and commercialized, encompassing a range of polyesters. However, their properties and costs have hindered wider application. Their biodegradability and degradation rate are also contingent on the specific end-of-life environment. Over the past half-century, polyester production volumes have surged and are projected to continue growing, primarily due to their versatility across various applications and their eco-friendly nature. For instance, polyesters are often more compatible with circular material flows compared to many conventional materials like polyolefins.

The Poly(butylene succinate) (PBS) and Polyhydroxyalkanoates (PHA) family of aliphatic polyesters, which includes Polyhydroxybutyrate (PHB) and, are notable family of eco-friendly materials. PHB, a carbon and energy storage material manufactured by different bacteria, demonstrates biodegradability, biocompatibility, and thermos-plasticity [13,14]. PBS, on the other hand, is a promising material in the field of bioplastics since it is generated from fossil fuels and natural sources and has excellent thermostability, biodegradability, and processability [15,16]. Its superior thermostability, biodegradability, and processability, especially its superior mechanical property comparable to isotactic polypropylene (PP), point to a promising future for this material in the field of bioplastics, but its poor water barrier, high light transmittance, and high production costs restrict its potential for further use. To address these limitation, numerous approaches have been explored, including the incorporation of various additives into PHB and PBS.

1.2 Challenges in Commercializing PHB and PBS

Among the mentioned polyesters, PHA and PBS, are more attractive for researchers due to their biodegradability and performance. PHAs are biodegradable polymers synthetized in the microbial cells as an energy store in the form of intracellular granules. Various substrates and monomers may be used to generate PHAs, and different microbes can manufacture the polymer, resulting in a variety of PHAs with a wide range of characteristics [17]. Although the majority of PHA research has been conducted on PHB and its copolymer with valerate (PHBV), over 140 varieties of monomers have been identified [18]. PHA is thus fully biobased and biosynthesized polymer and is quite readily and fully biodegradable in compost, soil, and water environments.

On the other hand, PHB and PBS both have a number of drawbacks while having promising qualities that have prevented their widespread commercial application. PHB has difficulties with respect to its mechanical qualities, flexibility, melting temperature, and relatively high manufacturing costs, which act as roadblocks to its widespread application in a variety of sectors [19]. Furthermore, because PBS and PHB degrades quickly, it cannot be used in several agricultural applications where long-term biodegradation management is crucial [20,21]. PBS's potential for usage has been constrained by factors such as its low water barrier, high light transmittance, and expensive production costs [22].

1.3 Ehancing PHB and PBS through Additive Modification

Researchers have looked at a variety of methods to improve PHB and PBS's characteristics in order to get over their drawbacks and increase their economic viability. Copolymers, crosslinking agents, natural chemicals, antimicrobial agents, and chain extenders are only a few of the methods that have been researched to improve the mechanical and thermal properties of PHB and PBS for various applications[23,24].

Essential oils, for example, have showed promise in improving PHB's characteristics while simultaneously providing modest antibacterial effects. The influence of essential oils on the has been investigated by several researchers as a high potential of its antimicrobial impact in soil [25–27].

Essential oils (EOs) are aromatic oily substances extracted from plants through various methods such as fermentation, extraction, and expression[28–30]. They are complex compounds comprising a blend of volatile and non-volatile components, with many having demonstrated efficacy in combating multi-drug-resistant (MDR) bacteria. Some EOs can even work synergistically with antibiotics to enhance their effectiveness. However, their limited solubility in water, susceptibility to oxidation, and volatility constrain their applications[31].

The effectiveness of each EO can be gauged by factors like the minimum inhibition concentration (MIC), which signifies the lowest concentration preventing visible growth of microorganisms[32]. Essential oils serve multiple purposes as additives in polyesters, such as functioning as plasticizers or antimicrobial agents [32]. Their primary application in polymers is for food packaging purposes. However, due to safety and environmental concerns, the use of additives in polymers in contact with food is regulated. EOs, being natural and recognized as generally safe (GRAS) by the Food and Drug Administration, can be added without adverse effects on food [31]. Active food packaging has recently gained traction, aiming to extend shelf life and enhance consumer safety [33]. Active ingredients in plant essential oils inhibit microorganisms by interfering with protein synthesis, damaging cytoplasmic membranes, disrupting proton motive force, electron flow, and active transport. Notably, carvone [34], oregano [35], carvacrol [36], and thymol [37] are particularly intriguing EOs for the food packaging sector due to their abundant presence and effectiveness in antimicrobial and antioxidant roles. They encompass phenolic compounds known for their antimicrobial properties against bacteria and fungi in food.

In certain cases, specific types of EOs can influence polymer biodegradation by altering crystallinity. This influence can either accelerate or slow down degradation. Some EOs, such as thymol and eucalyptol, possess antioxidative properties that enhance their appeal, particularly in the food packaging industry [33]. On the other hand, the ability of using this types of additives are still questionable in case of thermal and mechanical properties.

For biopolyesters, oxidative degradation mechanism can be explained in two main steps; 1) reduction in molecular mass that is caused by random chain scission, and 2) predominate production of anhydrides[38]. To eliminate this step of degradation or retard this process, blending even a low concentration of antioxidants or oxidation stabilizer is required [39]. Oxidation stabilizers classified in various types.

Several researchers used lignin as a suitable and cheap natural anti-oxidant for polyester's modification [40,41]. Incorporating organosolv, soda, and kraft lignin (KF) with various concentrations into the polyesters. Soda lignin is obtained by treating wood chips with sodium hydroxide (NaOH) and sodium sulfide (Na_2S) solution, while organosolv lignin is obtained by using an organic solvent, like ethanol or methanol to extract lignin from wood chips. Kraft lignin is a type of lignin that is obtained through the kraft pulping process. These additives cause to enhance oxidative degradation and matrix thermal degradation temperatures and hence, improve the stability of polymers. These additives could be interesting for researchers as they can have antimicrobial impact even at the low concentration [42]. It is worth noting that there is no significant difference between the effects of low and high concentrations of certain lignin; nevertheless, researchers aim to use high concentrations of lignin to enhance the mechanical properties, despite its cost [43]. The lower concentration of lignin is considered optimal since there is no significant disparity in the anti-bacterial and anti-oxidant efficacy of the additive between high and low lignin concentrations. However, regarding the mechanical properties such as tensile strength, high concentration of lignin would be more beneficial [44], owing to the low aspect ratio of this aromatic polyester, it can act as a filler.

Despite the potential advantages of adding lignin to PBS to reduce the drawbacks of composite materials, the use of lignin-based bioplastics is constrained by their subpar processability and mechanical characteristics [5]. In order to improve the lignin's processibility, researchers have used techniques like neutralization or acidification [45,46]. Additionally, it has been investigated to improve thermal behavior and crystallization by adding lignosulfonate calcium (LS), a natural filler made from lignin, to the PBS matrix, which would lower the cost [47]. Additionally, due to strong interactions between lignin and PHB, lignin has showed promise in enhancing the thermal characteristics of PHB, lowering the activation energy (Ea) and raising the glass transition temperature (Tg).

While there have been numerous studies dedicated to enhancing the mechanical properties and cost-effectiveness of PHB and PBS, the impact of lignin as an additive on their biodegradability and resistance to degradation in soil has not been thoroughly investigated. Furthermore, compared to other properties, the effect of lignin on the polymer matrix and structure of PBS and PHB has not been extensively studied.

1.4 Research Objectives

Although lignin and essential oils have been used as additives, their effects on PHB and PBS's biodegradability and resistance to breakdown in soil have not been adequately researched, despite the fact that many studies have explored additives to improve the mechanical qualities and economic viability of PHB and PBS. The impact of lignin on the polymer matrix and structure of PBS and PHB has also not received as much research as other features. This thesis contributes to the knowledge of how to maximize the performance of biodegradable polymers by thoroughly examining the impact of lignin as an addition on the biodegradability and mechanical qualities of PBS and PHB. This study also studies the influence of different types of essential oils on the biodegradability (their influence as antimicrobial and antifungal additives). The research has the potential to expand the uses of biodegradable polymers in packaging, agriculture, and other environmentally friendly industries.

Through a comprehensive investigation, this Ph.D. thesis endeavours to contribute to the sustainable development of biodegradable plastics, paving the way for their utilization in various eco-friendly applications.

2. AIM OF THE THESIS

The following query can be made in light of the data given above and the literature:

1. Is it possible to control the biodegradation of PBS and PHB with additives? The potential answer would be: yes, it is possible due to the controlling the activity of microorganisms in soil by using antimicrobial agents (terpenoids). Moreover, due to the structure of lignin, it can protect the contact of PBS molecular chain to the enzymes that are able to degrade it [48].
2. And is it possible to improve the mechanical properties of the mentioned polyesters by the additives that used for controlling the biodegradation? Concerning the thermal characteristics of PHB, the inclusion of lignin leads to a notable reduction in the activation energy (Ea), lowering it to half of the value observed in pure PHB. Furthermore, an increase in lignin content results in a higher glass transition temperature (Tg) for PHB, indicating the existence of robust interactions between lignin and PHB. Almost the same situation is expected for PBS. Moreover, the influence of terpenoids could be the same as lignin in this category.
3. Along with their environmentally friendly properties, the aim of this research study is to increase the number of industries that can accept these polymers such as food packaging.

The goal of this research is to study the biodegradation and mechanical properties of blended samples with two types of lignin and terpenoids. The main purpose of this study is to make a condition in which the compatibility of additives and our polyester will be optimised. These purposes will be followed by testing the samples by different experiment such as DSC, DMA, SEM, and biodegradation. The methodology of this research will be discussed in the following chapter.

3. THEORETICAL FRAMEWORK

Plastic pollution is one of the biggest world concerns nowadays. In this case, having, or making biodegradable plastics from one side and using less plastic (less using and using long-lasting polymers) are of actual importance.

Asian nations are the primary contributors to oceanic plastic pollution, accounting for approximately 81% (by the percentage of the plastic weight consumed) of the total global input. The top five Asian contributors include China, Indonesia, the Philippines, Vietnam, and Sri Lanka. Following Asia, Africa ranks as the second-largest source of ocean plastics, contributing about 8% of the total global input. The Americas, Europe, and Oceania each contribute to equal or less than 5% of the total input of ocean plastics [49].

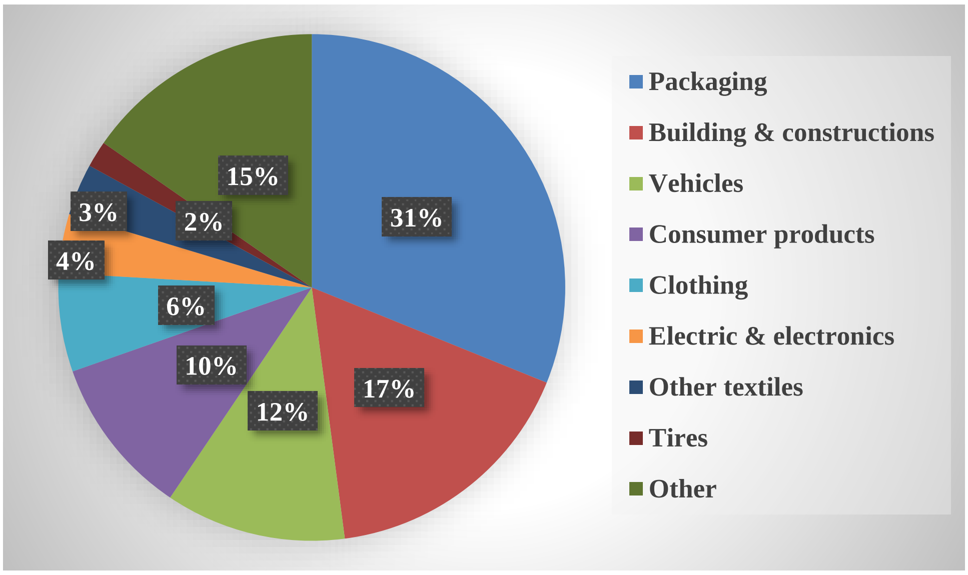


Fig 2. Plastic consumption worldwide in 2019, by application [13].

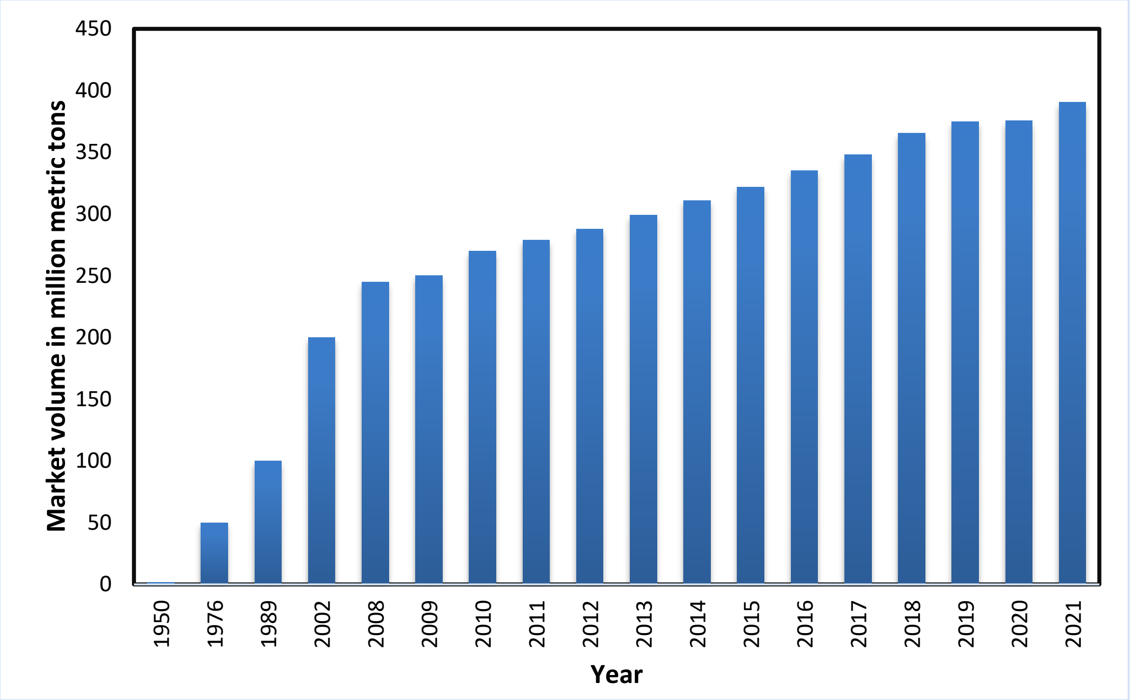


Fig 3. Annual worldwide production of plastic from 1950 to 2021[5]

Several attempts have been performed to address the aforementioned issues; however, using biodegradable plastic as well as attempt to making the plastic biodegradable is still known as the most useful technique. Biodegradation is the process of completely breaking down a substance into simple molecules, such as water, nitrate, and ammonium, through reduction or oxidation. The search for a naturally biodegradable substitute for conventional plastics was a compelling subject that attracted scholars from diverse fields of study [50]. However, biodegradable plastics necessitate specific environmental conditions to undergo effective biodegradation [51]. These conditions include appropriate levels of temperature, moisture, and oxygen that support the growth of microorganisms responsible for biodegradation of the plastic. Biodegradable materials, when used appropriately in specific applications, can contribute to reducing waste accumulation in the environment. However, effective waste management practices are still necessary. It is important to highlight that during the process of biodegradation, the resulting by-products may be more hazardous than the original chemical that is being decomposed [12]. Today, a number of similar materials have been studied and commercialized, including a variety of polyesters, but their properties and cost prevented their broader application. Their biodegradability and degradation rate also depends on the specific end-of-life environment. Over the past 50 years, production volumes of polyesters have been on the rise and are projected to continue increasing (as depicted in

Fig. 4) thanks to their versatility for numerous applications and environmentally friendly nature. As an example, polyesters are typically more suitable for circular material flows in comparison with many traditional materials such as polyolefins. Among all types of polyesters, there has been a slight increase in the use of recycled polyester between 2008 and 2021, highlighting a positive trend towards sustainability and environmental conservation (Fig. 5).

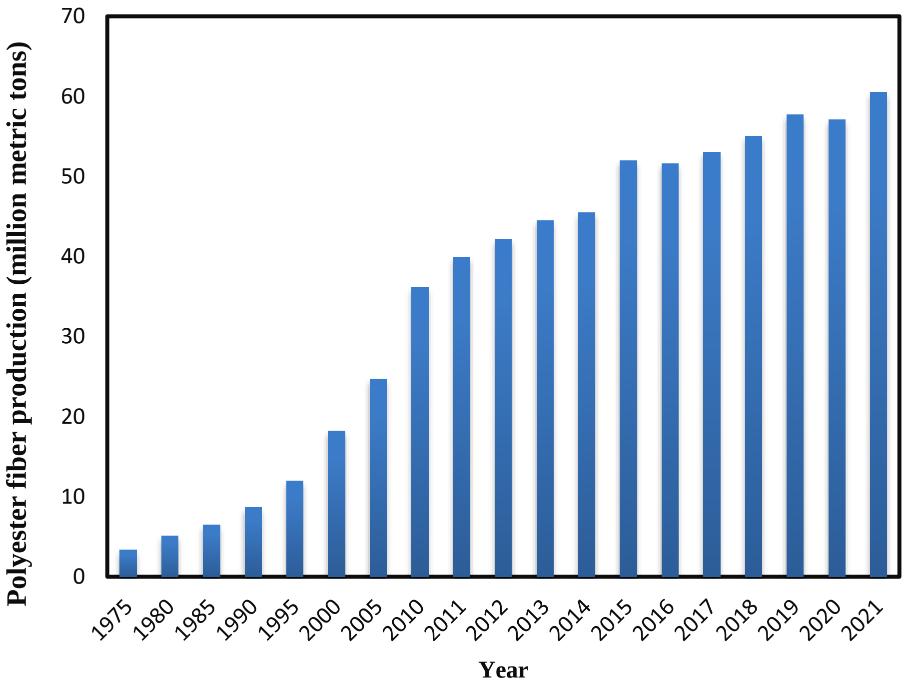


Fig 4. Worldwide production of polyester fibres from 1970 to 2022[52].

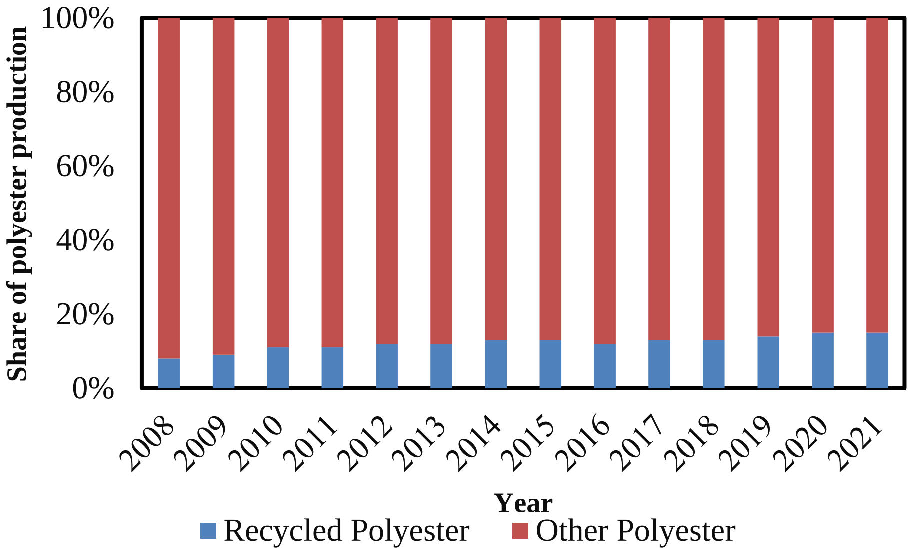


Fig 5. Worldwide production of polyester; recycled vs. non-recycled[53].

Among these polyesters, PHB and PBS, are among the attractive for researchers due to their biodegradability and performance. PHAs are biodegradable polymers synthetized in the microbial cells as an energy store in the form of intracellular granules. Various substrates and monomers may be used to generate PHAs, and different microbes can manufacture the polymer, resulting in a variety of PHAs with a wide range of characteristics [21]. Although the majority of PHA research has been conducted on PHB and its copolymer with valerate PHBV, over 140 varieties of monomers have been identified [22,23]. PHA is thus fully biobased and biosynthesized polymer and is quite readily and fully biodegradable in compost, soil, and water environments.

The drawbacks of biodegradable polyesters have been extensively studied through the use of various additives. However, there is a lack of a comprehensive review that considers all types of additives simultaneously. Such a holistic approach would allow for a thorough examination of the main limitations associated with each polyester and the specific additives used to address them. This is important because the addition of an additive can sometimes introduce new issues that need to be resolved. By systematically evaluating the effects of different additive characteristics across the various polyester systems, it would be possible to determine the optimal use of each additive type and develop more effective strategies for improving the performance of biodegradable polyesters.

The goal of this study is to explore the many facets of polymer science while concentrating on the modification of two well-known biodegradable polyesters, PHB and PBS. The main goal is to use essential oils and two types of lignin to enhance mechanical properties along with the control over the biodegradation of these polymers. This theoretical framework offers a thorough viewpoint to support the empirical investigation of these creative tactics.

3.1PHB and PBS biodegradation

As mentioned earlier, a crucial component of polymer science is biodegradation, which is the process by which microorganisms naturally break down polymers into harmless chemicals. Regarding PHB and PBS, there are several aspects that can influence their biodegradability.

One of the aspects to be mentioned is their chemical structure. PBS is an aliphatic polyester that degrades naturally and is made up of butylene and succinic acid repeating units. It has the chemical formula $[-(CH_2)\_4-COO-]_n$, where n stands for the level of polymerization. The repeating units' ester connections (-COO-) make PBS vulnerable to enzymatic hydrolysis during biodegradation. PHB is a thermoplastic polyester made of 3-hydroxybutyrate monomer units that is biodegradable. Its chemical formula is $[-(CH_2)\_2-C(=O)-CH_3]_n$, where n denotes the length of the polymer chain. Like PBS, PHB has ester bonds (-C(=O)-) that are susceptible to microbial deterioration. The phenolic and hydroxyl groups in essential oils and lignin can take part in antioxidant and antimicrobial processes. The ester linkages in PBS and PHB are important sites of enzymatic hydrolysis [54,55].

Microbial activity and environmental conditions are the other factors that should be taken into account. PHB and PBS are known to their fast biodegradation in soil, industrial and home composting. Essential oils are suitable for slowing down the activities of microorganisms living in soil and compost. In this regards, as we expect to have the essential oils on our polymer surface, it is expected that we will have the activity of microorganisms in soil retention [56].

Regarding lignin, it was found that it causes to reduce the PHB degradation temperature, although it cause to retar the degradation rate in a wide range of temperatures [57,58]. Moreover, due to the lignin structure, it can protect the contact of PBS molecular chain to the enzymes that are able to degrade it [48]. Due to its inherent resistance to enzymatic breakdown, lignin may also have a very small amount of antibacterial action. To be more specific, the microorganisms that can degrade lignin are limited in soil compare to the ones which are able to degrade PBD and PHB [59,60]. It is worth noting that increasing the content of lignin reduce the degradability sharply due to the higher protection potential of lignin for the microbial action against the materials.

3.2Crystallinity and Glass Transition Temperature (T_g)

A crucial characteristic of polymers that influences their mechanical behavior is their crystallinity. It describes the extent to which polymer chains are arranged in structured, crystalline areas throughout the substance. PBS and PHB's crystallinity may be determined using methods like differential scanning calorimetry (DSC) or X-ray diffraction (XRD). In this research we have tried DSC and we will evaluate the results in the next step. We will be able to comprehend how the addition of additives, including antioxidants produced from lignin and essential oils, affects the structural arrangement of the polymer by measuring crystallinity. Because ordered regions are often stiffer than amorphous parts, changes in crystallinity can directly affect mechanical qualities[61,62]. It is also expected that the crystallinity will reduce at the first days, while after a few weeks this factor can be increased. This phenomenon was asserted by Beltrami and her colleagues [63], who proposed that enzymatic degradation started first in the amorphous phase, thus increasing the crystallinity of the samples

Tg represents the temperature at which a polymer transitions from a glassy, rigid state to a rubbery, more flexible state [64,65]. It is an essential variable for comprehending how a polymer behaves throughout a variety of temperatures. The effect of lignin and essential oils on the thermal and mechanical transitions of PBS and PHB will be studied by measuring Tg[66]. Depending on how well the additives work with the polymer matrix, the addition of additives may affect Tg. it would be anticipated that although certain additions may have little or no effect on the polymer's flexibility at lower temperatures, others may reduce Tg. The decrease in Tg values can lead us to conclude that eucalyptol, thymol, and limonene will be miscible with the amorphous phase of PHB and that they will increase the molecular mobility of the polymer matrix [18].

3.3Mechanical Properties

Through the measurement of loss and storage moduli, the dynamic mechanical behavior of polybutylene succinate (PBS) and polyhydroxybutyrate (PHB) will be characterized in this work. These characteristics shed light on how the materials react to mechanical stress and temperature variations.

The energy lost as heat during cyclic deformation of a material is represented by the loss modulus[67]. It shows the polymer's capacity to take in energy and transform it into heat, which can be very important in applications with dynamic loads. By measuring E'', we may determine how the addition of lignin and essential oils affects PBS and PHB's damping ability, potentially changing how resistant they are to mechanical wear and dynamic stress.

The energy that is stored during cyclic deformation is represented by the storage modulus, which measures a material's elastic nature[68]. It offers details on stiffness and elasticity and represents the material's capacity to hold and release energy. By analysing E', we may determine how PBS and PHB have been modified and how that has affected their stiffness and resistance to deformation, revealing prospective gains in their mechanical characteristics.

3.4. Additives to address PBS and PHB drawbacks

3.4.1.1. Plant oil (Essential oils)

Currently, the major portion of the industrial oil resources used in the food industry, petroleum products such as lubricating hydraulic and cutting oils as well as the transportation sector (e.g., as engine oil) are of petroleum origin that are leaving behind a huge deal of oleochemical pollutants (Fig. 6). Plant oils are considered by many as ideal environmentally-friendly, renewable, and sustainable feedstocks that could potentially replace petroleum-derived oil in the above-mentioned industries. Moreover, it is important to highlight that the market value of the fossil-oriented industrial oils is approximately equal to that of the fossil-oriented fuels. This indicates the economic viability of strategic replacement of fossil oils with plant oils.

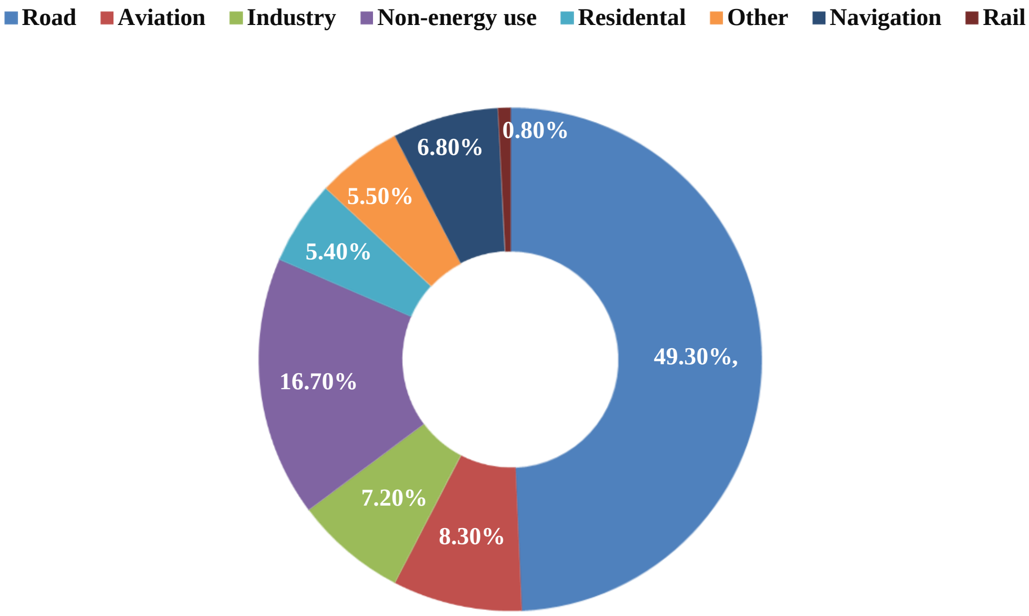


Fig. 6. Shares of world oil consumption in various sectors and industries in the year 2018. IEA, World Energy Balances, 2020. (IEA, 2018). Other: includes agriculture, commercial and public services, non-specified other, pipeline and non-specified transport.

It is noteworthy to mention that, more than 85% of the plant oils produced worldwide is used for human nutrition making it unrealistic to replace all fossil oils used in the industry and the transportation sector with plant oils. It has been anticipated that to replace only 40% of the fossil oils used in the above-mentioned industries with plant oils, global production of plant oils should be trebled till the year 2030. However, given the growing scarcity of renewable water resources (Fig. 7) and arable land (Fig. 8), this trebling will be very challenging specially with using the existing oil crops whose yields and oil contents have reached a plateau.

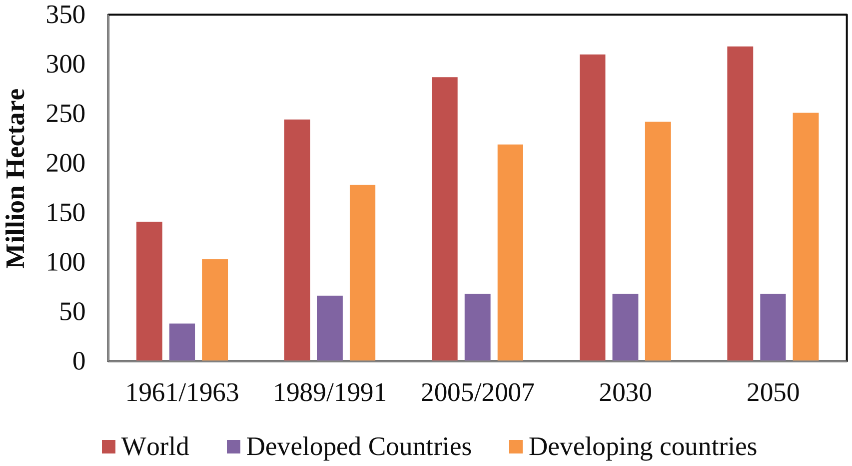


Fig. 7. Area equipped for irrigation (OECD, 2012).

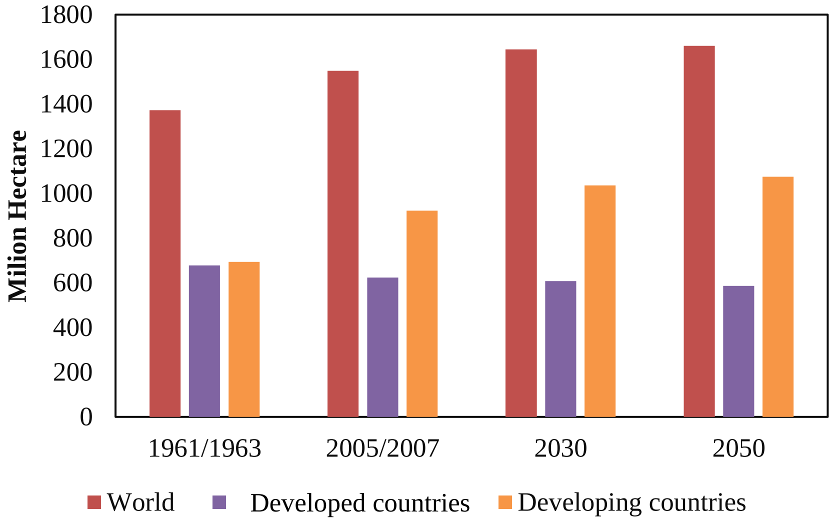


Fig. 8. Total arable land in use (FAO, 2011)

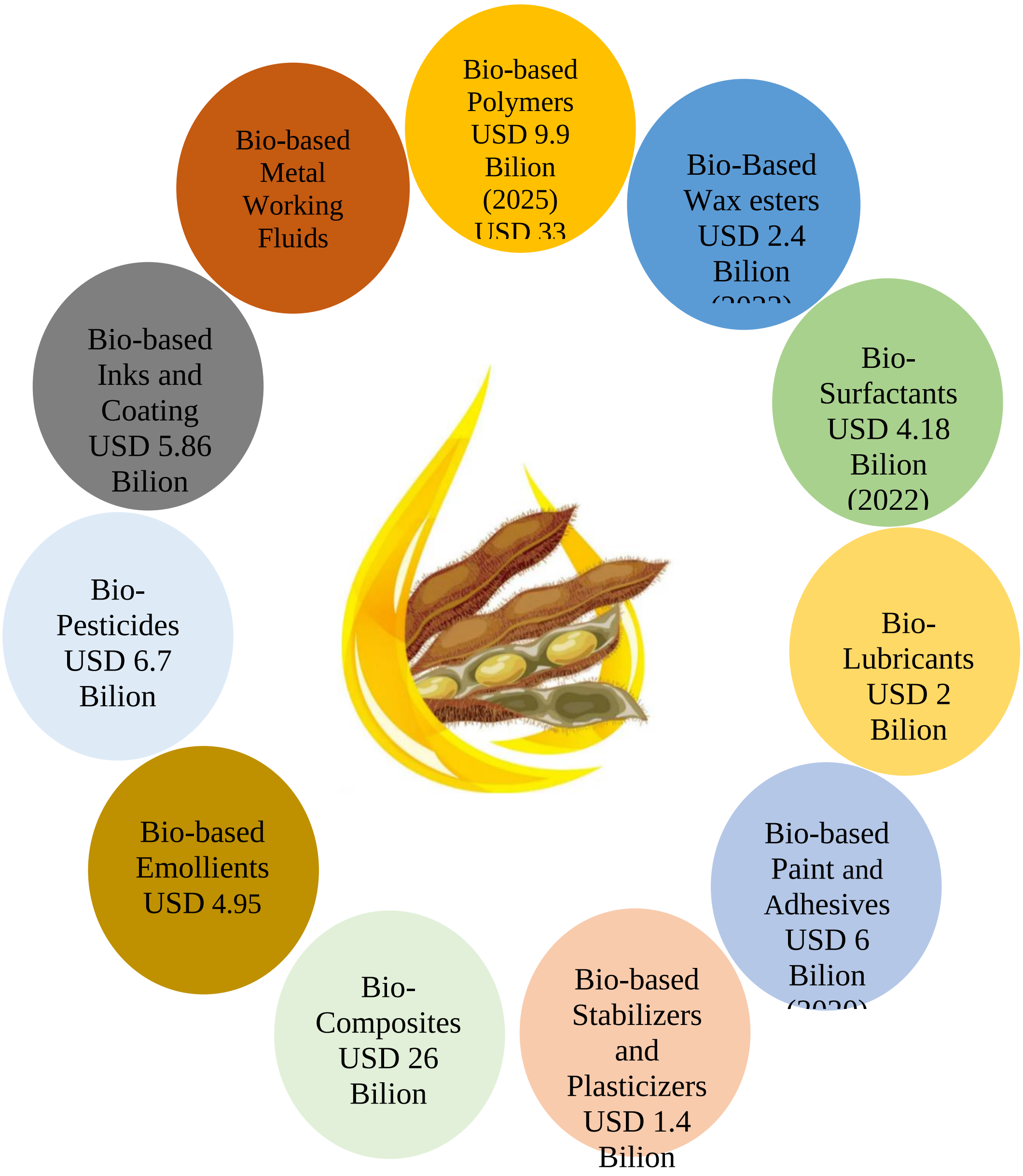


Fig. 9. Industrial applications of plant oils and their market size

Over the last decades, commercially available polymers have been fabricated from non-renewable fossil resources. The global annual consumption of polymers stands at 300 million tonnes with an annual growth rate of 5 %. Such a huge quantity and the resultant waste streams (disposed of into various ecosystems without treatment in many places in the world) have on one hand led to growing environmental and health concerns over the use of these materials, i.e., petrochemical based polymers, while on the other hand, caused a surge in interest in biobased polymers. These polymers are not only renewable in nature but they are also biodegradable, and eco-friendly. Biobased polymers can be synthesized from polysaccharides, fibers, and polylactic acid while triacylglycerol (TAG) oils and fatty acids can also be used as reliable starting materials during the production process. In 2019, the total production volume of bio-based polymers was 3.8 million tonnes (https://www.bioplasticsmagazine.com).

Plant oil-based polymers could be fabricated through different copolymerization techniques, (i.e., cationic, free radical, and thermal) of plant oils and a number of petroleum-based co-monomers. However, it should be noted that most plant oils need some modifications in their naturally-occurring reactive sites (e.g., ester groups and carbon-carbon double bonds) before they can be used as biopolymer. Therefore, these reactive sites such as the carbon–carbon double bonds present in the fatty acid chains are of critical importance during the. In better words, these double bonds serve as excellent starting points for the production of biopolymers. For instance, conversion of double bonds of fatty acids into hydroxyl groups, and the subsequent reaction of the resultant 'polyols' with isocyanate could lead to the formation of polyurethanes. Other polymerization techniques such as acyclic metathesis polymerization and ring-opening metathesis polymerization (ROMP) have also been employed to synthesize plant oil-based polymers reported that modified vegetable oils with acrylic double bonds were highly reactive and formed thermosetting biopolymers through free radical polymerization.

One of the most used additives nowadays not only for polyesters, but also for most of the common used polymers are essential oils [69,70]. The antimicrobial agent is an agent that protects the activity of microorganisms. Several additives have been added into polymeric matrix, especially in PHB and PBS matrix in recent years, including natural additives (such as essential oils), enzymes, chelating agents, antibiotics, peptides, and metals to provide antimicrobial activity [8].

Essential oils (EOs) are oily aromatic materials extracted from plants by different techniques such as fermentation, extraction, and expression [71] and known as complex compounds that contain a mixture of volatile and non-volatile parts, and many of them have been found to be efficient in destroying multi-drug-resistant (MDR) bacteria and can be used with antibiotics to increase efficacy synergistically. However, the insolubility in water, susceptibility for oxidation, and volatility limit their application [31]. Each EO's effectiveness can be determined by factors such as minimum inhibition concentration (MIC), which shows the lowest concentration of a chemical substance that prevents the visible growth of a microorganism[32]. There are several purposes for using essential oils as an additive to introduce into polyesters, such as plasticizers, , antioxidants, antimicrobial and barrier agents, etc.[72].

EOs are gaining increasing attention in the food industry, particularly in polymers for use in food packaging[73,74]. In fact, because the active components in essential oils migrate, their addition to packaging films and coatings has resulted in products with improved optical and barrier properties, as well as antioxidant and antibacterial activity [75]. Alkyl polymers such as PLA and PHA and starch-based polymers are examples of commercially used biopolymers in the production of sustainable food packaging films. However, the challenge associated with the use of these polymeric materials is to meet the requirements of improved mechanical and barrier performance, as well as market competitiveness. The addition of active ingredients such as EOs allows not only to improve the physicochemical properties of biopolymer-based films but also to increase food safety and quality[76]. The use of additives in polymers in contact with food is restricted due to safety and the environment. EOs are natural and also approved by FDA as GRAS additives [31] without any harmful influence on food [77]. For this reason, active food packaging has become increasingly popular in recent years as a way of extending the shelf life of food products while improving consumer protection [33].

Plant essential oils' active ingredients inhibit microorganisms by inhibiting protein synthesis, destroying the cytoplasmic membrane, disrupting the proton motive force, electron flow, and active transport [34]. Carvone[34], oregano[35], carvacrol [36], and thymol [37] are the most interesting EOs for the food packaging industry due to their abundance and performance in antimicrobial and antioxidant activities. They include phenolic compounds that have antimicrobial effects against bacteria and fungi that are present in food.

To some extent, some types of EOs can influence the biodegradation of polymer by their influence on crystallinity. In this case, the degradation could be enhanced or retarded as well as the antioxygenic activity of some EOs such as thymol and eucalyptol that made them more attractive, especially in the food packaging industry[78].

Furthermore, the barrier properties of the films are enhanced by the inclusion of EOs, with EOs playing a significant role in improving water barrier properties. Specifically, water molecules predominantly diffuse through the continuous polymer phase, where EO lipid droplets are situated. These discontinuities contribute to an increased tortuosity factor for water transfer within the matrix[79].

In particular, films incorporating citrus essential oil demonstrated a more substantial reduction in water barrier qualities compared to films incorporating tea tree essential oil [80]. This observation is elucidated by the higher hydrophobicity of the primary constituents of citrus essential oil (limonene) compared to those of tea tree oil (terpineol)[81]. Numerous studies posit that this effect is contingent on various structural factors, including the matrix type, composition and quantity of added oil, and interactions with the matrix.

The introduction of EOs into the films resulted in a noteworthy decrease in oxygen permeability values. This drop can be attributed to the increased solubility of the gas in the lipid phase, with lipid addition generally fostering improved oxygen permeability in the films [82]. The positive effect of EOs on the oxygen barrier properties of films can be attributed to the lower oxygen solubility in the more polar oils, as thyme and basil EOs, and the presence of antioxidant compounds have an oxygen scavenging role.

The worldwide essential oils market is anticipated to reach a value of USD 16.0 billion by 2026 (from 10.3 billion in 2021), increasing at a CAGR of 9.3%[83].

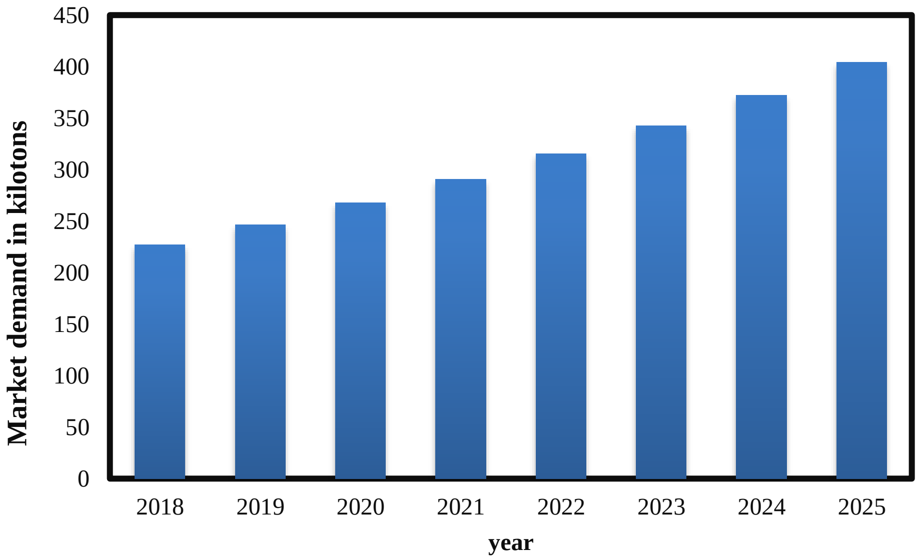


Fig 10. Market demand of essential oils with a forecast to 2025[84].

In terms of antimicrobial agent, the selection of the most effective additive hinges on the specific requirements of the application, with diverse options explored in recent years for polymeric matrices, particularly in PHB and PLA. In most industries, among the noteworthy candidates, EOs, specially thymol and carvacrol, stand out for their demonstrated antimicrobial and antioxidant activities, making them versatile choices for enhancing polymer properties. Not only their antimicrobial potential, but also the level of their influence that can be found by their MIC make them of actual value. Their and other EOs‘ ability to contribute to active food packaging, with FDA recognition as generally safe additives, adds to their appeal. Additionally, the increasing market demand for essential oils further underscores their potential as a preferred additive in this chapter. The choice of the best additive is influenced by factors like solubility, volatility, and impact on biodegradation, emphasizing the need for a nuanced selection process tailored to the targeted application.

3.4.1.2. Antioxidant

For biopolyesters, oxidative degradation mechanism can be explained in two main steps; 1) reduction in molecular mass that is caused by random chain scission, and 2) predominate production of anhydrides [38]. To eliminate this step of degradation or retard this process, blending even a low concentration of antioxidants or oxidation stabilizer is required [85]. Oxidation stabilizers classified in various types.

Several researchers used lignin as a suitable and cheap natural anti-oxidant for polyesters modification[40,41]. Incorporating organosolv, soda, and KF, with various concentrations into the polyesters. Soda lignin is obtained by treating wood chips with NaOH and sodium sulfide (Na_2S) solution, while organosolv lignin is obtained by using an organic solvent, like ethanol or methanol to extract lignin from wood chips. Kraft lignin is a type of lignin that is obtained through the kraft pulping process. These additives cause to enhance oxidative degradation and matrix thermal degradation temperatures and hence, improve the stability of polymers. These additives could be interesting for researchers as they can have antimicrobial impact even at the low concentration [42]. It is worth noting that there is no significant difference between the effects of low and high concentrations of certain lignin; nevertheless, researchers aim to use high concentrations of lignin to enhance the mechanical properties, despite its cost[43]. The lower concentration of lignin is considered optimal since there is no significant disparity in the anti-bacterial and anti-oxidant efficacy of the additive between high and low lignin concentrations. However, regarding the mechanical properties such as tensile strength, high concentration of lignin would be more beneficial[44], owing to the low aspect ratio of this aromatic polyester, it can act as a filler.

Lignin also possesses attributes such as antioxidant properties, substantial rigidity, thermal resilience, and UV-blocking capabilities [86]. Due to the previous research studies, PHB can be mixed with various types of commercially available lignin, without alteration, to enhance its mechanical, thermal, and rheological characteristics [87].

Despite the potential benefits of incorporating lignin into traditional polymers to mitigate the shortcomings of composite materials, the utilization of lignin-based bioplastics is limited due to their inferior processability and mechanical properties [88]. The problem that caused by poor processibility of some types of lignin such as Alkali can be solved by neutralization or acidifying of lignin [57].

Organosolv lignin is a type of lignin extracted from biomass through the organosolv process. Lignin is a complex organic polymer found in the cell walls of plants, providing structural support. The organosolv process involves using organic solvents, such as ethanol, methanol, or a mixture of both, along with an acid or a base, to break down the lignin and separate it from the cellulose and hemicellulose components of biomass materials like wood, agricultural residues, or grasses. Organosolv lignin used by several researchers to address the poor properties of different polymers, specially polyesters[89,90]. Due to its structure, it can possess more complexity to the polymer matrix, resulting in higher resistance against the biodegradation. Moreover, its low price, sustainability, and its potential to be use as a reinforcing filler in polymer matrices make it a valuable additive[91].

Although the incorporation of hydrophilic lignin led to fragility and increased water uptake, preventing the composites from meeting the required mechanical properties for certain applications, Lin utilized lignosulfonate calcium (LS), a natural filler, to enhance the thermal behavior and crystallization of composites within the PBS matrix, resulting in a noteworthy 40% reduction in cost [92]. Regarding the thermal properties of PHB, lignin can reduce the activation energy (Ea) to two times less than the pure PHB. Moreover, as the lignin content increased, the glass transition temperature (Tg) of PHB also increased, indicating the presence of strong interactions between lignin and PHB [93].

4. EXPERIMENTAL

The experimental part of this thesis will be related to the preparation of the thin films for PLED device, which will be organized to these separate segments:

4.1Chemicals and Materials

The study utilized PHB in its powdered form, sourced from Tiatan Biologic Materials Co., Ltd. in Beilun, Ningbo, China, with a molecular weight of 66,500 g mol−1. Additionally, PBSA or bio PBS used in the research was acquired from Mitsubishi Company in Japan, possessing an average molecular weight of 120,000 g mol−1. The terpenoids used in this research summarised in table 1.

Additive (Purity)	Molecular weight	Made in	Other Properties Melting point (MP), Bubble point (BP)
Camphor (98%)	152.23	USA	MP=179-181˚C
Thymol (98.5%)	150.22	India	PB=232 ˚C, MP=48-51˚C
Carvacrol (≥98%)	150.22	India	MP=3-4 ˚C, BP=236-237 ˚C
Trans-Anethole (99%)	148.20	Spain	MP=20-21 ˚C, BP=234-237 ˚C
Eugenol (99%)	164.2	Germany	MP= 12- -10, BP=254 ˚C
Eucalyptol (99%)	154.25	USA	MP=1-2 ˚C, BP=176--177 ˚C
Carvone (98%)	150.22	China	BP=227-230 ˚C
Limonene (96%)	136.23	Spain	BP=175-177 ˚C
Trans-Cinnamaldehyde (99%)	132.16	China	MP=-9 - -4 ˚C, BP=250-252 ˚C
Nerol	154.25	USA	BP=103-105 ˚C

Table 1. The properties of essential oils used to blend with PHB

The additives that have been used in this research have natural sources. Regarding the essential oils, that are derived from various natural sources, each possessing distinct chemical compositions and aromatic profiles. Camphor, known for its strong, minty scent, is extracted from the wood of camphor trees, particularly the Cinnamomum camphora species. Thymol, characterized by its pungent, herbal aroma, is sourced primarily from the leaves and flowering tops of thyme plants, such as Thymus vulgaris. Carvacrol, with its warm, spicy scent, is abundant in oregano and thyme essential oils, obtained from Origanum vulgare and Thymus capitatus, respectively. Trans-Anethole, recognized for its sweet, licorice-like fragrance, is predominantly found in anise seeds, obtained from the Pimpinella anisum plant. Eugenol, boasting a rich, clove-like aroma, is derived from clove buds, harvested from the Syzygium aromaticum tree. Eucalyptol, renowned for its fresh, menthol-like scent, is extracted from the leaves of eucalyptus trees, such as Eucalyptus globulus. Carvone, possessing a distinct minty aroma, is abundant in the seeds of caraway and spearmint plants, sourced from Carum carvi and Mentha spicata, respectively. Limonene, characterized by its citrusy fragrance, is prevalent in the peels of citrus fruits, including lemons, oranges, and limes. Trans-Cinnamaldehyde, known for its warm, spicy aroma reminiscent of cinnamon, is derived from the bark of cinnamon trees, particularly Cinnamomum verum. Lastly, Nerol, prized for its sweet, floral scent, is found in high concentrations in the essential oils of rose and neroli, obtained from Rosa damascena and Citrus aurantium var. amara, respectively. These diverse sources underscore the rich botanical diversity from which these essential oils are extracted, each contributing unique olfactory characteristics and therapeutic properties.

Alkali lignin and organosolv lignin are derived from different processes of lignin extraction, each originating from distinct biomass sources and extraction methods. Alkali lignin, also known as lignosulfonates, is primarily obtained as a byproduct from the pulping process in paper and pulp industries. During this process, wood chips or other lignocellulosic materials are treated with strong alkaline solutions, such as sodium hydroxide (NaOH) or sodium sulfite (Na2SO3), to remove cellulose fibers, leaving behind lignin as a byproduct. Alkali lignin is typically sourced from softwood species like pine and spruce due to their high lignin content and suitability for pulping.

On the other hand, organosolv lignin is obtained through an organic solvent-based extraction process. In this method, lignocellulosic biomass, such as wood chips, agricultural residues, or grasses, is treated with a mixture of organic solvents, such as ethanol, methanol, acetone, or ethyl acetate, under high temperature and pressure conditions. This treatment breaks down the lignin structure and dissolves it into the organic solvent, leaving behind cellulose and hemicellulose fractions. Once separated, the solvent is recovered, and the lignin is precipitated out by adding water or acid. Organosolv lignin extraction is typically more selective and results in higher purity lignin compared to the alkali process. The choice of biomass source for organosolv lignin extraction can vary and may include hardwoods, softwoods, agricultural residues, or dedicated energy crops, depending on factors such as availability, cost, and desired lignin properties for specific applications.

It is of actual importance to note that several preliminary studies have been conducted to find the most optimum additive for PHB and PBS. In this cae, different additives from different categories as well as different techniques were applied in this studies. One of the techniques was plasma treatment. For this technique, plasma was exposed to the samples with different gases. The most important gases were argon and air. After this step, burial test started in two different temperatures; 25 and 37 °C. Finally, the samples were monitored every two weeks to see the changes in terms of their shape and color. The other additives to be mentioned was silan, which was used as a crosslinker with decumyl peroxide as initiator. In the result section, we are going to explain these experiments more in details.

4.2Samples preparation

The preparation of samples for experimentation involved a series of meticulous steps to ensure consistency, reproducibility, and optimal performance of the materials under investigation. The process commenced with the thorough blending of the provided concentrations of additives with pure polyhydroxybutyrate (PHB) powder in a controlled environment. This blending process was meticulously conducted in a bowl to achieve homogeneity of the mixture, ensuring uniform dispersion of the additives throughout the PHB matrix. Subsequently, the blended mixture was loaded into a state-of-the-art twin-screw micro-extruder, specifically a HAAKE Minilab model manufactured by Thermo Fisher Scientific, operating at a predetermined speed of 50 rpm. The micro-extruder provided precise control over processing parameters, with temperatures set at 185 °C for PHB and 120 °C for polybutylene succinate (PBS), respectively. A predefined mixing duration of 2 minutes was determined as optimal under the specified conditions, ensuring thorough blending without inducing undesired material degradation. Prior to extrusion, the PHB powder underwent a meticulous drying process at 100 °C for 10 hours to eliminate any residual moisture and maintain material integrity.

Following extrusion, compression molding was employed to transform the extruded materials into films with consistent thickness and dimensions. The compression molding process utilized the same temperatures as the micro-extruder (185 °C for PHB and 120 °C for PBS), ensuring continuity and uniformity in material processing. The heating duration for molding was carefully controlled, with an approximate time of 2 minutes to achieve optimal material flow and consolidation within the mold cavity. Subsequently, the molded films were allowed to cool down to room temperature for approximately 10 minutes, facilitating solidification and dimensional stability. The resulting film specimens exhibited a uniform thickness ranging from 120 to 130 µm, with dimensions of 50mm × 300mm, ensuring consistency across samples for subsequent testing and analysis.

To facilitate the biodegradation and burial tests, the prepared film specimens were meticulously cut into small pieces of two different sizes: 5 × 5 mm for biodegradation testing and 5 × 50 mm for burial testing. This standardization of sample dimensions ensured uniformity and reproducibility in testing conditions, enabling accurate assessment of material performance under simulated environmental conditions. Overall, the meticulous preparation of samples following standardized protocols and utilizing advanced equipment and techniques laid the foundation for robust experimentation and insightful analysis of material properties and behavior.

4.3Experiments

4.3.1 Biodegradation

Throughout the process of aerobic decomposition of organic compounds, oxygen serves as a crucial reactant, facilitating the conversion of carbonaceous materials into gaseous carbon dioxide (CO_2). The evaluation of mineralization, which quantifies the extent of organic carbon conversion to CO_2, is integral to understanding the biodegradation process. To assess mineralization, experiments were conducted in 500 mL biometric flasks, adhering to ISO 17556 standards [7]. Each flask contained meticulously measured components: 50 mg polymer film fragments, precisely cut to 2 mm in size, 15 g of dry soil, 5 g of perlite, and 11 mL of mineral medium. These components were meticulously selected and combined to simulate environmental conditions conducive to biodegradation. Similarly, for burial tests and additional analyses such as dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM), identical percentages of perlite, mineral medium, and soil were employed to maintain consistency across tests [8]:

$$D_t = \frac{[CO_2]_t - [CO_2]_b}{ThCO_2}$$

The mineralization percentage (D_t) was calculated using a formula that compares the released $CO_2$from the sample ($[CO_2]_t$) to the accumulated CO_2 released from blank flasks ($[CO_2]_b$), relative to the expected theoretical amount of CO_2 (Th CO_2) from the test material. This calculation was vital for quantifying the degree of carbon transformation during biodegradation. To measure the released CO_2, a state-of-the-art mass spectrometer, the HPR-40 DSA, manufactured by HIDEN Analytical in 2020 and located in Warrington, UK, was employed. This sophisticated instrument provided precise and sensitive detection of CO_2, enabling accurate quantification of biodegradation rates. Each sample was tested in triplicate to ensure reproducibility, with four blank flasks included in the experiment to account for background CO_2 levels and ensure data accuracy. By meticulously adhering to standardized protocols and utilizing advanced analytical instrumentation, the mineralization experiments provided valuable insights into the biodegradation kinetics and environmental impact of the tested materials.

Before starting the main experiments, a preliminary biodegradation test along with a burial test (to see the physical shapes of the samples in different time steps) to determine the influence of the additives before main test. After this test, we decided to chose the aforementioned oils; thymol, eucalyptol, and limonene as antimicrobial agents and organosolv and neutralized alkali lignin as antioxidants for the further development.

Composting biodegradation tests followed the adapted and miniaturized ISO 14855 method, using 500 mL biometric flasks with septum-equipped stoppers. Mature compost from a local municipal composting facility (TSZ Ltd., Zlín, Czech Republic) was utilized for this study. Tests were conducted at 58°C for industrial composting and 28°C to simulate home-composting conditions. Each flask contained 2.5 g of dry-weight compost, 5 g of perlite, and 1 mL of mineral salt medium, with the substrate mixture's water content adjusted to 60% using sterile drinking water. Sample fragments, each 100 mg cut into 5 x 5 mm pieces, were placed in the flasks. Three flasks were prepared for each sample, along with four blank flasks. CO2 production from blank incubations was subtracted to determine the net mineralization of the samples.

4.3.2 Scanning Electron Microscope

Surface changes on the films were meticulously examined utilizing advanced microscopy techniques, specifically employing a Phenom Pro Desktop Scanning Electron Microscope (SEM) device manufactured by ThermoFisher Scientific, headquartered in Waltham, MA, USA. This sophisticated SEM apparatus facilitated high-resolution imaging of the film surfaces, allowing for the detailed analysis of microstructural alterations induced by biodegradation processes. Operating under optimal conditions, a 10 kV acceleration voltage was meticulously applied in the high vacuum mode to ensure optimal imaging quality and resolution. Prior to imaging, meticulous preparation of the samples was conducted to enhance imaging efficacy and minimize potential sample damage. To mitigate the risk of sample charging and ensure accurate imaging results, the samples were meticulously coated with a thin layer of Au/Pd using state-of-the-art sputter coating technology. This coating served a dual purpose: enhancing the surface conductivity of the samples to minimize charging effects and providing a uniform, conductive layer to facilitate optimal electron beam interaction and imaging resolution. By meticulously adhering to these standardized protocols and leveraging cutting-edge microscopy technology, the SEM examination offered invaluable insights into the microstructural changes occurring on the film surfaces during the biodegradation process, thereby enriching our understanding of the underlying mechanisms driving polymer degradation and informing the development of novel strategies for enhancing material durability and sustainability.

4.3.3 Differential Scanning Calorimetry

In this chapter, the DSC analysis was conducted using a state-of-the-art DSC1/700 analyser manufactured by Mettler Toledo, a renowned company based in Columbus, OH, USA. This instrument was equipped with a sophisticated mechanical cooling system, ensuring precise temperature control during the analysis. The analysis was performed in a controlled nitrogen atmosphere to prevent oxidation or other chemical reactions that could influence the results. To ensure accuracy, the instrument was calibrated using an indium standard, a common practice in DSC analysis.

The primary objective of the DSC analysis was to investigate key thermal properties of the samples, including their melting point, crystallinity, and glass transition temperature (Tg). These properties play crucial roles in understanding the material's behavior and performance under different conditions.

To conduct the analysis, the samples were carefully placed in aluminium pans specifically designed for DSC measurements. These pans provide excellent thermal conductivity and ensure uniform heat transfer to the samples during the analysis.

The temperature scanning range employed in this study ranged from -40 °C to 200 °C, covering a broad spectrum of temperatures relevant to the thermal behavior of the samples. Initially, the samples were subjected to heating from -40 °C to 200 °C at a constant rate of 10 °C per minute. This heating process allowed the samples to undergo thermal transitions, such as melting or crystallization, while recording the associated heat flow changes.

Following the first heating cycle, the samples were then cooled from 200 °C back to -40 °C at a rate of -10 °C per minute. This controlled cooling step served to reset the samples' thermal history, ensuring that any effects from prior heating cycles were eliminated. The subsequent heating cycle provided in-depth insight into the thermal characteristics of the samples, including the determination of their melting point, crystallinity, and Tg. By analysing the DSC curves obtained during this second heating cycle, researchers were able to precisely identify and quantify these critical thermal properties. Overall, the two-step process involving heating and subsequent cooling followed by a second heating cycle enabled comprehensive characterization of the samples' thermal behavior, providing valuable insights for further analysis and interpretation.

4.3.4 Dynamic mechanical analysis

In this section, Dynamic Mechanical Analysis (DMA) was employed as a pivotal tool to delve into the intricate mechanical properties exhibited by the samples under scrutiny. The DMA analysis was meticulously conducted utilizing a state-of-the-art DMA Analyzer manufactured by Mettler Toledo, a renowned leader in analytical instrumentation headquartered in Columbus, OH, USA. This cutting-edge equipment ensured precise and reliable characterization of the mechanical behavior of the samples across varying temperature regimes.

During the DMA analysis, a comprehensive temperature sweep spanning from -40 to 100 °C was meticulously orchestrated. This extensive temperature range was deliberately selected to encompass a spectrum of environmental conditions, enabling a thorough exploration of the samples' mechanical response under diverse thermal scenarios. Such comprehensive analysis is crucial for deciphering the materials' performance across a broad range of operational temperatures.

The DMA analysis was executed in the film-tension mode, a methodical approach that entails subjecting the samples to controlled tensile forces while meticulously monitoring their mechanical responses. To ensure methodical consistency and accuracy, a controlled heating rate of 2 °C per minute was meticulously maintained throughout the experiment. This gradual temperature increment facilitated uniform thermal transitions within the samples, enabling precise characterization of their mechanical properties.

During the analysis, a frequency of 1 Hz and a load of 0.5 N were meticulously applied to the samples. These parameters were meticulously calibrated to emulate real-world mechanical stresses encountered by the materials, thereby facilitating a robust assessment of their mechanical integrity and resilience. It's worth noting that DMA analysis was conducted both before and 8 days after the burial test, enabling researchers to track and evaluate any temporal changes in the samples' mechanical properties. This iterative approach provided invaluable insights into the materials' stability and durability under evolving environmental conditions.

By meticulously analysing the DMA data gleaned from these experiments, researchers can glean valuable insights into a plethora of mechanical characteristics exhibited by the samples. This encompasses the viscoelastic behavior, modulus, damping properties, and other pivotal mechanical attributes, all of which play a pivotal role in determining the materials' performance and suitability for diverse applications. This comprehensive dataset serves as a cornerstone for informed decision-making in material design and optimization endeavours, paving the way for the development of tailored materials that meet specific performance criteria in real-world scenarios.

5. RESULTS AND DISCUSSION

In this section, different experiments will be explained in two steps; preliminary and main experiment. It is worth noting that some of the tests conducted just in the preliminary section and were not accepted as practical additives with our purposes.

5.1Test just with preliminary step

5.1.1 Plasma treatment

In this test, air and argon were used as gases for treatment. In this experiment, which was conducted just for PHB, samples that were treated by air were less resistant to the degradation. The reason can be owing to the fact that in can make the soil more suitable for micoorganisms. In this case, microoganisms that can degrade PHB can attack the polymer network and degrade it. One of the most important factors in this test was the temperature, increasing the temperature caused to make the environment even more suitable for the microorganisms to grow.

On the other hand, in terms of argon treatment, the samples stayed with the same physics for quite long time and even more than the sample without treatment. Figure 11 shows the shapes of the samples for burial test in 37 °C afte 42 days. As can be seen, argon had a better shape than the other samples and it could stay as the only sample after 55 days; however, it was not that long to make the main test for this technique.

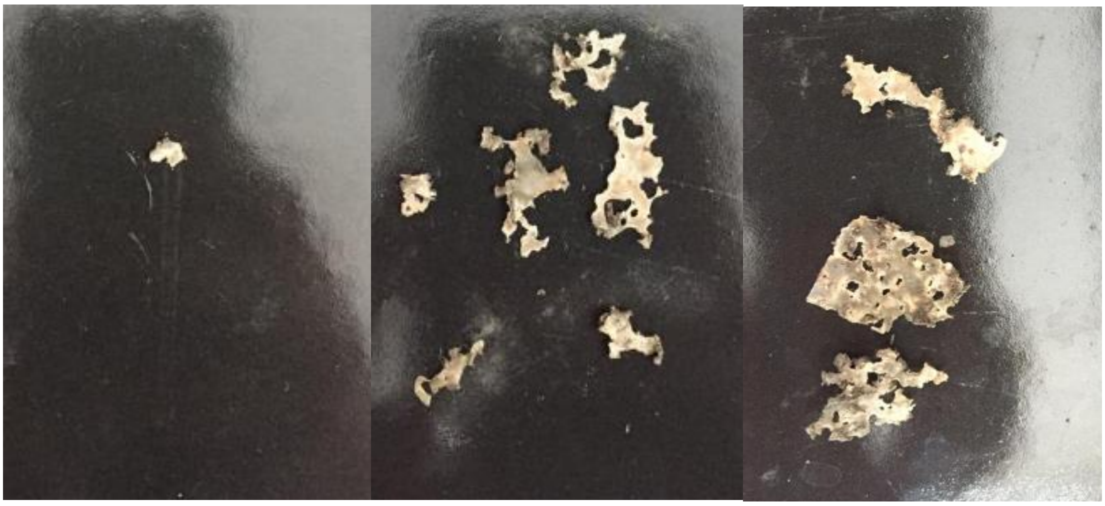


Fig 11. From left to right: PHB treated with air, PHB without treatment, and PHB treated with argon

5.1.2 Crosskining agent

In chemistry, cross-link is a bond links one polymer chain to another. These links may take the form of ironic, covalent or and metallic bonds and the polymers can be natural or synthetic polymers. In polymer, cross-linking usually refers to the applying cross-links to make a change in the polymers' physical properties [94]. In some research it is has been shown that by blending cross-linking agent with polyesters, we can produce a promising elastomeric materials [95]. Generally, the main properties of crosslinking agents that should be taken into account are; their cost, compatibility, thermal resistance, reactivity, and toxicity, etc[96–98]. Although there were several attempts to crosslink polymers especially polyesters with mechanical mixing and radiation exposure, not true crosslinking happened[99]. On the other hand, those attempts triggered improved properties such as mechanical properties.

To see whether or not the base polyester is already crosslinked by a crosslinker, several techniques can be used [99,100]. The most used method is gel content, which can show the amount of insoluble crosslinked material, that can be so fast and in the majority of time precise. DSC (specially studying the elevation in glass-transition temperature (Tg), Dynamic Mechanical Analysis (DMA), Infrared spectroscopy (IR), and microscopy, such as Transmission electron microscopy (TEM) and Scanning electron microscope (SEM) are the techniques that used to show the effectiveness of additives used as crosslinking agent.

Moreover, as usually an initiator is employed to initiate the crosslinking, find a good initiator is of actual importance. Initiator acts as a catalyst and starts and accelerate the mechanism and without an initiator, the crosslinking process might no longer be placed or will be so slow [101]. Azo compounds (decomposed by light or heat to produce free radicals) [102,103], peroxides (decompose at high temperature)[104], and redox systems (free radicals provide by electron transformation) [105] are three types of the most used initiators. Sometimes it is valuable to study the influence of crosslinker and initiator on the crystallinity and glass transition temperature to see whether or not it influence the solidity of polymer matrix as there can be used sometimes as hardeners[106].

There are different types of crosslinking agents for polyesters, such as silane [107], isocyanates, epoxy resins, acrylics, and melamine formaldehyde resins, peroxides, etc. Epoxy resins are usable as they contain epoxy group which can react with hydroxyl group of polyesters to make a crosslinked material with boosted tensile strength, toughness, and temperature resistance [108]. Moreover, chemical resistance and the electrical properties of polymers can be improved with this type of crosslinker [109].

Sometimes adding even a low amount of an initiator such as dicumyl peroxide or radiation could cause unpreferred chain branching or chain scission predominantly. The chain branching in the polymer blends triggers a difficulty in polymer chain crystallization [110]. Consequently, the crystals of smaller sizes are formed and leads to blends with decreased melting temperatures. In this case, the temperature of extrusion is so important for choosing a suitable crosslinker and initiator.

In this part of the study, crosslinking agent was used to change the structure of PHB. Silane was the crosslinker with decumyl peroxide as an initiator. As it mentioned earlier, an initiator can increase the functionality of the crosslinking agents. To measure the amount of crosslinking, gel content test was performed or different content of crosslinker and decumyl peroxide. This approach uses peroxide radicals to graft silane molecules, and then hydrolysis and condensation processes in hot water produce connections [111]. Another factor that was considered was the time of hot water treatment. In this experiment, it was concluded that due to the high hydrolysis degradation, increasing hot water treatment cause to reduce the gel content. Finally, a burial test was conducted to see the influence of the aforementioned additives on the shape of PHB. Table 2 shows the gel contents of te samples with different properties.

Table 2. Gel content of the samples with crosslinker and initiator

Amount of PHB [phr]	M_{PHB}	Crosslinking [phr]	M_{Silane}	Initiator[phr]	M_{DCP}	Water treatment time	%Gel
100		0		0	0	0	0
100	6.88	1.5	0.1018	0	0	0	0
						4	0
						17	0

100	6.84	3	0.2022	0	0	0	0
						4	0
						17	0
100	6.843	4.5	0.3110	0	0	0	0
						4	0
						17	0
100	6.8	1.5	0.1120	0.1	0.0068	0	10.72
						4	27.87
						17	11.92
100	6.7	3	0.2087	0.1	0.0076	0	10.11
						4	33.7
						17	12.88
100	6.78	4.5	0.3013	0.1	0.0069	0	13.19
						4	10.8
						17	13.72
100	7	1.5	0.1050	0.3	0.0213	0	10.7
						4	20.55
						17	19.74
100	6.83	3	0.2145	0.3	0.0214	0	11.11
						4	16.7
						17	14.75
100	6.852	4.5	0.3157	0.3	0.0198	0	26.61
						4	18.47
						17	27.75

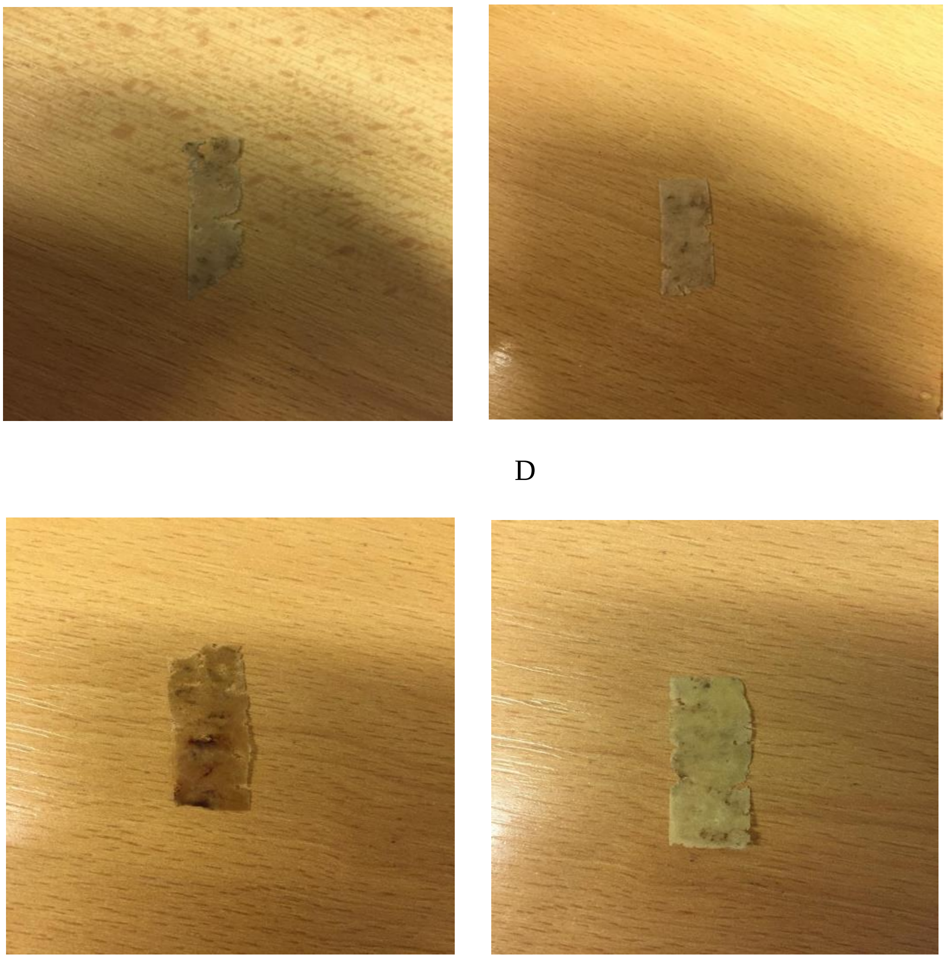
As can be seen, higher amount of crosslinker and initiator trigger higher gel content. Surprisingly, the shapes of the samples didn't show sensible difference with different contents. It is worth noting that these types of additives such as crosslinkers and chain extenders are more practical in terms of using them for PLA.

5.1.3 Plant Oils (Trees' Extracts)

In this experiment, three different plant oils were used to examin the biodegradation of PHB when they blend with it. In this step, the same standard as the previous experiments was used. Cocoa oil, oil from green tangerine and the pyrolysis oil of tangerine were applied as additives for PHB to see their influence on the biodegradation.

Fig 12 shows the samples after a month of burial test. The samples had been monitoring during that period. Figure 12 presents the biodegradation rates of several PHB blends over time. The different blends are depicted by their names; Pyrol means 5% of pylolysis oil blended with PHB, cocoa and green tangerine are the same. Each blend shows distinct biodegradation patterns, reflecting the impact of the additives. Pure PHB serves as the control sample in this study. The biodegradation rate of pure PHB increases steadily over time, eventually plateauing at around 80%. This consistent degradation rate makes it a reliable benchmark for comparing the effects of different additives. Adding 5% Pyrol to PHB results in a slower biodegradation process. Initially, the rate is low, but it shows a continuous and steady increase over time, reaching a maximum biodegradation rate of about 60%. The presence of Pyrol seems to retard the biodegradation, likely due to its pyrolyzed nature, making it less susceptible to microbial breakdown. Incorporating 5% cocoa oil into PHB accelerates the initial biodegradation rate compared to Pure PHB. This blend reaches a biodegradation level similar to Pure PHB, around 80%, but achieves this level more rapidly. Cocoa oil enhances the early stages of degradation, suggesting that it may attract microbial activity, thus speeding up the biodegradation process initially. Regarding green tangerine blend, it exhibits a degradation pattern similar to Pure PHB but with a slightly faster initial rate. The biodegradation rate of PHB with 5% green tangerine oil exceeds almost 73%, indicating an improvement in controllingoverall biodegradation rates. This reduction could be due to the organic nature of green tangerine oil antimicrobial property, which potentially reduce microbial activity.

A B



C

D

Fig 12. Physical shapes of PHB and PHB blended with plant oils; A)Pure PHB, B)PHB blended with 5% Cocoa, C)PHB blended with 5% pyrolysed oil, and D)PHB blended wit 5% green tangerine oil

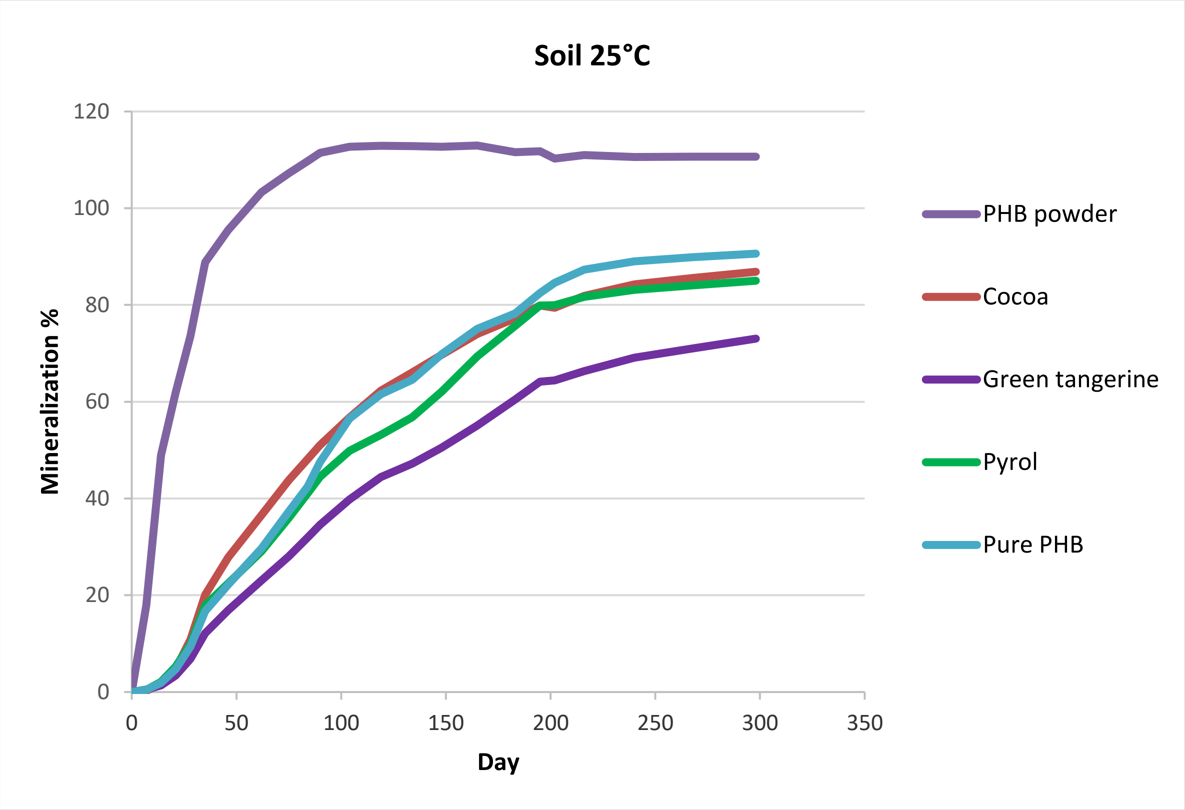


Fig 13. The biodegradation of PHB and PHB blended with some plant oils

As can bee seen, there is a high similarity between the visual and biodegradation tests. It shows that the biodegradation test was performed in a correct and acceptable way. From the experiments, it is concluded that although the rate of the biodegradation was retarted, specially by adding green tangerine, the reduction was not high enough to consider these types of additives as the main ones. This decision as made due to almost the same lag phase, biodegradation trend, and almost the same physical shapes.

5.2 The Main Experiments

In this part, the main experiments that could pass the requirements after preliminary is discussed as the main experiments. These experiments contain two sections. The first one is the blending of PHB with the selected essential oils and the second section is about the blending of PBS and PHB polymers with two types of lignin. The reason behind blending only PHB with terpenoids wa the project (SEALIVE, Horizon 2020) aim that was focused on PHB, then they have changed the main polymer to PBS. For this reason, in the second experiments, we used both polymers to meat their requirements.

5.2.1 Essential Oils

5.2.1.1 Biodegradation Test

Essential oils are using wildly in different industries due to their unique properties such as their antimicrobial properties. In this study, several essential oils (all of them were terpenoids) were used to show their influence in controlling the biodegradation and PHB. In the preliminary study, different terpenoids with different percentages were performed for biodegradation test. Moreover, burial test was conducted alongside to monitor the samples' shapes every two weeks. Figure 14 shows the biodegradation of PHB blended with all selected terpenoids. As can be seen, all of those additives were practical in reducing the biodegradation of PHB; however, three of them were selected not only due to their sown influence in the biodegradation test, but also their shapes in burial test. Burial test also showed almost the same results, which support the biodegradation test.

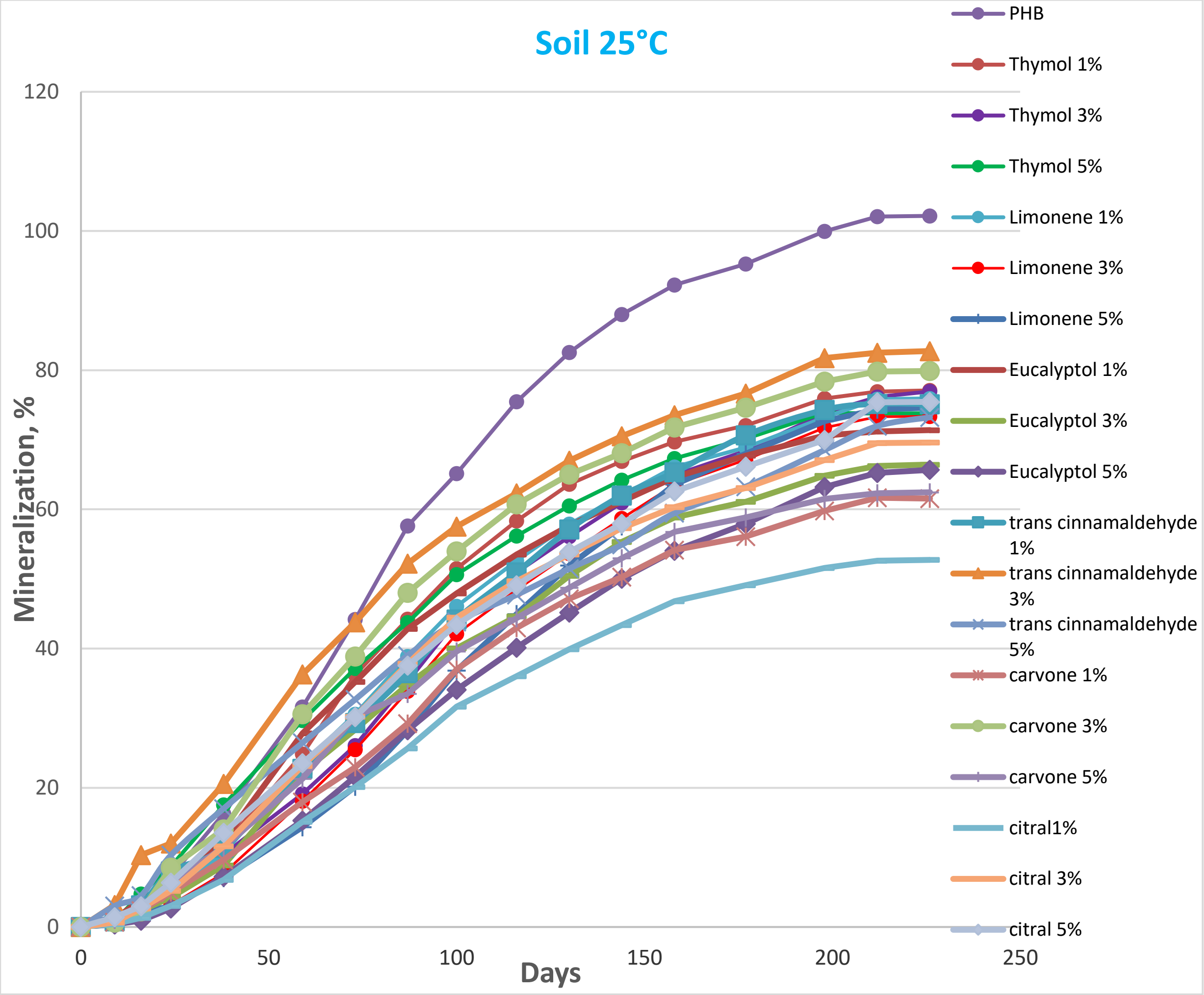


Fig 14. The preliminary study of incorporating essential oils in PHB

The results of mineralization showed reasonable retardations in biodegradation for all additives (Fig. 15). As can be seen, the blend with 3% eucalyptol has shown the best resistance against degradation. Although pure PHB was degraded completely before 200 days, PHB blended with 3% limonene was the second best sample in retarding biodegradation, and 3% thymol showed moderate retardation in biodegradation. In this regard, 3% eucalyptol, 3% thymol, and 3% limonene after 226 days of incubation reached 66.4, 77, and 73.3% of mineralization, respectively, due to their antimicrobial activities [112,113]. The influence of limonene in retarding biodegradation was more substantial than thymol due to its higher antifungal activity [78]. The film degradation in the preliminary study proved the more substantial influence of eucalyptol in PHB degradation. It is also due to its high antimicrobial and antioxidant activities [114]. Besides, blending essential oils with PHB is a technique to enhance the polymer's crystallinity that reduces biodegradation.

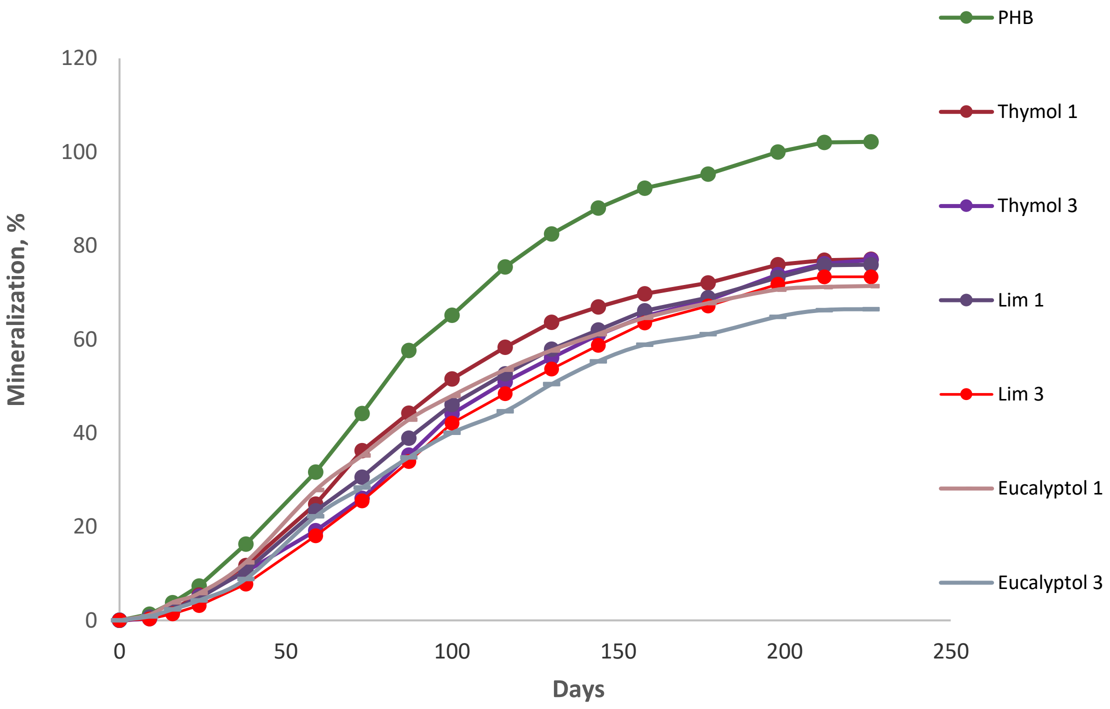


Fig. 15. Mineralization of pure PHB and PHB blended with the selected terpenoids

After finalizing the three terpenoids and making the first biodegradation test, they were used to show if they can have the same reduction in biodegradation when they are using as plasticizers.

Plasticizers, being non-volatile low molecular weight substances, possess significant potential as an additive for polymer blending. They can effectively address the aforementioned drawbacks of polyesters, while also enhancing their ductility and toughness [115]. By using plasticizer, some of biodegradable polyesters can be make thier applications in flexible packaging, medical devices like tubing, and biodegradable bags even more. The schematic of influence of plasticizer on the polymer matrix is shown in Fig. 16. The main reason for using plasticizer is to improve the mechanical and thermal properties of polyesters [116] especially by reducing the Tg. The incorporation of plasticizers in polyesters can result in an improvement in their low-temperature properties, as well as other relevant properties. Furthermore, the addition of plasticizers can reduce the processing temperature of polyesters, thereby improving their overall processability [117].

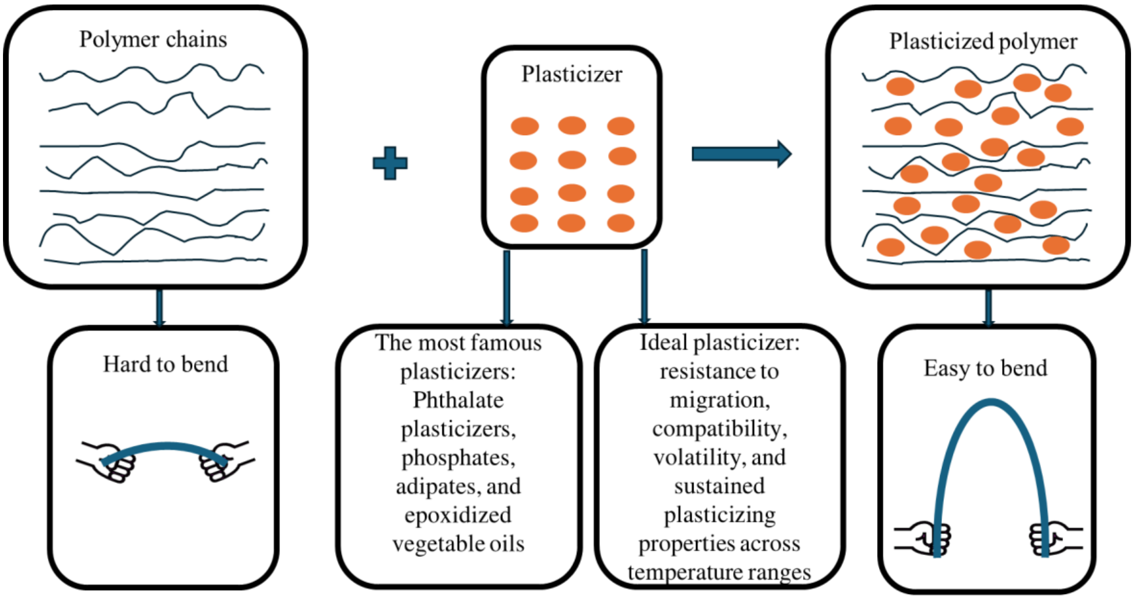


Fig. 16. The schematic of plasticizer influence on the polymer matrix

As can be seen in Fig 17, the biodegradation after almost 6 months the biodegradation rate reduction was almost the same as when we used lower content of essential oils. It should be noted that due to the main purpose of using essential oil in this research, the influence of them as plasticizers was studied just in terms of biodegradation experiment and thermal and mechanical tests were conducted for the lower percentages of selected terpenoids.

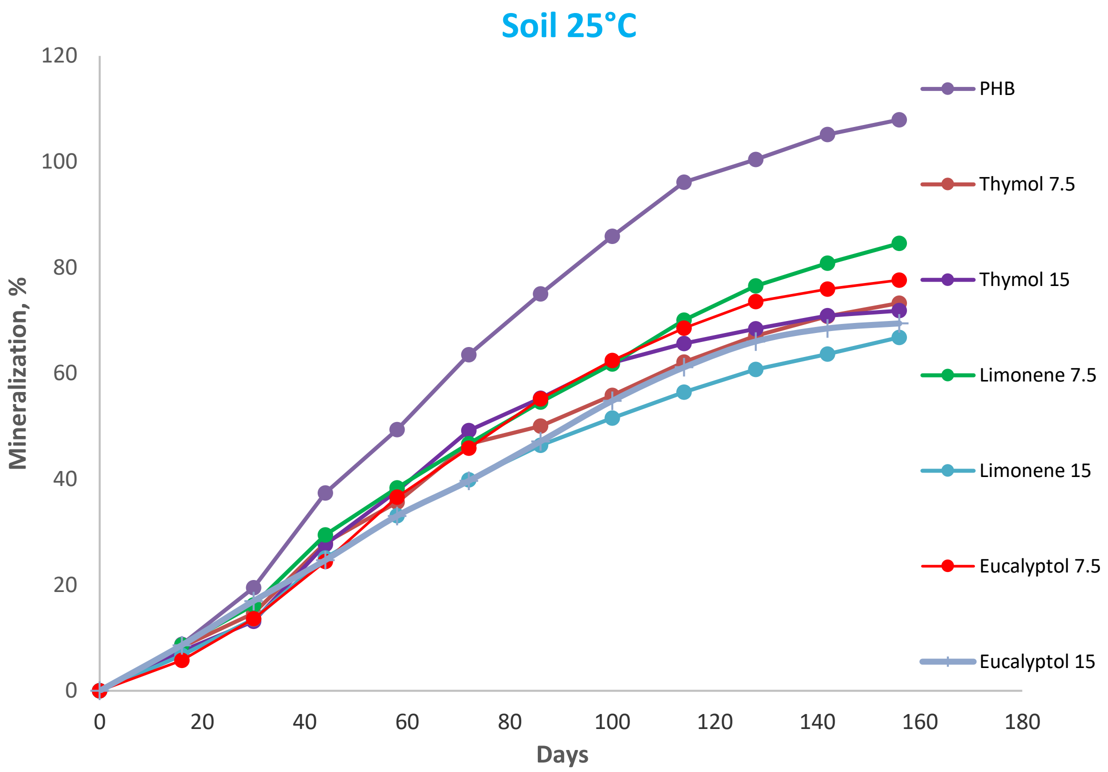


Fig. 17. The influence of selected terpenoids as plasticizer

5.2.1.2 Visual and Microscopic Analysis

The physical shapes of the samples are shown in Fig.18. As can be seen, the blend with 3% of eucalyptol was the only sample that could be found after 32 days, the other samples had disintegrated before that time. The images also depicted that samples with thymol and limonene were more resistant than pure PHB.

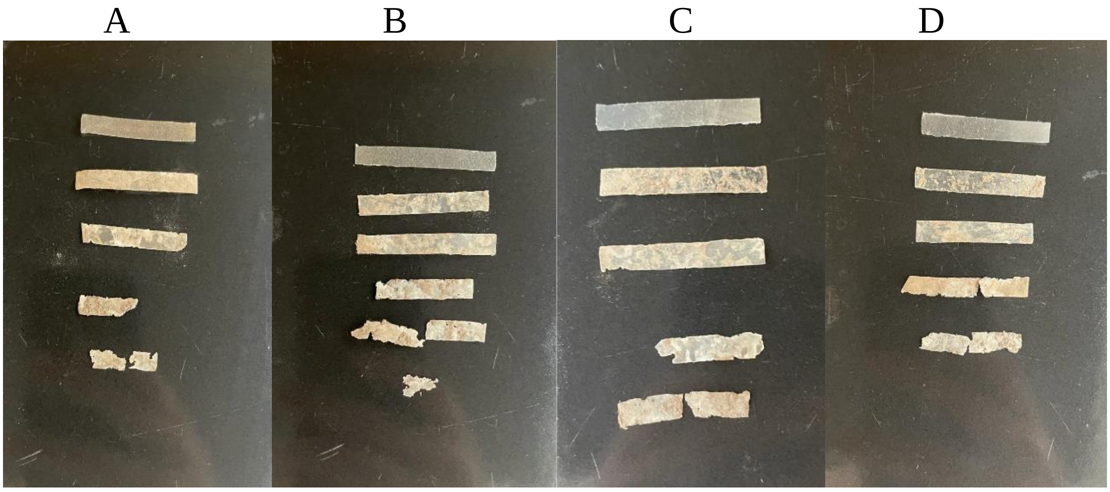


Fig. 18. Physical shapes of the samples through incubation at different times 0, 2, 4, 8, 16, and 32 days. A) pure PHB, B) PHB+3% eucalyptol, C) PHB+3% limonene, D) PHB+3% thymol

The results of the biodegradation were proved qualitatively by SEM images (Fig. 19). These images show that pure PHB has a higher potential to degrade compared with other samples due to several holes in the structure. Regarding these images, the matrix with 3% of eucalyptol showed a relatively smooth structure, meaning higher degradation resistance than other samples, especially pure PHB.

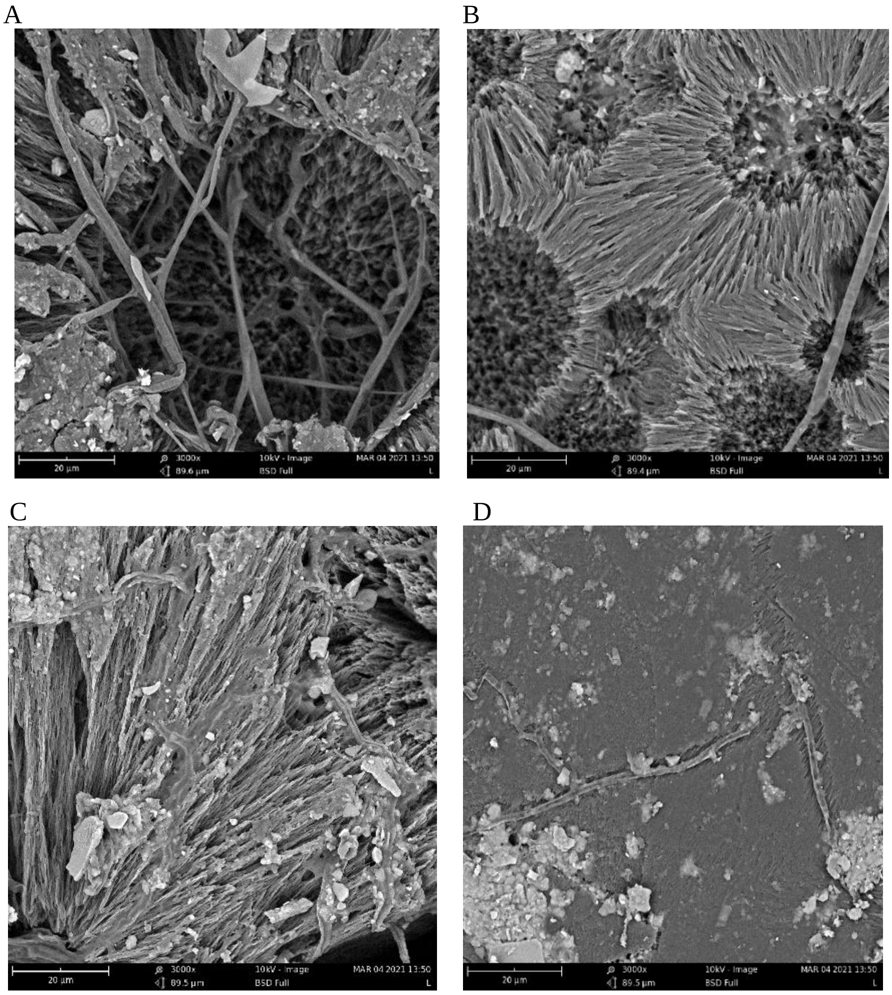


Fig. 19. SEM images of the samples after 16 days of incubation. A) pure PHB, B) limonene 3%, C) thymol 3%, D) eucalyptol 3 %

Besides, the PHB/eucalyptol 3% matrix indicated that this film could start to degrade after 32 days of incubation (the only sample that could analysed by SEM) (Fig. 20). Moreover, the blend with limonene and thymol exhibited a better structure than neat PHB on day 16. Fungi hyphae are well discernible in the pictures, supporting the assumption that fungi play an important role in PHB biodegradation in soil [72,118,119]. The materials, however, were not covered by a dense biofilm of cells.

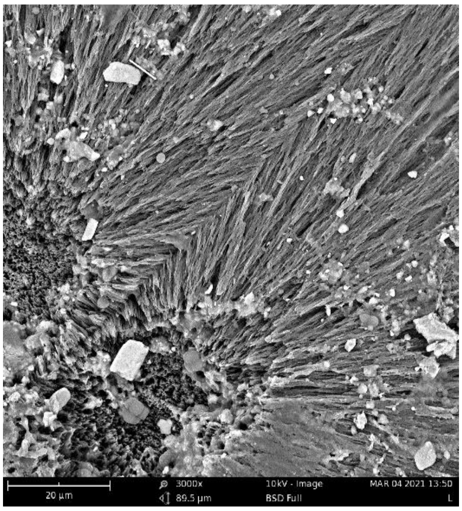


Fig. 20. SEM image of PHB/eucalyptol 3% after 32 days of incubation

5.2.1.3 Thermal and Mechanical Properties

Thermal properties, including melting point, glass transition temperature (Tg), and crystallinity of PHB samples, were analyzed using differential scanning calorimetry (DSC). The results are presented in Tables 3 and 4. The data indicate that the incorporation of the selected compounds led to a reduction in Tg (Table 3). This decrease in Tg values suggests that eucalyptol, thymol, and limonene were miscible with the amorphous phase of PHB, thereby enhancing the molecular mobility of the polymer matrix [18]. The most significant Tg changes were observed in materials containing limonene (29%). Additionally, the melting temperature (Tm) was assessed. After adding the selected compounds, two melting transitions (Tm1 and Tm2) appeared in the melting region of the PHB blends, while pure PHB exhibited only one sharp peak at 172 °C (Tm2). Following partial biodegradation, all tested compositions showed two melting transition temperatures, indicating that the mixtures experienced melting and recrystallization of their subphases. During biodegradation, only minor changes in Tm were noted in PHB modified with terpenoids. Moreover, all mixtures exhibited a very weak degree of cold crystallization (Tcc) (Table 2). It was observed that Tcc shifted slightly towards higher values (maximum change of 3%) with prolonged biodegradation time. It appears that Tcc is not significantly influenced by either the presence of terpenoids or the degradation duration.

The influence of the material crystallinity on its biodegradation was also obtained from DSC data (Table 3). Most of the time, additives slightly enhanced the crystallinity of the matrix. As can be seen in Fig. 17, the samples started to degrade by microorganisms from the amorphous part, and crystalline parts remained. However, the DSC results in our research (Tables 3,4) revealed that microorganisms degrade crystalline parts of the samples after amorphous parts. As can be seen, pure PHB was degraded after 16 days, which was faster than other samples. The difference between crystallinity percentage of PHB at different times was lower than in PHB blended with essential oils. This phenomenon was asserted by Beltrami and her colleagues [63] i.e. enzymatic degradation starts first in the amorphous phase, promoting the crystallinity of the samples.

Table 3. Crystallinity of PHB and PHB blended with essential oils

Sample	Crystallinity (%)				
	0 day	4 days	8 days	16 days	32 days
Pure PHB	69	67	61	63	-
Eucalyptol 3%	70	64	62	62	66
Limonene 3%	70	66	68	67	66
Thymol 3 %	66	67	66	65	-

Table 4. DSC results of PHB/terpenoids blends

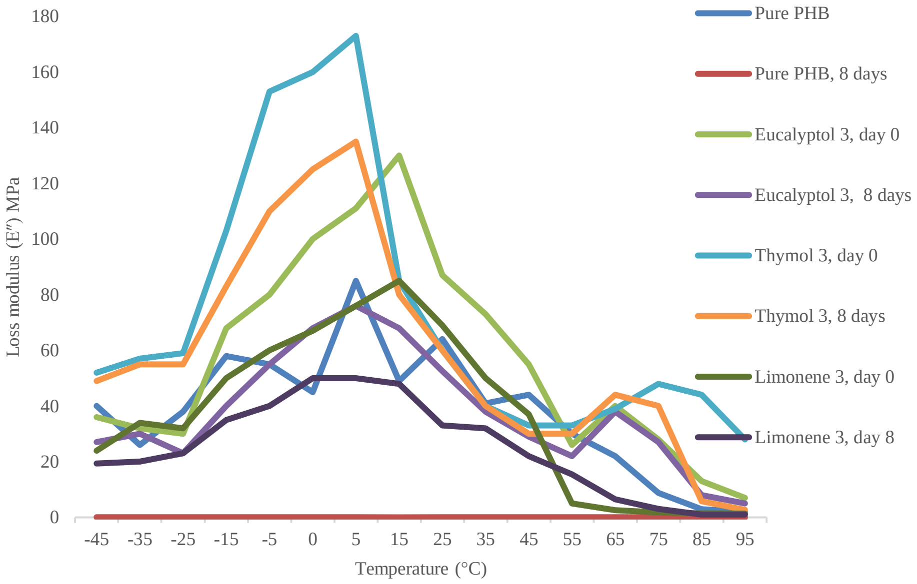
Sample	Incubation time (day)	T_g(°C)	T_c(°C)	T_{cc}(°C)	T_m(°C)	
					T_{m1}	T_{m2}
Pure PHB	0	5.66	82.85	94.25	-	172
	16	5.8	83.06	94.23	168.23	173.58
	32	-	-	-	-	-
PHB+Eucalyptol 3%	0	4.9	84.37	93.4	167.73	172.89
	16	5.5	87.26	95.07	167.42	172.77
	32	5.67	85.1	97.56	166.2	172.93
PHB+Limonene 3%	0	4.05	77.33	94.56	166.79	172.86
	16	4.73	85.07	94.23	166.11	172.56
	32	4.84	88.28	95.08	166.63	172.16
PHB+Thymol 3%	0	4.65	69.49	87.75	167.14	172.75
	16	4.87	86.77	94.91	166.9	172.11
	32	-	-	-	-	-

The mechanical properties of the materials during biodegradation were investigated in DMA. Loss modulus (E″) determines the quantity of energy lost by a polymer when subjected to cyclical external loading [120]. The results of E″ are shown in Fig.21. A. The highest E″ of 173 MPa was achieved by blending 3% thymol, which showed 92% enhancement from pure PHB. Loss modulus results showed three drops at -45, 35, and 55°C for PHB, and it was almost zero after eight days (Fig.19. A). According to the findings, the interactions between the terpenoids and PHB inhibited the ester motion of the polymer main chain [18]. The highest peak was reported for thymol (day 0) and showed higher E″ even after eight days of incubation. Two big reduction in the E″, correspond to Tg (around 5-6.5 °C) and cold crystalization temperature (Tcc) or post crystalization temperature, that led the samples′ E″ to almost zero.

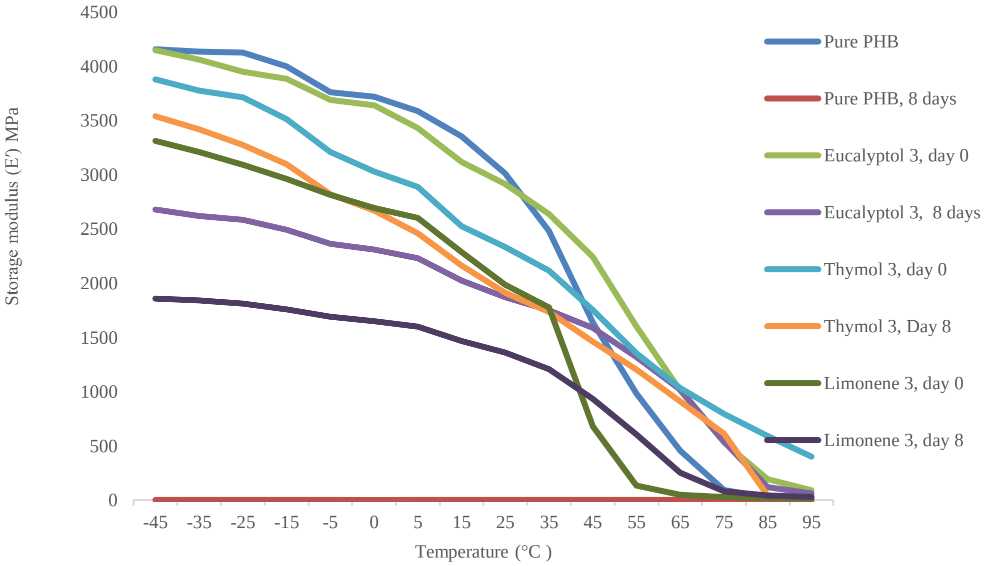
The storage modulus (E′) results for pure PHB and PHB blended with 3% limonene, thymol, and eucalyptol as a function of temperature are depicted in (Fig. 21. B). In general, the E′ remained constant and high in the glassy state, then dropped dramatically following the Tg before stabilizing in the rubbery state. As can be seen, the neat PHB has E′ value of 4.1 GPa at -45 °C. This value dropped sharply after 8 days of incubation in soil. On the other hand, the differences in storage modulus of modified PHB before and after incubation were less than those of pure PHB. Besides, at 35 °C and higher as well as in the rubbery zone (40-60 °C), thymol and eucalyptol modified PHB had a higher modulus than neat PHB. This phenomenon is due to restricting the motions of polymer chains with eucalyptol or thymol [121].

The last factor related to mechanical properties analyzed in the research was tan δ. Internal friction or damping causes energy dissipation in polymers, and intermolecular friction at the filler-matrix interface causes energy dissipation in a polymer matrix. This factor is defined as the ratio of loss modulus to storage modulus (tan δ) and is a measure of energy loss [122,123]. The tan δ (Fig. 21. C) peaks of modified samples slightly shifted in different temperatures. The first peak shows the glass transition temperature that has a suitable correlation with the results from loss modulus for this factor. The biggest peaks were shown at temperatures behind the samples′ Tcc. The reduction in Tg and change in Tcc were observed by adding terpenoids, which caused an enhancement in molecular motion in the amorphous phase [124].

A


Loss modulus (E") MPa
180
160
140
120
100
80
60
40
20
0
-45
-35
-25
-15
-5
0
5
15
25
35
45
55
65
75
85
95
Temperature (°C)
Pure PHB
Pure PHB, 8 days
Eucalyptol 3, day 0
Eucalyptol 3, 8 days
Thymol 3, day 0
Thymol 3, 8 days
Limonene 3, day 0
Limonene 3, day 8

B


Storage modulus (E') MPa
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-45
-35
-25
-15
-5
0
5
15
25
35
45
55
65
75
85
95
Temperature (°C)
Pure PHB
Pure PHB, 8 days
Eucalyptol 3, day 0
Eucalyptol 3, 8 days
Thymol 3, day 0
Thymol 3, Day 8
Limonene 3, day 0
Limonene 3, day 8

C

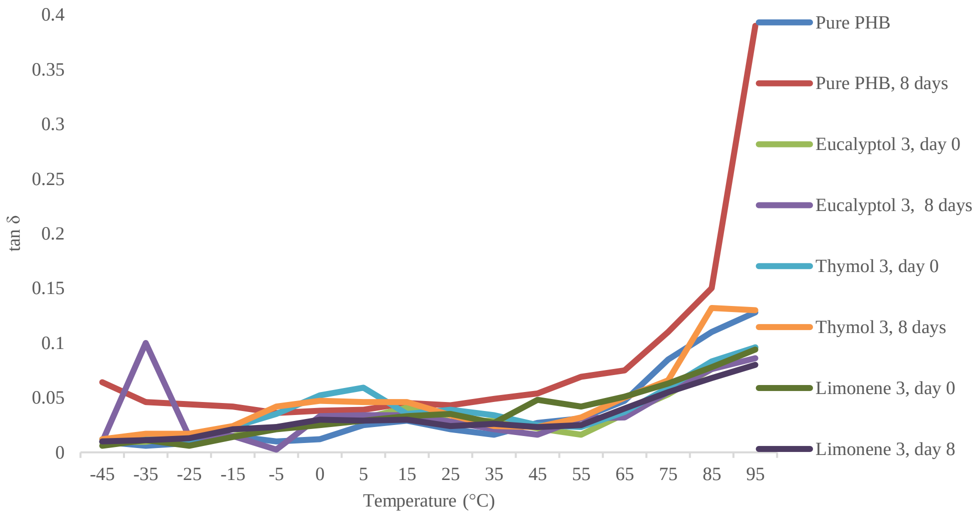


Fig. 21. A) Loss modulus, B) storage modulus, and C) tan δ as a function of temperature for PHB and PHB blended with terpenoids at different times.

The E′ curve formed three distinct areas: a shorter plateau below 4°C, a continuous decrease until 60-85 °C, and a second plateau region. In the first plateau region, pure PHB maintained a storage modulus of around 4060 MPa in this experimental study. Eucalyptol in this experiment showed higher E′ than other samples (PHB blended with eucalyptol showed almost the same results in that region). Oil in this PHB matrix decreases intermolecular stresses throughout the polymer chain, enhancing chain mobility and flexibility, which is the main reason for using essential oils as plasticizers [125]. In the second region of the first experiment, eucalyptol and thymol showed higher E′ than pure PHB at higher than 35 °C and 50 °C, respectively. As can be seen in fig 19B, the reduction in the storage modulus was occurred at higher temperatures (higher than Tg).

5.2.2 Lignin

5.2.2.1 Biodegradation

For this part of the study, biodegradation and visual tests were performed. The biodegradation test followed the same standard as the previous test in soil. The collected data clearly indicated a significant deceleration in biodegradation when all additives were included (Fig. 22 and 23). It can be observed that organosolv lignin had a relatively lesser impact on the retardation of PBS and PHB biodegradation, particularly at lower content levels. However, at higher percentages, it exhibited a high potential for this purpose. Conversely, neutralized alkali lignin demonstrated opposite effects. As can be seen in Figure 20, organosolv, in the lower content showed lower impact on the retardation of PHB degradation than alkali lignin. Conversely, at higher lignin content, organosolv lignin demonstrates superior performance in reducing PHB degradation compared to alkali lignin. This shift in behavior may be attributed to the increased presence of active functional groups in organosolv lignin, which could interact more effectively with the degradation products of PHB, thereby mitigating degradation. In Figure 21, it showed a bit different behavior by having the same influence in high and low contents of two types of lignin; alkali lignin showed better performance than organosolv one for enhancing PBS resistance against the degradation. This finding suggests that the chemical composition or structural properties of alkali lignin may be more conducive to forming stable interactions with PBS chains, thereby providing better protection against degradation factors.

Biodegradation test also showed a slight difference in the lag phases of PHB and PBS samples. PHB lag phase was shorter that could be the reason for the more availability of microorganisms that are interested in degrading it. The rate of biodegradation can prove that hypothesis not only by the shorter lag phase but also for the rest of the trend, which showed sharper rise in degrading PHB than PBS.

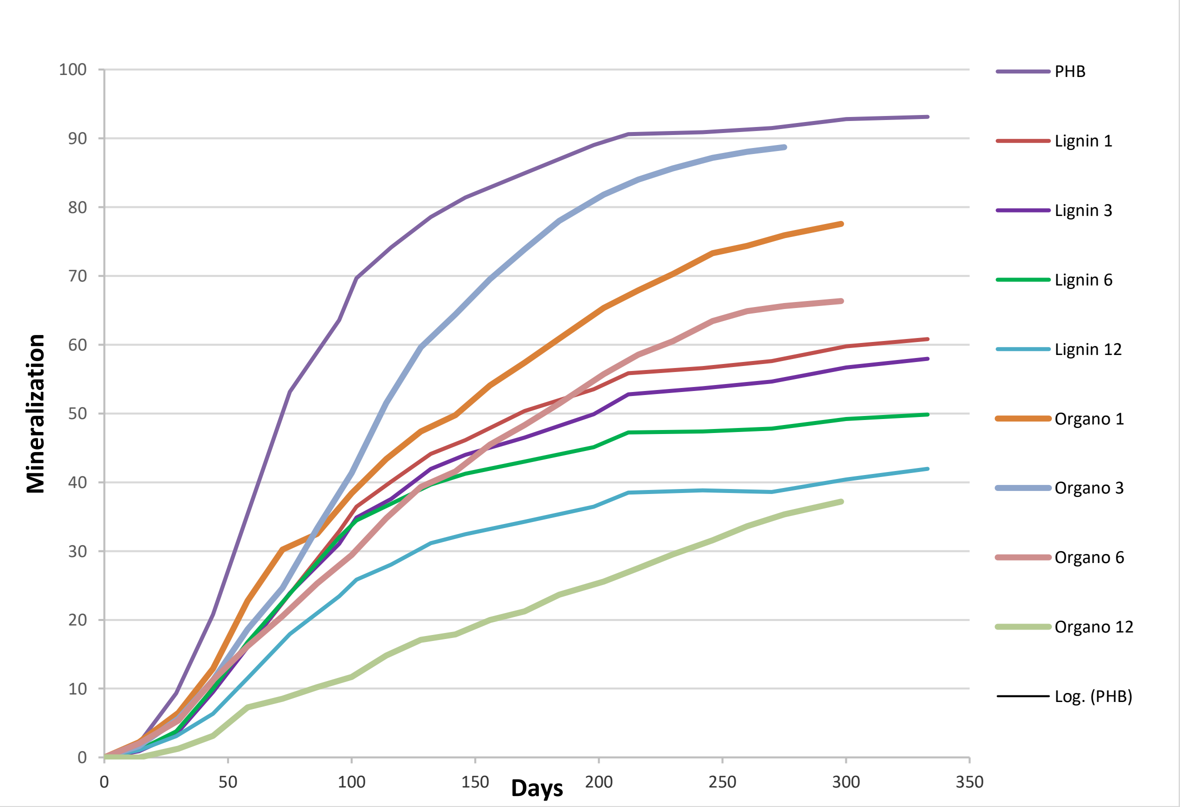


Fig 22. Mineralization of the PHB and its additives at room temperature.

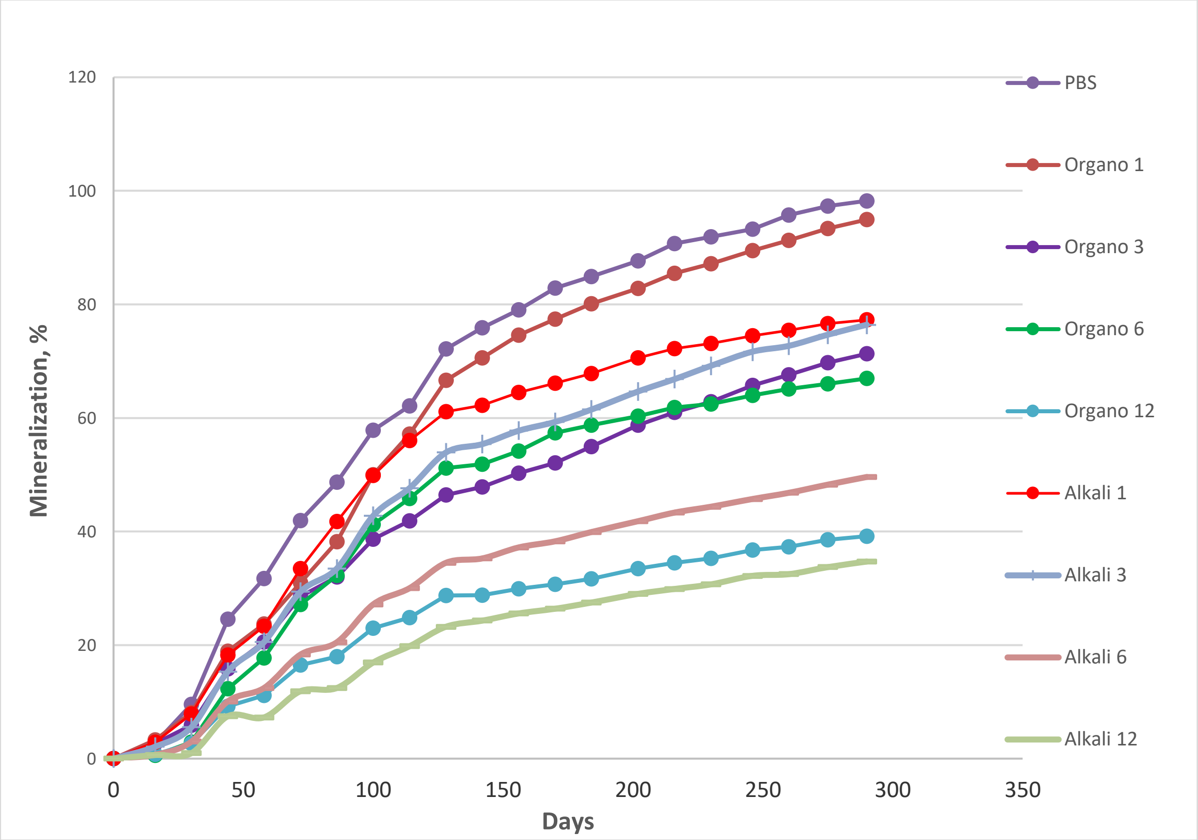


Fig 23. Mineralization of the PBS and its additives at room temperature.

5.2.2.1 Visual and Microscopic Analysis

By analyzing the SEM results for the PBS polymer (Table 5) samples treated with different types and concentrations of lignin to enhance resistance against biodegradation, biodegradation results were proven. After 4 days, minor surface irregularities were visible for pure PBS, while by 32 days, a noticeable increase in surface degradation was shown, indicating that pure PBS is susceptible to biodegradation. With 1% alkali, a slight improvement in resistance compared to pure PBS was shown. However, after 32 days a smoother surface than PBS was exhibited. By increasing the percentage of alkali to 6%, a significant improvement was detected in both 4 and 32 days of incubation. Furthermore, the surface remained relatively smooth even after extended incubation. Blending organosolv showed less impact on the resistance of PBS with low content; however, enhancing the content of organosolv lignin showed more impact even with the extended incubation time. As it was shown by biodegradation results, 6% of alkali lignin had the highest performance in terms of SEM results in improving the resistance of PBS against the biodegradation.

In addition, by analyzing the SEM results for the alkali and organosolv lignin blended with PHB, the same results were found as the biodegradation, but with a bit a bit difference. Table 6 depicted SEM images of the surface morphology of PHB polymer samples after 4 and 32 days of incubation in soil. As can be seen, alkali lignin could improve the resistance of PHB more than organosolv, showing the results that was found by biodegradation results.

Table 5. SEM images of the samples after 4 and 16 days of incubation for PBS blended with lignin

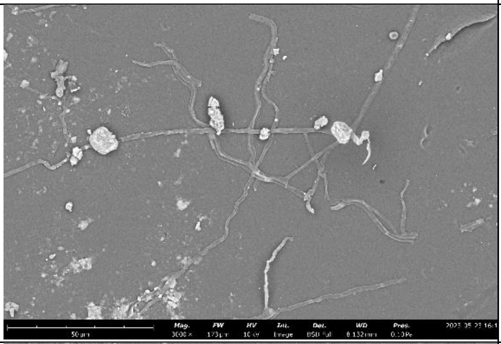
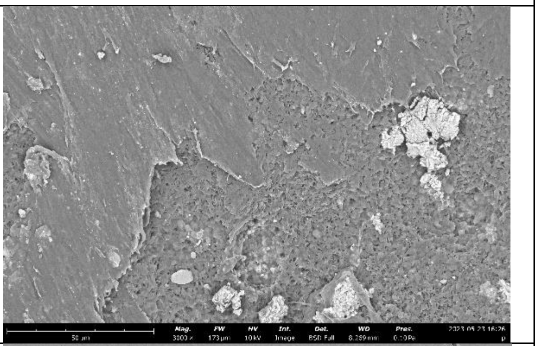
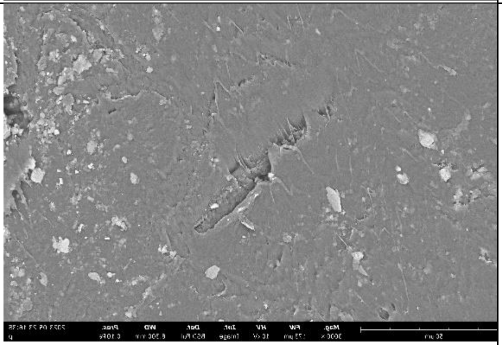
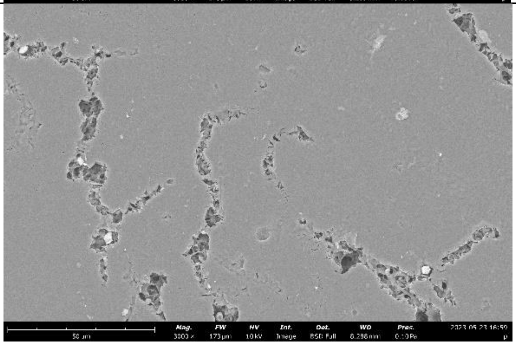
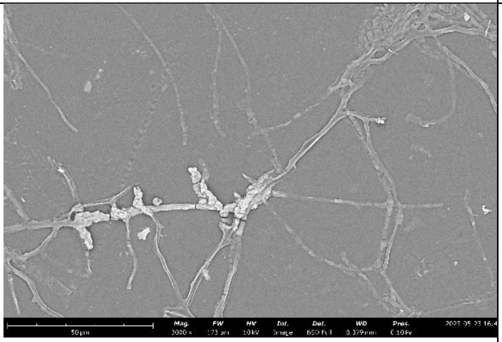
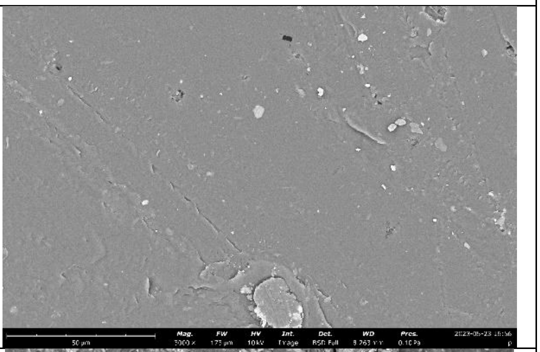
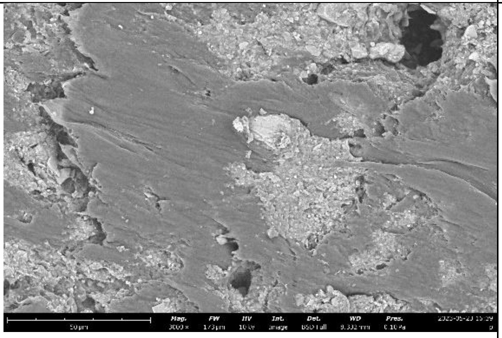
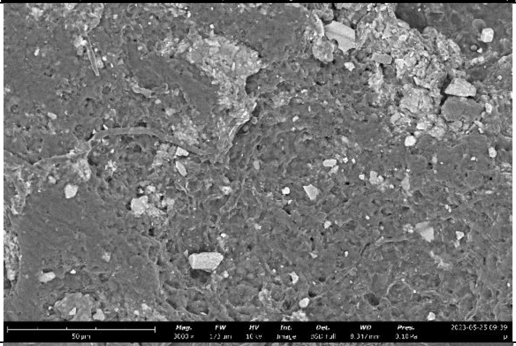
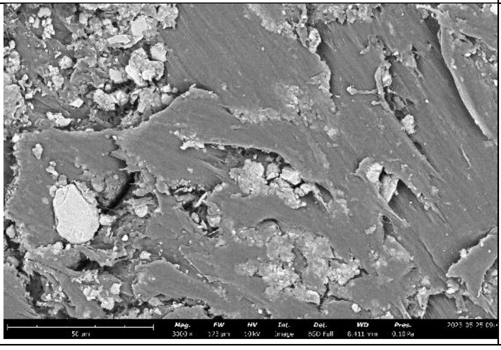
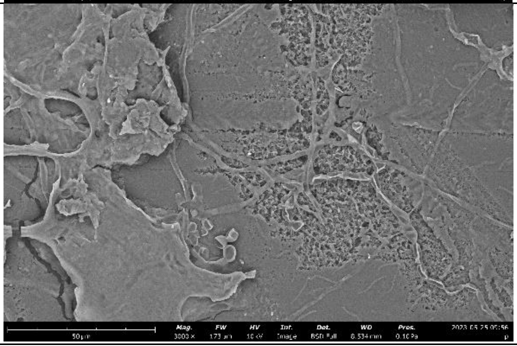
Sample	Day 4	Day 32
Pure PBS		
PBS/Alkali 1		
PBS/Alkali 6		
PBS/Org 1		
PBS/Org 6		

Table 6. SEM images of the samples after 4 and 16 days of incubation for PHB blended with lignin

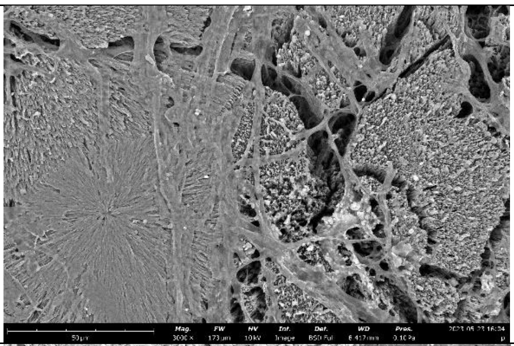
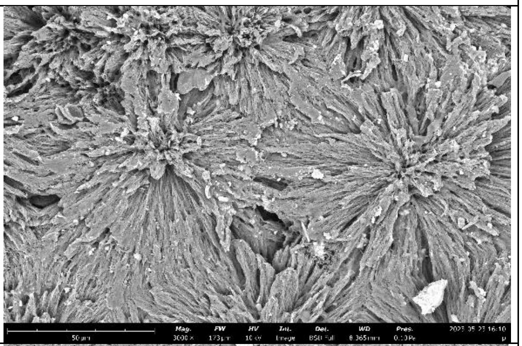
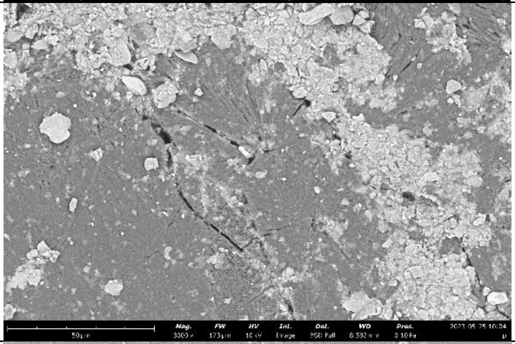
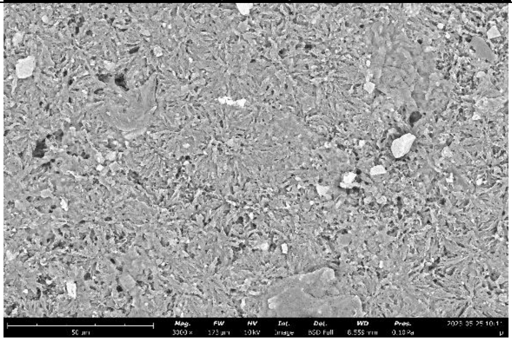
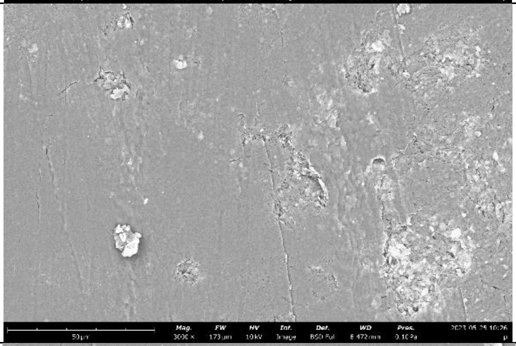
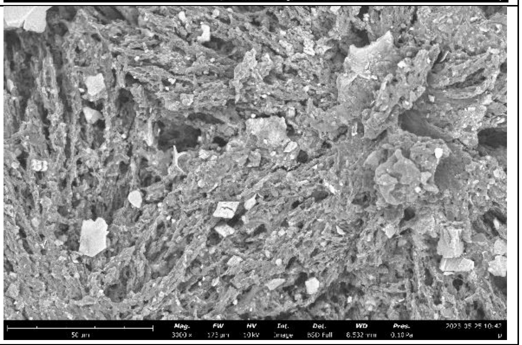
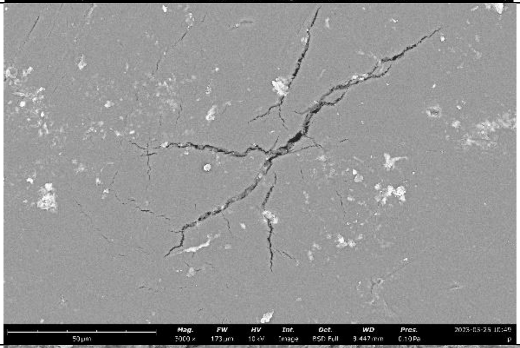
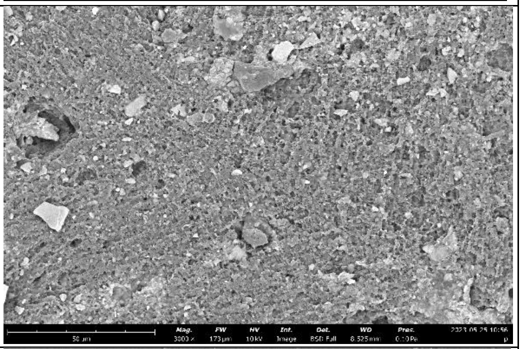
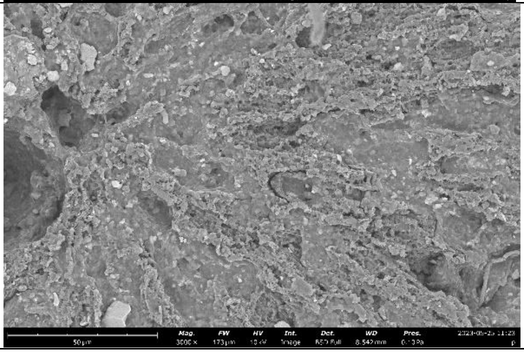
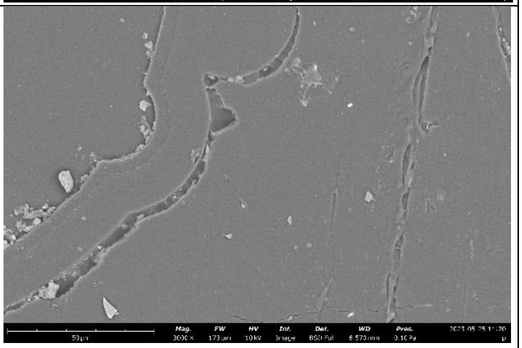
Sample	Day 4	Day 32
Pure PHB		
PHB/Alkali 1		
PHB/Alkali 6		
PHB/Org 1		
PHB/Org 6		

Figure 24 showed the physical shapes of the samples with PHB and alkali lignin that were observed at different time intervals: 0, 4, 8, 16, and 32 days. The images show the following samples: (A) pure PHB, (B) PHB + 1% alkali lignin, (C) PHB + 3% alkali lignin, and (D) PHB + 6% alkali lignin, and (E) PHB + 12% Alkali lignin. Tables 5 and 6 depicted the influence of the lignin in the surface of PBS and PHB. As can be seen, for PBS, the influence of Alkali lignin to make the surface smoother was more than the second additive. However, for PBS, the influence of the additive was almost the same. It is shown that pure PHB and pure PBS were not that resistant to degrade compared with the blended samples that is in accordance to the results of biodegradation.

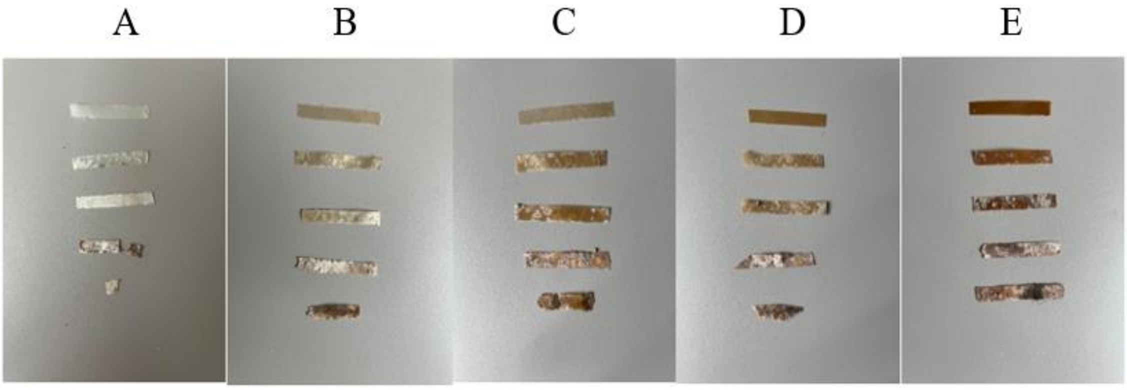


Figure 24. physical shapes of the samples with PHB and neutralized alkali lignin during incubation

5.3 Collaborative Studies

In this part, collaborative works that were performed as a part of the European project will be discussed

5.3.1 Biodegradability of PLA/PHB for cups

This experiment was performed with a group of researchers in in a private company for some confidential products. The tested materials were the final products. These materials were blended with each other and thermoplast starch (TPS), which ae not allowed to be known. This experiment was conducted in two environments; home and industrial compostings.

The materials were designed to be compostable in industrial composting and home-composting environments, while maintaining favorable processing and service properties. They contain a significant proportion of PLA, a widely available bio-based polymer typically considered non-biodegradable in home-composting conditions. Additionally, film samples (D, E, F) underwent biodegradability testing in a laboratory under home-composting conditions. These samples were selected for home-composting due to their relatively low thickness and the assumption that home-composting conditions are less aggressive than industrial composting, particularly for the PLA component [126,127].

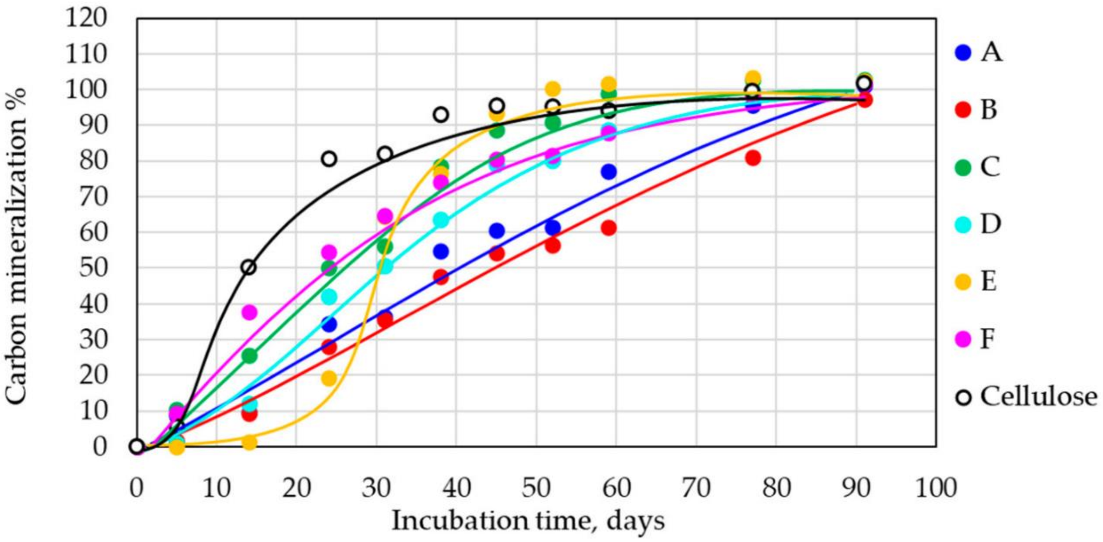


Figure 25. Mineralization of samples under industrial composting conditions, 58 °C.

All samples were subjected to laboratory testing under industrial composting conditions at 58°C. Based on their composition, it was expected that all samples would achieve complete mineralization under these conditions, although thick-wall samples without TPS (A and B) were anticipated to require more time to reach 100% mineralization. Three samples for each composition, including a reference sample (cellulose), were measured, with an average standard deviation of ±8.6 for industrial composting conditions. Complete mineralization was observed for all samples after approximately 90 days of incubation (Figure 25). Except for sample E, no sample exhibited a lag phase. Sample E, containing the highest amount of PLA (70%), displayed a typical PLA compost biodegradation characteristic, demonstrating a lag phase [128].

Other samples, which degraded without a lag phase, contained at least 30% of easily biodegradable PHB and/or TPS, which mitigated the lag phase in the biodegradation curve under industrial compost conditions. For sample E, the PHB phase was likely enclosed within the dominant PLA phase. After the lag phase, mineralization proceeded exponentially, with sample E achieving complete mineralization first. Film samples D and F also mineralized quickly, with sample F mineralizing faster initially, likely due to its higher content of easily biodegradable TPS and plasticizers (40%) compared to D (5%). Surprisingly, the relatively thick (1 mm) sample C, with high PHB and TPS contents (65%), also mineralized rapidly.

The slowest degradation occurred in thick samples A (4 mm) and B (1 mm). TPS-containing cups degraded slightly faster, correlating well with the construction (thickness) of the cups. Interestingly, the thickness of the samples played a less significant role than expected. The thin film F, composed of a PLA/PHB/TPS blend, exhibited a biodegradation pattern similar to the thick sample C. Both samples had comparable formulations. However, in the absence of TPS, thickness became more significant (samples B, D, and E, which were TPS-free formulations). The presence of TPS likely facilitated early disintegration of the samples, reducing the importance of thickness.

The selected samples were removed from the compost after incubation and examined using SEM to assess microbial colonization and surface deterioration (Figure 26). After just 10 days in the compost, all materials were densely colonized, with the biofilm density increasing over time. Although the specific microorganisms could not be identified, their morphology suggested filamentous thermophilic actinobacteria with distinct round endospores. Surface erosion was also clearly evident.

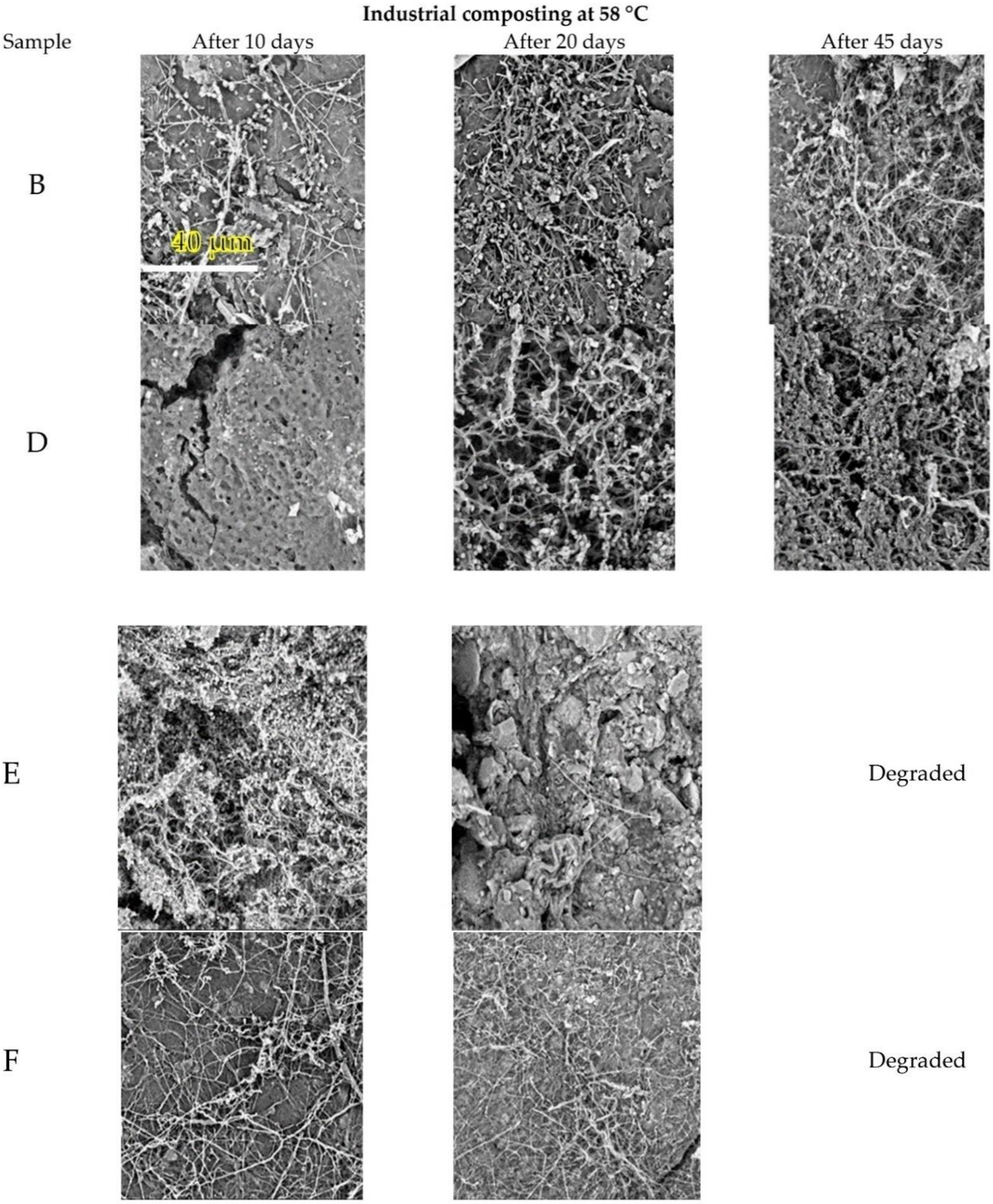


Figure 26. Scanning electron microscopy survey of the sample surface during the biodegradation test at 58 °C (industrial composting condition). Magnification of 5000×.

Film samples D, E, and F were chosen for biodegradation testing under home-composting conditions. Based on previous studies, it was expected that the PLA component of the materials would not fully mineralize under these conditions. Three samples for each composition, including a reference sample (cellulose), were measured. All samples achieved total mineralization within approximately 180 days, with an average standard deviation of ±3.9 for home-composting conditions. A lag phase of about 15 days was observed for all samples.

The biodegradation curves for the tested samples closely matched that of the cellulose reference and followed the anticipated order (Figure 27). The thin film of the PLA/PHB/TPS blend (F) exhibited the fastest biodegradability, closely followed by the thin film sample without TPS (E). In this case, thickness and plasticizer content were significant factors; the thick film made of PLA/PHB without TPS and with lower plasticizer content (D) degraded significantly slower than the thin film with higher plasticizer content (E).

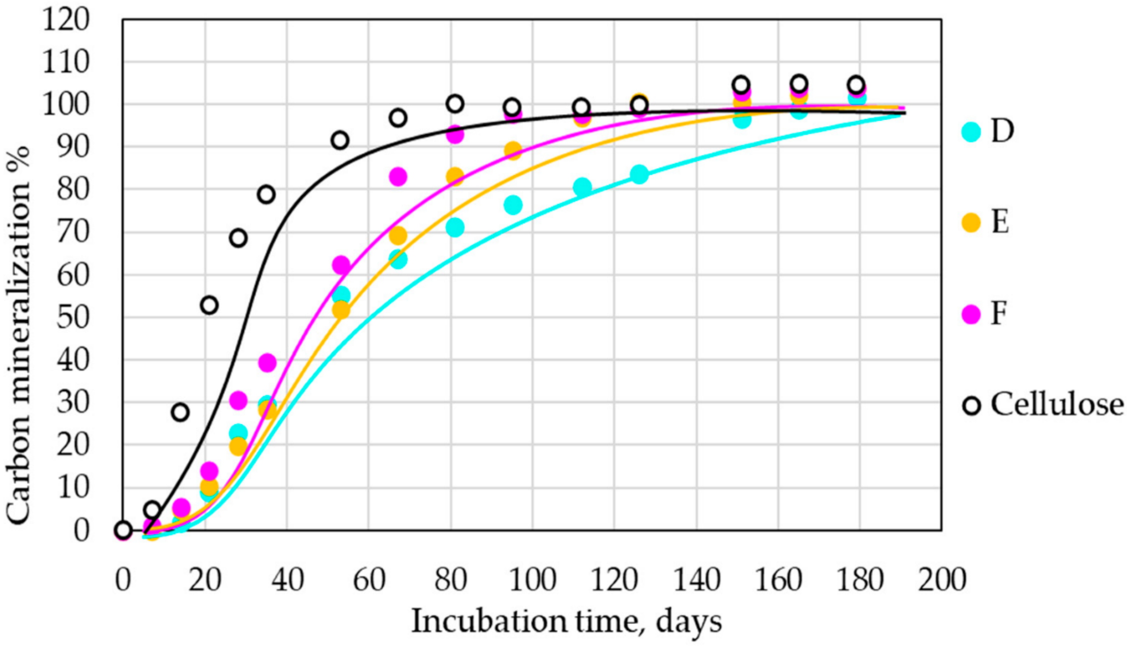


Figure 27. Mineralization of samples under home-composting conditions, 28 °C

When observed under SEM (Figure 28), samples from the home-compost experiments generally exhibited a much lower degree of surface colonization compared to those from the industrial compost experiment. This difference can be attributed to the distinct microbial communities present at different temperatures. Filamentous bacteria (likely actinomyces) and rod-shaped bacteria were observed (e.g., Figure 26F, 30 days). Cavities and cracks gradually formed over time. Fungi were highly active at this temperature, likely degrading the material through their extracellular enzymes, even though they were not visibly attached to the surface.

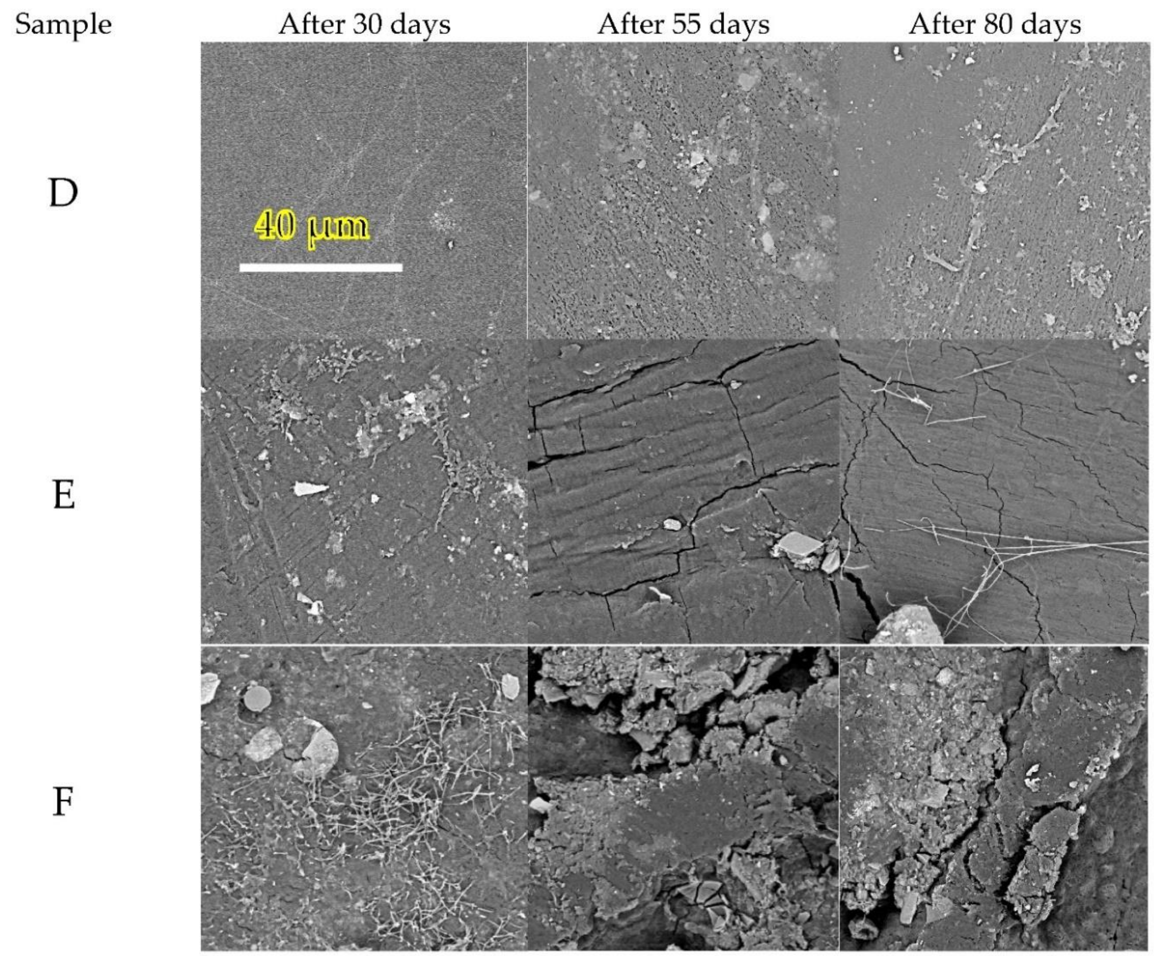


Figure 28. Scanning electron microscopy survey of the sample surface during the biodegradation test at 28 °C (home-composting conditions). Magnification of 5000×.

A significant finding from both environmental and practical perspectives is that PLA/PHB-blend samples achieved complete degradation under home-composting conditions. This result is notable because it challenges the prevailing belief that PLA cannot biodegrade at temperatures below its glass transition temperature (about 55°C) under home-composting conditions. Typically, only the mineralization of the non-PLA components of the blends was expected. The blending of PLA and PHB in the hot melt state likely induces re-esterification reactions, resulting in the formation of PLA/PHB co-polyesters. The easily biodegradable PHB segments in such co-polyesters can facilitate the release of low molecular weight fragments that are susceptible to further biodegradation [127].

Standard analytical methods struggle to investigate the occurrence and extent of re-esterification, but the results from the home-composting biodegradation tests can be seen as evidence of this process. This discovery has substantial implications not only for home composting but also for industrial composting facilities. In these typically municipal plants, the composting process is often simple and not always well-controlled, which can result in a thermophilic phase that is too brief or not sufficiently hot to ensure complete PLA mineralization. Issues have been reported with various PLA-based items labeled as "compostable," leading to their rejection by some composting plants. This finding could prevent the formation of microplastics, a significant environmental concern currently under scrutiny.

5.3.2 Biodegradability of polymer blends

In this research that was in collaboration with an institute, three polymers; PHB, PLA and PBSA were mixed to investigate their biodegradability in two environments; soil at 25°C and home composting (at 28°C). The main purpose of this study was to investivage if PLA can be degraded in soil or if it is possible to accelerate the biodegradation in home composting. The test performed with the same laboratory conditions as the previous tests.

The figure 29 presents the mineralization rates of various polymers and their blends with PLA in a soil environment at 25°C over a period of nearly six months. As expected, cellulose shows the highest rate of mineralization, approaching 100% by the end of the study period, demonstrating its rapid and complete biodegradability in soil. Similarly, both pure PHB and PBSA also degrade almost completely, with mineralization rates nearing 100%. This indicates that these polymers are highly biodegradable under soil conditions, likely due to their more amorphous structures and greater accessibility to microbial attack compared to PLA. It's important to note that similar results were observed in the composting environment, where PHB and PBSA also degraded completely, highlighting their consistent biodegradability across different environments.

In stark contrast, pure PLA demonstrates the lowest biodegradability, with mineralization barely reaching 30% by the end of the study. PLA's slow degradation can be attributed to its crystalline structure and hydrophobic nature, which make it less accessible to microbial attack under typical home composting conditions. The composting environment at 28°C is relatively mild, and PLA typically requires higher temperatures (closer to 60°C) found in industrial composting facilities to break down more efficiently.

When PLA is blended with other polymers like PHB and PBS, the biodegradability improves, but the extent of this improvement is limited. The 50/50 blend of PLA and PHB reaches around 40% mineralization after six months, while the 75/25 PLA/PHB blend achieves a slightly lower rate of around 30%. PHB itself is more biodegradable than PLA due to its more amorphous structure and higher susceptibility to enzymatic degradation. However, when blended with PLA, the overall biodegradability is tempered by the presence of PLA's more resistant crystalline regions.

Similarly, the PLA/PBS blends exhibit improved biodegradability compared to pure PLA, with the 50/50 blend reaching just over 30% mineralization and the 75/25 blend reaching around 25-30% by the end of the experiment. PBS is more flexible and amorphous than PLA, which aids in its degradation. However, the presence of PLA in these blends still limits the overall mineralization due to the reasons mentioned earlier its crystalline structure and the fact that the composting temperature is not high enough to significantly accelerate its breakdown.

Overall, while blending PLA with more biodegradable polymers like PHB or PBS does enhance its biodegradability in home composting conditions, the improvement is modest. The results suggest that the composting environment, particularly the temperature, plays a critical role in the biodegradation of these materials, and even with the addition of more biodegradable polymers, PLA-based materials may still require conditions closer to those in industrial composting facilities to achieve complete mineralization.

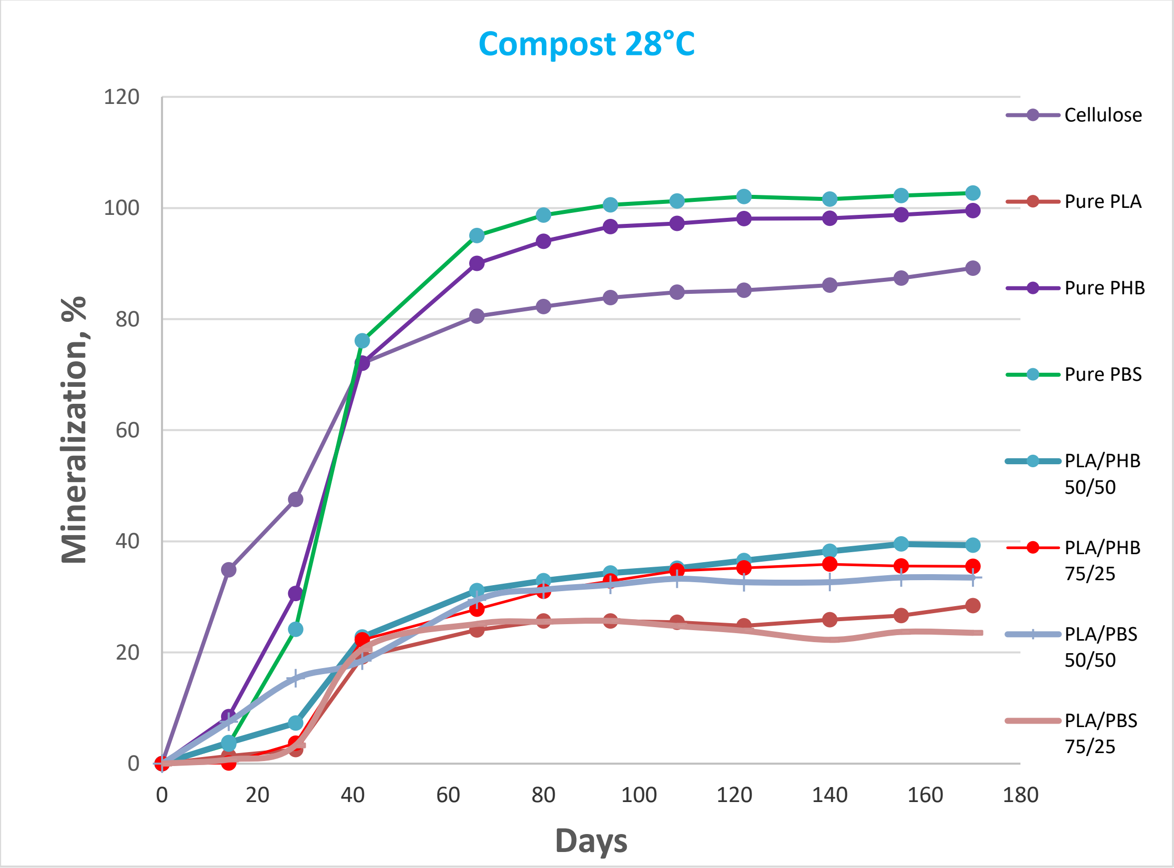


Figure 29. The biodegradation of PLA and its blends in home composting

The figure 30 presents the mineralization rates of various polymers and their blends with PLA in a soil environment at 25°C over a period of nearly six months. As expected, cellulose shows the highest rate of mineralization, approaching 100% by the end of the study period, demonstrating its rapid and complete biodegradability in soil. Similarly, both pure PHB and PBSA also degrade almost completely, with mineralization rates nearing 100%. This indicates that these polymers are highly biodegradable under soil conditions, likely due to their more amorphous structures and greater accessibility to microbial attack compared to PLA.

On the other hand, pure PLA exhibits very poor biodegradability in soil, with mineralization barely exceeding 5% over the entire six months. This limited degradation is due to the inherent properties of PLA, such as its semicrystalline structure and hydrophobic nature, which make it resistant to microbial attack under the relatively mild conditions of soil at 25°C. Soil conditions, especially at this temperature, are not conducive to the breakdown of PLA, which typically requires higher temperatures (closer to 60°C) and specific microbial environments found in industrial composting facilities to degrade more effectively.

When PLA is blended with other polymers like PHB and PBSA, there is only a slight improvement in biodegradability, but the overall rates remain low. The 50/50 PLA/PHB blend reaches about 15% mineralization by the end of the experiment, while the 75/25 PLA/PHB blend achieves around 10% mineralization. PHB is more biodegradable on its own, but when blended with PLA, the overall mineralization is significantly limited, likely due to the dominance of PLA’s resistant properties in the blend. Similarly, the PLA/PBSA blends exhibit minimal biodegradation, with the 50/50 blend reaching about 10-15% mineralization, and the 75/25 blend achieving slightly lower mineralization rates of around 10%. PBSA is more flexible and typically degrades more readily than PLA, but as with the PHB blends, the presence of PLA hinders the overall biodegradability in the soil environment. The limited degradation observed for these blends suggests that even when blended with more biodegradable polymers, PLA’s inherent resistance to degradation persists, particularly under the less aggressive conditions of soil composting at 25°C.

Overall, the results indicate that while blending PLA with PHB or PBSA slightly enhances its biodegradability in soil, the extent of improvement is minimal, and none of the blends achieve substantial mineralization within the six-month period. This highlights the challenge of biodegrading PLA and its blends in soil, especially under lower temperature conditions that are not optimal for rapid degradation. These findings suggest that while such blends may be somewhat better than pure

PLA, they are not well-suited for applications requiring significant or complete biodegradation in soil environments. This reinforces the need for considering environmental conditions and the choice of materials when designing biodegradable products, particularly when aiming for effective breakdown in natural soil settings.

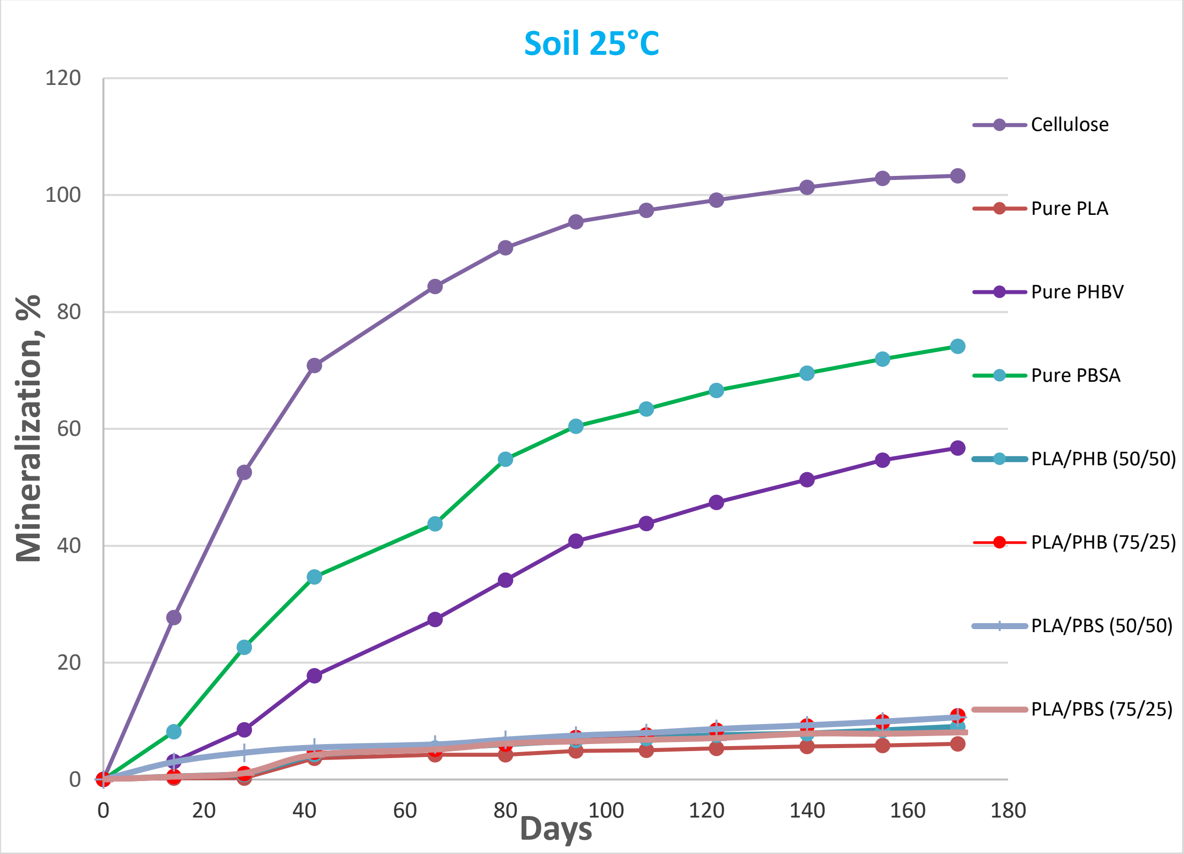


Figure 30. The biodegradation of PLA and its blends in soil

Comparing the biodegradation of these materials in soil and composting environments reveals significant differences in the rates and extent of mineralization. In the composting environment at 28°C, both PHB and PBSA degraded almost completely, reaching near 100% mineralization within six months, similar to the natural polymer cellulose. The warmer and more biologically active composting conditions provide a more favorable environment for the breakdown of these polymers, which is reflected in their rapid and complete degradation. In contrast, the soil environment at 25°C shows much slower and incomplete degradation for the same materials. While PHB and PBSA still exhibit high biodegradability, their mineralization is somewhat slower compared to composting, likely due to the lower temperature and reduced microbial activity in the soil.

5.3.3 Antimicrobial agents

In this experiment that was conducted for Horizon 2020 project, several additives were used for PHB as antimicrobial agents. These additives were controlled by starting a burial test in soil to see their influence on the degradation of PHB. The purpose was aligned with the main purpose of this study, which is controlling the biodegradation of PHB and PBS.Potassium sorbate, Didecyldimethylammonium chloride, Dimethyloctadecyl(3-trimethoxysilylpropyl)ammonium chloride, 1,2-benzodiazole-3(2H)-one, 2-phenylphenol, Sodium metabisulfite, and Thiabendazole were used for the first step of this study.

Burial test showed that Thiabendazole and 1,2-benzodiazole-3(2H)-one were the best additive in making PHB matrix more resistant to degradation. Figure 31 shows the physical shapes of PHB, PHB blended with the two selected and some of the additives that were not selected for the further experiment, which is biodegradation.

As can be seen, the selected ones showed better shapes after 4 weeks and the rest not only didn’t show good shapes with 1% during the same period, but also with higher content, it caused to make the polymer matrices more degradable with higher content. The main reason could be due to the fact that those antimicrobial agents were not affective for microorganisms that degrade PHB in soil.Moreover, their colors showed that those matrices were degraded by both fungi and bacteria.

Material	Two weeks	4 weeks
Pure PHB		
Matrix 1 = PHB+1%1,2-benzodiazole-3(2H)-one		
Matrix 2 = PHB+1% Thiabendazole		
PHB+1%Sodium metabisulfite		
PHB+1%5. 2-phenylphenol		

Fig 31. The physical shapes of PHB and PHB blended with some antimicrobial additives

The graph (Figure 32) demonstrates the influence of two different additives 1,2-benzodiazole-3(2H)-one (Matrix 1) and Thiabendazole (Matrix 2) on the biodegradation of PHB in soil at 25°C, highlighting their retarding effects on PHB mineralization. PHB, shown by the purple line, serves as the control and exhibits a high mineralization rate, reaching around 80% within the first 75 days It is shown that pure PHB, as expected, reached 100% degradation after almost three months. This indicates that pure PHB is highly biodegradable under these conditions, and showed that the biodegradation conducted correctly.

When PHB is blended with Thiabendazole (Matrix 2), the biodegradation process is increasingly retarded as the concentration of the additive rises. At lower concentrations (0.2% and 0.5%), the mineralization rates are only slightly lower than that of pure PHB, suggesting that the microbial community can still largely overcome the additive's presence to degrade PHB. However, as the concentration increases to 2% and 5%, the inhibitory effects become more pronounced, likely due to the additive interfering with microbial activity or the bioavailability of PHB, resulting in a significant retardation of biodegradation.

1,2-benzodiazole-3(2H)-one (Matrix1) exhibits an even stronger retardation effect on PHB biodegradation, especially at higher concentrations. Even at the lower concentrations of 0.2% and 0.5%, the mineralization rates are noticeably reduced compared to both pure PHB and Matrix 2 blends, indicating that 1,2-benzodiazole-3(2H)-one more effectively inhibits microbial activity. At concentrations of 2% and 5%, the degradation process is severely retarded, with the 5% blend showing minimal mineralization by the end of the study. This substantial retardation is likely due to 1,2-benzodiazole-3(2H)-one’s potent biocidal properties, which inhibit a broad spectrum of soil microorganisms essential for the biodegradation of PHB. Thus, both additives retard the biodegradation of PHB, with 1,2-benzodiazole-3(2H)-one exerting a significantly stronger inhibitory effect than Thiabendazole, particularly at higher concentrations.

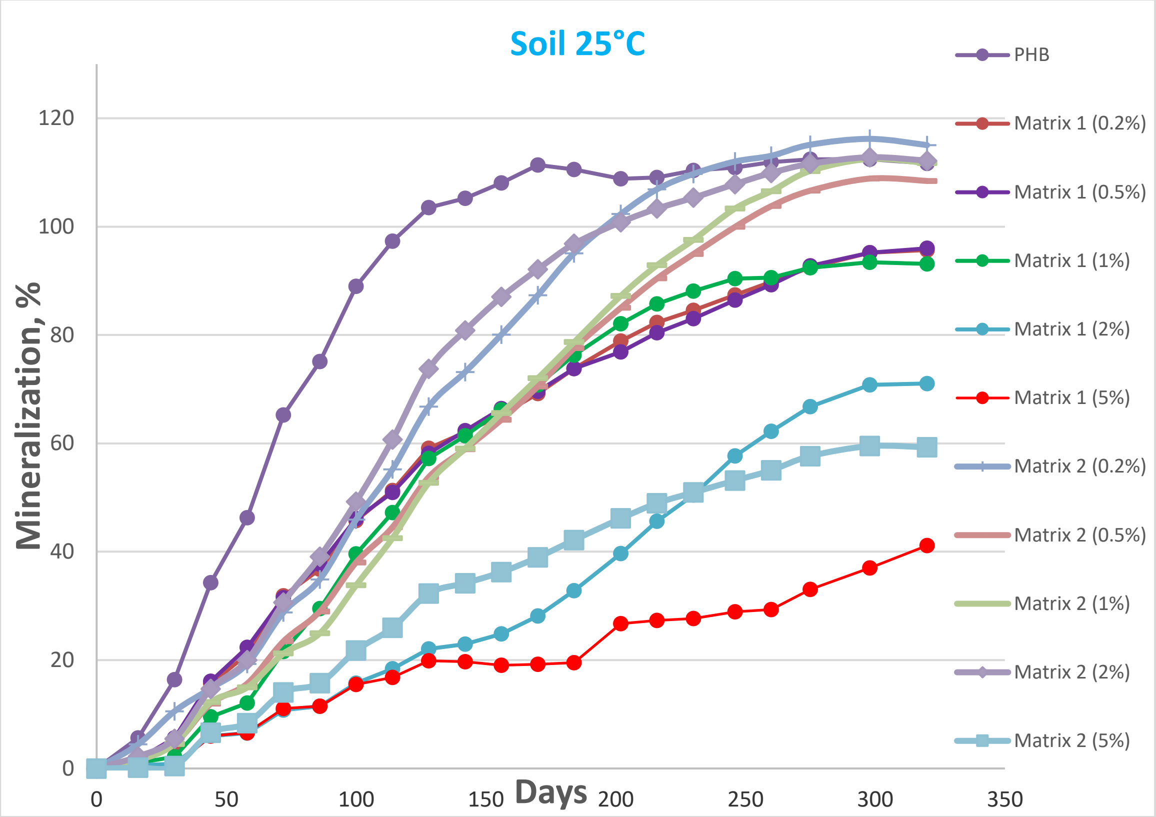


Fig 32. The biodegradation of pure PHB and PHB blended with two antimicrobial agents

5.3.4 PLA blends

In this experiment, different types of additives were blended with PLA to make them biodegradable specially in home composting, which is more challenging. This experiment like some of the previous ones was performed in composting environment.

In this experiment, different physical shapes and sizes were considered. The thickness of the final product was the main factor for this test. In this regard, thin (less than 1 mm) and thick (2 mm) were used to measure their biodegradation in industrial and home composting. Different thicknesses selected due to the final productrs' applications in industry. Due to the policy of the project, additives names and other details regarding blendings are confidential.

One of the most important outcome of this experiment was the fact that these additives and blend could make PLA fully biodegradable in less than 6 months (Figure 33). Among the PLA-based blends, there are noticeable variations. The "PLA based blend 2/A- Thin film" shows the highest mineralization rate among the PLA samples, reaching about 90% mineralization in roughly 80 days, and achieving close to 100% by 180 days. This outcome laid in the high content of the additives that is highly degradable in the matrix. PLA based blend 1/B- Thin film follows closely, showing a similar mineralization trend but with a slightly slower rate compared to the green line. However, up to 70% of biodegradation, blend of 2/B showed slightly higher biodegradation than 1/B.

The “PLA based blend 1/A- Thermoforming” was shown moderate mineralization rates in comparison with the mentioned blends, with reaching approximately 80-90% by the end of the 180-day period. It is logical that thinner materials can be degraded faster due to the higher or wider contact surface, which let the microorganisms to attack the matrix easier and sooner.

As expected, in industrial composting (Figure 34) the biodegradation was even fster. PLA-based blends in thin film form (such as PLA based blend 1/A- Thin film and PLA based blend 1/B- Thin film) exhibited the highest rates of biodegradation. These materials reached over 90% mineralization within 40 days and achieved nearly complete degradation by around 50-60 days. The high surface area-to-volume ratio of thin films allows for greater exposure to microbes, facilitating quicker degradation. Additionally, the elevated temperature in industrial composting enhances the breakdown of the polymer chains in these PLA blends [129].

PLA-based blends in thermoformed form (like PLA based blend 1/A- Thermoforming) and thicker specimens (such as PLA based blend 1/B- Thick specimen) showed slower mineralization rates compared to thin films, but still performed well under industrial conditions. The thicker materials took longer to degrade because their lower surface area-to-volume ratio limits microbial access to the entire material [130,131]. However, by the end of the experiment, even these thicker materials reached high levels of mineralization (around 80-90%), demonstrating that industrial composting can effectively handle a variety of material structures.

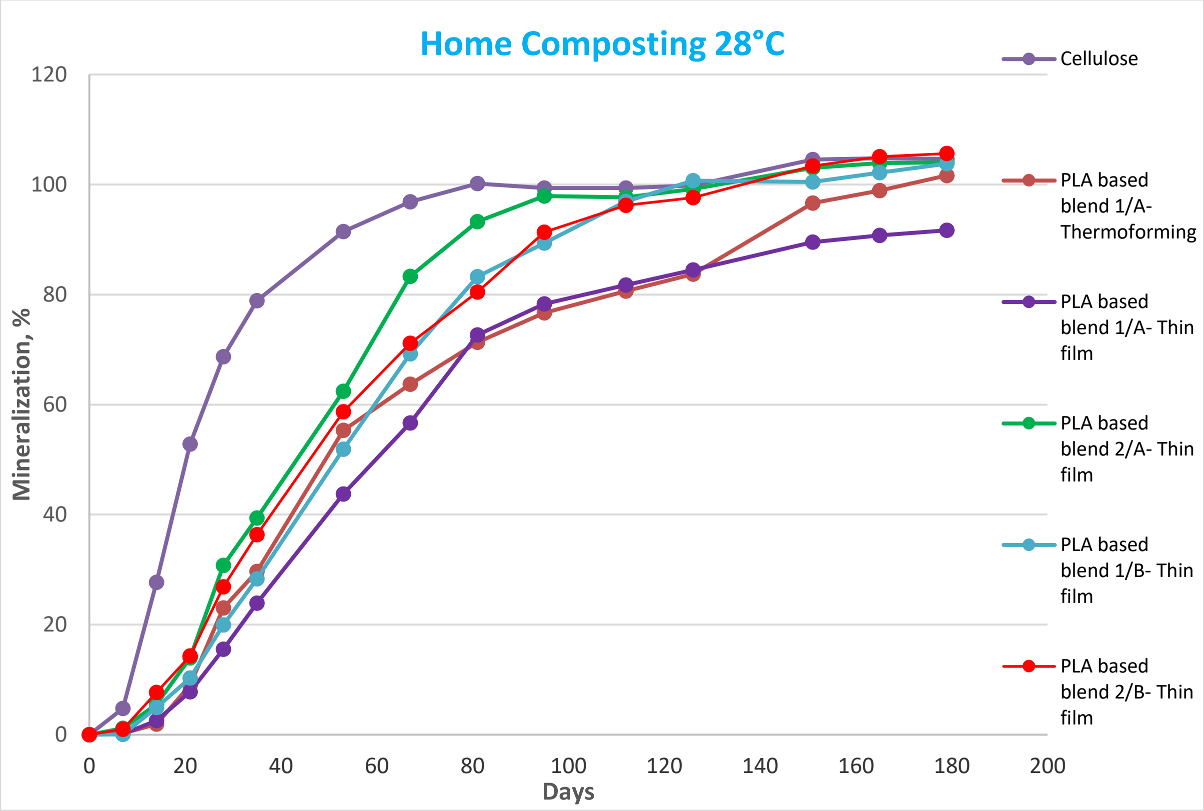


Fig 33. The biodegradation of PLA blends in home composting

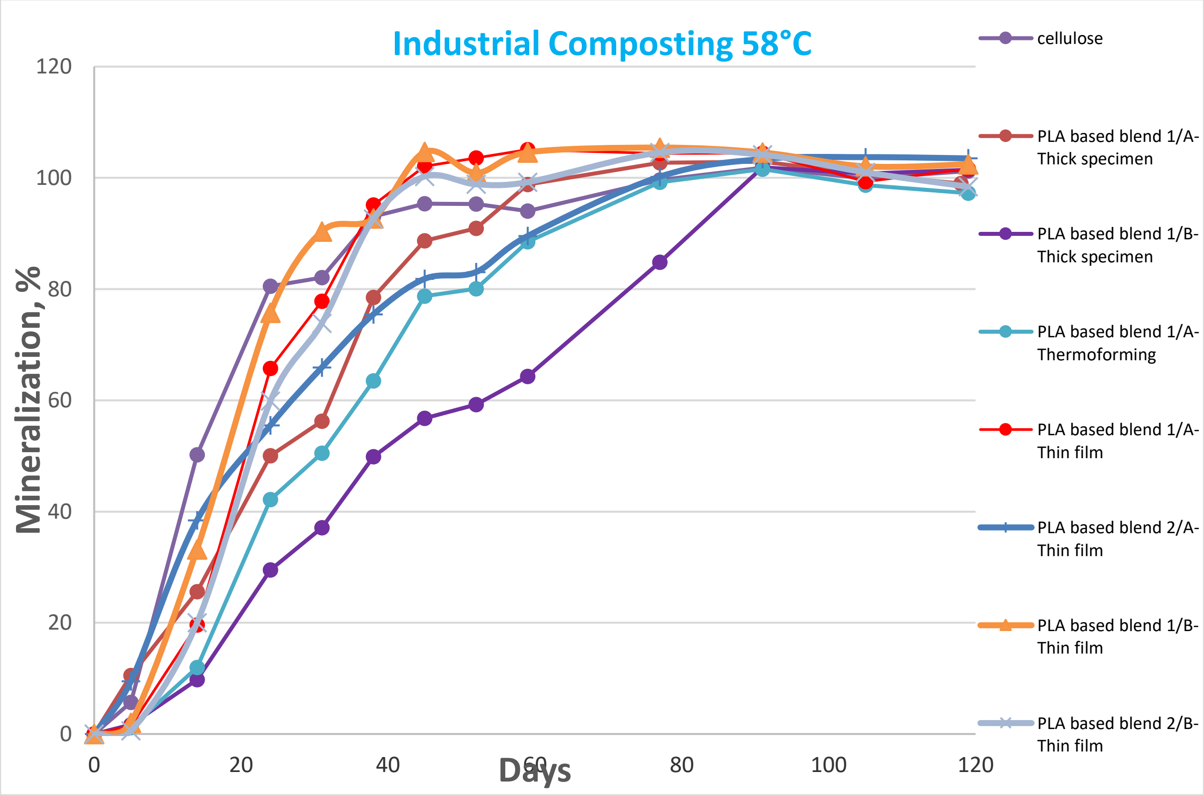


Fig 34. The biodegradation of PLA blends in Industrial composting

6. CONCLUSION

The utilization of biodegradable polymers such as poly(3-hydroxybutyrate) (PHB) and poly (butylene succinate) (PBS) represents a promising avenue in addressing the environmental challenges posed by conventional plastics. However, their inherent susceptibility to biodegradation, especially when exposed to soil environments, necessitates innovative approaches to enhance their resistance while maintaining their eco-friendly attributes. This thesis has undertaken a multifaceted exploration, focusing on the incorporation of lignin additives and monoterpenes to bolster the biodegradation resistance of PHB and PBS.

The initial investigation delved into the efficacy of blending monoterpenes specifically eucalyptol, limonene, and thymol into PHB matrices. These compounds, selected for their documented antimicrobial properties, exhibited considerable potential in retarding biodegradation processes in soil environments. Notably, eucalyptol emerged as the most efficacious additive, prolonging the stability of PHB-based materials even under conditions conducive to maximal biodegradation. This discovery underscores the applicability of such compounds in agricultural contexts and other sectors where PHB materials interface with soil, promising extended functional lifespans and reduced environmental impact.

Subsequently, attention was directed towards incorporating alkali and organosolv lignin into PHB and PBS matrices to fortify their resistance against biodegradation. The inherent complexity of lignin structures endowed the polymer matrices with increased intricacy, rendering them more resilient to microbial degradation. Furthermore, the minimal antimicrobial influence exerted by lignin further impeded biodegradation processes, affirming its efficacy as a biostabilizing agent. The meticulous selection of lignin types and concentrations emerged as pivotal determinants, underscoring the need for tailored approaches aligned with specific application requirements. This study underscores the transformative potential of lignin additives in augmenting the sustainability and durability of biodegradable polymers, offering economically viable solutions across diverse industries.

In synthesis, these findings collectively underscore the imperative of exploring diverse additives and blending methodologies to optimize the performance of biodegradable polymer materials. Future investigations could explore an expanded array of lignin types, concentrations, and blending techniques to further refine their efficacy. Additionally, elucidating the synergistic effects of combining multiple additives holds promise for unlocking novel avenues to enhance biodegradation resistance and surface properties of biodegradable polymers.

In conclusion, the insights gleaned from this thesis endeavour hold a significant stride towards advancing the development of environmentally conscious materials with augmented biodegradation resistance. By fostering broader adoption across industries, these innovations stand poised to mitigate the pervasive environmental ramifications of plastic waste, heralding a more sustainable trajectory for global material consumption and waste management practices.

7. THESIS CONTRIBUTION TO SCIENCE AND PRACTICE

The research that have been conducting is crucial because it addresses a pressing environmental concern: the pervasive presence of non-biodegradable plastics in our ecosystems. These plastics, like the ones we use in packaging, agriculture, and everyday items, persist in the environment for centuries, contributing to pollution, harming wildlife, and degrading natural habitats. Finding solutions to this problem is paramount, and that's where my work comes in.

This research focuses on enhancing the durability and lifespan of biodegradable plastics, specifically poly(3-hydroxybutyrate) (PHB) and poly (butylene succinate) (PBS). These biodegradable plastics offer an eco-friendlier alternative to traditional plastics, but they still degrade relatively quickly, especially in soil environments. By making them more resistant to biodegradation, we can extend their usefulness and reduce the frequency of replacements, thereby lessening their environmental impact.

One approach that this research explored was the incorporation of natural oils called monoterpenes into the biodegradable plastic matrices. These monoterpenes, found in plants like eucalyptus and citrus fruits, possess antimicrobial properties that inhibit the microbial activity responsible for breaking down plastics. Through careful experimentation, I found that certain monoterpenes, such as eucalyptol, limonene, and thymol, effectively slowed down the biodegradation process, thereby prolonging the lifespan of the plastic. This has significant implications, particularly in agricultural settings where plastic mulches are commonly used to control weeds and conserve moisture. By incorporating these additives, we can reduce the frequency of mulch replacement, leading to cost savings and less environmental disruption.

Additionally, this research investigated the use of lignin, a natural polymer derived from plant cell walls, as a reinforcing agent for biodegradable plastics. Lignin, typically a byproduct of paper and biofuel production, is abundant and inexpensive. By blending lignin with PHB and PBS, we were able to create composite materials with improved mechanical strength and resistance to microbial degradation. These lignin-enhanced plastics show promise in applications such as food packaging, where durability is essential to protect perishable goods during transportation and storage.

What's particularly exciting about this research is its potential to leverage existing waste streams. For example, the lignin used in the experiments is sourced from agricultural residues and industrial byproducts that would otherwise be discarded. By repurposing these materials, we not only enhance the performance of biodegradable plastics but also reduce waste and promote a circular economy.

In conclusion, this research contributes to the ongoing efforts to develop sustainable alternatives to traditional plastics. By fortifying biodegradable plastics with natural additives like monoterpenes and lignin, we can extend their lifespan, reduce environmental pollution, and promote responsible resource utilization. As we continue to refine these techniques and explore new avenues, we move closer to a future where plastics are not a burden on the environment but a boon to sustainability.

References

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Activation energy (Ea)

Bubble point (BP)

Carbon Ddioxide (CO_2)

Cold Crystallization Temperature (Tcc)

Differential Scanning Calorimetry (DSC)

Dynamic Mechanical Analysis (DMA)

Essential Oils (EOs)

Glass Transition Ttemperature (Tg)

Lignosulfonate Calcium (LS)

Loss Modulus (E″)

Melting point (MP)

Poly(butylene succinate) (PBS)

Polyhydroxyalkanoates (PHA)

Polyhydroxybutyrate (PHB)

Storage Modulus (E′)

Curriculum vitae

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Status

Looking for a Job Position

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Research Interests

Environmental Engineering, Process Engineering, Optimization, Energy Forecast, Power Improvement

Education

Ph.D. Candidate in Environmental protection engineering department. Tomas Bata University, Czechia,(2020-July 2024)

Project: Sealive , Horizon 2020

Expected Graduation: August 2024.

Thesis Title: Investigating the influence of different additives on the mechanical properties and biodegradation of PHB and PBS

M.Sc. in Chemical Engineering Department, Central Tehran faculty of Azad University, Tehran, Iran

Thesis Title(2016): Reduce the air pollution and greenhouse gases generated by diesel, Under the supervision of Dr. V. Pirouzfar

GPA: **18.55/20 (3.71/4) Ranked 1st**

B. Sc. In Chemical Engineering Department, Abadan faculty of Azad University, Abadan, Iran

Thesis Title (2014)**:** Investigate ways to improve the energy efficiency of chemical manufacturing processes . Under Supervisor of Dr. A. Alizadeh.

GPA: **16.51/20 (3.30/4)**

N, Hajinajaf; A, Fayyazbakhsh; S, Kamal Shahsavar; F, Sanjarian; H, Rahnama. **Boosting plant oil yields: the role of genetic engineering in industrial applications.** Biofuel Research Journal 2024 (Link)

Julinová, M.; Dagmar, S.; Kaszonyiov, M.; Kalendov, A.; Fayyazbakhsh, A.; Koutny, M. **Comprehensive Biodegradation Analysis of Chemically Modified Poly (3-Hydroxybutyrate) Materials with Different Crystal Structures**. Biomacromolecules 023. (Link)

PUBLICATION

Fayyazbakhsh, A.; Bell, M.L.; Zhu, X.; Mei, X.; Koutný, M.; Hajinajaf, N.; Zhang, Y. **Engine Emissions with Air Pollutants and Greenhouse Gases and Their Control Technologies.** J. Clean. Prod.2022. (Link)

ARTICLES

Fayyazbakhsh, A.; Koutný, M.; Kalendová, A.; Šašinková, D.; Julinová, M.; Kadlečková, M. **Selected Simple Natural Antimicrobial Terpenoids as Additives to Control Biodegradation of Polyhydroxy Butyrate**. Int. J. Mol. Sci. 2022. (Link)

Fogašová, M.; Figalla, S.; Danišová, L.; Medlenová, E.; Hlaváčiková, S.; Bočkaj, J.; Plavec, R.; Alexy, P.; Repiská, M.; Přikryl, R.; Fayyazbakhsh, A.; et al. **PLA / PHB-Based Materials Fully Biodegradable under Both Industrial and Home-Composting Conditions.** 2022. (Link)

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Nguyen, D.D.; Moghaddam, H.; Pirouzfar, V.; Fayyazbakhsh, A.; Su, C.H. **Improving the Gasoline Properties by Blending Butanol-Al2O3 to Optimize the Engine Performance and Reduce Air Pollution.** Energy 2021. (Link)

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Fayyazbakhsh, A.; Pirouzfar, V. **Comprehensive Overview on Diesel Additives to Reduce Emissions, Enhance Fuel Properties and Improve Engine Performance.** Renew. Sustain. Energy Rev. 2017. (Link)

Khorramshokouh, S.; Pirouzfar, V.; Kazerouni, Y.; Fayyazbakhsh, A.; Abedini, R. **Improving the Properties and Engine Performance of Diesel-Methanol-Nanoparticle Blend Fuels via Optimization of the Emissions and Engine Performance.** Energy and Fuels 2016. (Link)

Fayyazbakhsh, A.; Pirouzfar, V. **Investigating the Influence of Additives-Fuel on Diesel Engine Performance and Emissions: Analytical Modeling and Experimental Validation.** Fuel 2016. (Link)

Fayyazbakhsh, A.; Pirouzfar, V. **Determining the Optimum Conditions for Modified Diesel Fuel Combustion Considering Its Emission, Properties and Engine Performance.** Energy Convers. Manag. 2016. (Link)

Books

Pirouzfar, Vahid, Narimani, Mastane, Fayyaz Bakhsh, Ahmad, Su, Chia-Hung and Gharebaghi, Milad. **Gasoline Additives**. De Gruyter, 2022. (Link)

Pirouzfar V, Fayyazbakhsh.A. **Diesel Fuel Additives**. Lambert Academic Publisher, 2015. (Link)

Honors and Awards

Recipient of a paper award for publication in a journal ranking among the top 10% From Tomas Bata University

Acknowledged with three additional awards in the form of "Extraordinary Scholarships" for outstanding publications by Tomas Bata University.

Honored as one of the distinguished students in Chemical Engineering in Iran, awarded by the Chemical Engineering Society of Iran

Achieved the 1st rank among a cohort of 25 M.Sc. students in the Department of Chemical Engineering at Azad University, Central Tehran Branch.

Language Competencies

English (Professional)
Arabic (Native)
Persian (Native)
German (Elementary)

Computer skills

Engineering Software:	Design expert, H.X net, PVSyst (intermediate), Gnuplot
Scripting Software:	Python **(**Intermediate), Gnuplot
General Software:	Microsoft Office

Research Experiences

Research in Bachelor under Prof. Hossein Hosseini Supervision(Head of Department)

- Work on a combination of chemical and physical methods to improve the polymer recycling

Course Projects, Azad University, Central Tehran Branch, Tehran, Iran (2014 – 2016)

- **Analysis of the Effect of Ethanol and n-Butanol blended with Diesel Fuel:** Analysis (Experimental).
- **Analysis of the Effect of nitro additives blended with diesel fuel:** analyzing (Experimental).
- **Analysis of the Effect of Nano Metal additives blended with diesel fuel:** analyzing (Experimental).
- **Simulation of the effect of different additives on engine power and air pollution:** designing the object by considering experimental data and analyzing
    - Software used: Design Expert
- **The study, comparison, and assessment on the performance of zeolite catalyst:** Studying a lot of papers and writing an article with a group. (2016)
- **Worked with a group of students and a professor** (Dr. Vahid Pirouzfar) on different membranes (Membrane synthesis) and studied the effect of various Nanoparticles blended with a membrane in different temperatures and pressures. (2017)

Teaching Experiences

Teaching Assistant for "Heat Transfer" course (Fall 2011)

Under supervision of Dr. H. Hosseini (Pedram465@yahoo.com)

Teaching Assistant for "Fluid Mechanics" course (Winter 2012)

Under supervision of Dr. H. Hosseini (Pedram465@yahoo.com)

Teaching Assistant for "Process Integration" course(Fall 2015)

Under supervision of Dr. V. Pirouzfar

Tutor for Mathematics (summer 2013)

Tutor for Advanced Mathematics (summer 2015)

Tutor for Advanced fluid mechanics (summer 2015)

Presentations

Conferences

- Presenting the results of my research on five reference books on the effect of nano additive blended with diesel fuel on increased power of diesel engine (summer 2015)

  Seminar course, Azad University, Tehran Branch, Tehran, Iran, 2015.
- Presenting the effect of nanofluid for decreasing the influence of hydration on gas transportation, Nano Material Symposium, Azad University, Abadan branch, Abadan, Iran. (summer 2013).
- Presenting my M.Sc thesis, Azad University, Tehran Branch, (2016)
  - Got the maximum score (18/18 +2 score for writing article+20/20 or 4/4)

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