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

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Doctoral Thesis Summary

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Faculty of Technology

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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 will be exposed to simulated environmental conditions in order to assess the effect on biodegradability. The study also thoroughly will study 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 will be 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 budou vystaveny simulovaným environmentálním podmínkám, aby byl posouzen vliv na biodegradovatelnost. Studie také důkladně prozkoumá mechanické vlastnosti modifikovaných materiálů PBS a PHB. Po stanovení skladovacího modulu, ztrátového modulu a dalších kritických mechanických vlastností bude možné získat hlubší znalosti o vlivu přísad na celkovou výkonnost a strukturální integritu polymerů.

Cílem této práce je nejprve zvýšit odolnost PHB a PBS proti biodegradaci, protože jsou velmi biodegradovatelné. Za tímto účelem byly a budou použity různé techniky, jako jsou různé druhy přísad. Druhým cílem této práce je zvýšit mechanické vlastnosti zmíněných polyesterů. Konkrétně se bude studovat mechanické vlastnosti spolu s biodegradací. K dosažení těchto cílů budou použity různé testy, jako jsou biodegradace, skenovací elektronová mikroskopie (SEM), dynamická mechanická analýza (DMA) a diferenciální skenovací kalorimetrie (DSC).

Výzkum uvedený ve finální práci ukáže, jak důležité mohou být esenciální oleje a antioxidanty z ligninu jako efektivní přísady pro kontrolu biodegradovatelnosti a mechanických vlastností PBS a PHB.

Contents

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].

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. However, biodegradable plastics necessitate specific environmental conditions for effective degradation to take place [10]. 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 [11].

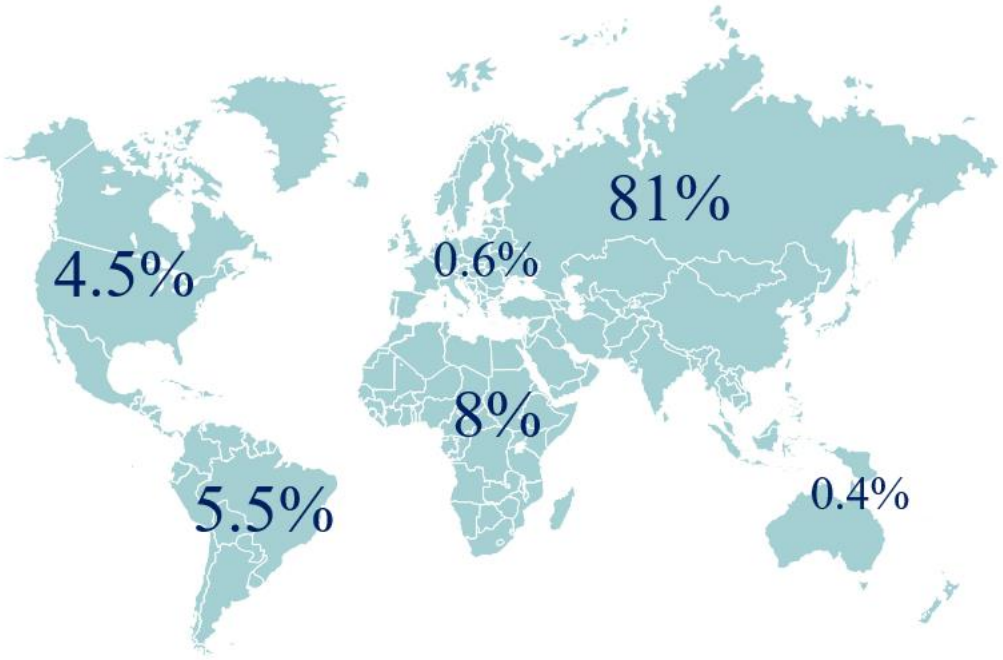

Fig 1. Continents that emit most ocean plastics in 2021.

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[12,13]. 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 [14,15]. 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

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[16]. Furthermore, because PBS and PHB degrades quickly, it cannot be used in several agricultural applications where long-term biodegradation management is crucial [17,18]. PBS's potential for usage has been constrained by factors such as its low water barrier, high light transmittance, and expensive production costs [19].

1.3. Enhancing 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[20,21]. 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 [22–24]. This ability made those additives interesting not only to postpone the biodegradation, but also made them good option for being used in food packaging industry [25–27].

On the other hand, the ability of using this types of additives are still questionable in case of thermal and mechanical properties.

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 [28,29]. 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 [30]. 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).

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 [31].
2. And is it possible to improve the thermo 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.

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. 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:

3.1. Chemicals 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

3.2. Samples preparation

The provided concentrations of additives were thoroughly blended with pure PHB powder in a bowl prior to loading into a micro-extruder. In this study, a twin-screw micro-extruder (HAAKE Minilab, Thermo Fisher Scientific, Waltham, MA, USA) was used, operating at a speed of 50 rpm, and the processing temperatures were set at 185 °C for PHB and 120 °C for PBS. A mixing duration of 2 minutes under the specified conditions was determined to be sufficient without causing any undesired material degradation. Before extrusion, the PHB powder was dried at 100 °C for 10 hours.

Next, compression molding was carried out at the same temperatures as the micro-extruder (185 °C and 120 °C) to produce the films. The heating time for molding was approximately 2 minutes, and afterward, the films were allowed to cool down to room temperature for about 10 minutes. The resulting film specimens had a thickness ranging from 120 to 130 μm, with dimensions of 50mm × 300mm. The same process was applied to create pure PHB and PBS films, which served as control samples. The samples later cut into small pieces with two different sizes(5 × 5mm for biodegradation and 5 × 50 mm for burial test).

3.3. Experiments

3.3.1.Biodegradation

Throughout the process of aerobic decomposition of organic compounds, oxygen is utilized, leading to the transformation of carbon into gaseous carbon dioxide (CO_2). The assessment of mineralization involves determining the proportion of solid organic carbon in the tested sample that undergoes conversion into CO_2. The experiments were carried out in 500 mL biometric flasks. These flasks contained the following components: 50 mg polymer film fragments measuring 2 mm, 15 g of dry soil, 5 g of perlite, and 11 mL of mineral medium, all placed in ISO 17556 compliant flasks [8]. For burial test, the same percentages of perlite, mineral medium and soil were added in to the boxes to perform other

tests; DMA, DSC, and SEM. The calculation for mineralization percentage (Dt) was performed using the following formula [7]:

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

The release of CO_2 from each sample is represented as $(CO_2)t$, while $(CO_2)b$ stands for the accumulated CO_2 released from the blank flasks. ThCO2 refers to the expected theoretical amount of carbon dioxide from the test material in the test flasks. To measure the released carbon dioxide, a mass spectrometer HPR-40 DSA (manufactured by HIDEN Analytical in 2020, located in Warrington, UK) was used. Each sample was tested in three parallel flasks, and four blank flasks were also included in the experiment.

3.3.2. Scanning Electron Microscope

Surface changes on the films were examined using a Phenom Pro Desktop SEM device from ThermoFisher Scientific (Waltham, MA, USA). For the SEM examination, a 10 kV acceleration voltage was applied in the high vacuum mode. Prior to imaging, the samples were coated with a thin layer of Au/Pd to minimize sample damage and prevent charging effects.

3.3.3. Differential Scanning Calorimetry

A DSC1/700 analyzer (manufactured by Mettler Toledo in Columbus, OH, USA) equipped with a mechanical cooling system was utilized to conduct the analysis of the samples using differential scanning calorimetry (DSC). The measurements were carried out in a nitrogen atmosphere and calibrated using an indium standard. The DSC analysis aimed to determine the melting point, crystallinity, and Tg (glass transition temperature) of the samples. The samples were placed in an aluminum pan specifically designed for DSC and subjected to temperature scanning ranging from -40 °C to 200 °C. Initially, the samples were heated from -40 °C to 200 °C at a rate of 10 °C per minute. Subsequently, they were cooled from 200 °C back to -40 °C at a rate of -10 °C per minute. This two-step process involving heating was employed to reset the sample's previous thermal history, and the second heating cycle of the DSC curves provided the thermal characteristics of the samples.

3.3.4. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was conducted using a DMA Analyzer (Mettler Toledo, Columbus, OH, USA). The temperature was varied from -40 to 100 °C, and the film-tension mode employed a heating rate of 2 °C per minute, a frequency of 1 Hz, and a load of 0.5 N. The DMA analysis of the samples took place both before and 8 days after the burial test.

4. Results and Discussion

The main focus of the research is on modification of the two main polyester by blending additives with them. The blending process that performed by two different extruders, followed by four tests to achieve our goals; controlling biodegradation along with the mechanical properties' improvements of the mentioned polyesters. This chapter provides a comprehensive summary of the experimental results in detail. The results are accompanied by discussions, ensuring that the reader maintains context throughout the presentation.

4.1 Biodegradation

The CO_2 evolution measurement was utilized to monitor the mineralization process of the materials. The data obtained clearly demonstrated a significant influence in biodegradation caused by all of the additives. It is worth mentioning that before starting the main experiment, preliminary studies have shown that the majority our samples have the potential to control the biodegradation. In this regard we had set an experiment to see if the terpenoids can control the biodegradation. The results after 65 days showed a promising influence and led us to make the main experiment with different contents of terpenoids. Figure 1 showed the biodegradation results from the main experiment. As can be seen, terpenoids had promising effect on inhibition of microorganisms in soil. The best additives were citral, carvone and eucalyptol; however, we have concentrated on limonene, eucalyptol and thymol. The reason was their availability, their potential in improving the mechanical properties, their price, and their ability to be used as plasticizers. The literature [26,32,33] showed that essential oil can be used in polymer as plasticizer and it was the reason why we used the second experiment (in the next step of this research) with the three mentioned additives (with higher percentage) to see if we can have the plasticizing effect long with the biodegradation control. As we expected from the first experiment, eucalyptol has the higher influence on the biodegradation of PHB. Moreover, blending essential oils with PHB serves as a technique to enhance the polymer's crystallinity, thereby reducing its biodegradation rate.

Organosolv and alkali (neutralized) lignin were used as antioxidants in both PHB and PBS. The biodegradation results of this parts are in progress and almost in the last step. It is just clear that they showed promising influence as additives. The final results along with discussion will be conducted in the next step.

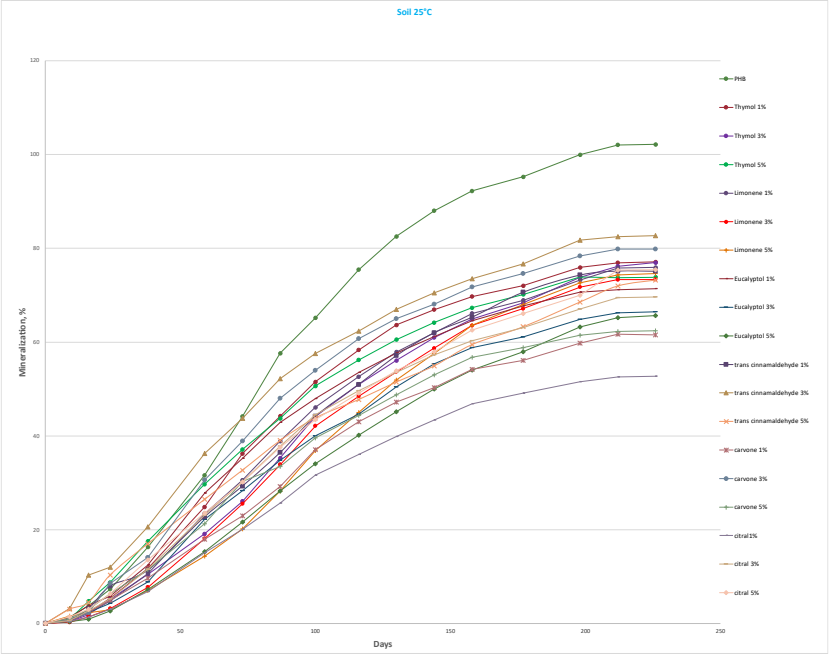

Figure 1.Biodegradation of pure PHB and PHB blended with terpenoids

4.2 Visuals and Microscopic Analysis

Figure 2 illustrates the physical shapes of the samples. During incubation, the physical shapes of the samples were observed at different time intervals: 0, 2, 4, 8, 16, and 32 days. The images show the following samples: (A) pure PHB, (B) PHB + 3% eucalyptol, (C) PHB + 3% limonene, and (D) PHB + 3% thymol. It is evident that the blend containing 3% of eucalyptol was the only sample identifiable after 32 days, while the other samples had already disintegrated by then. Additionally, the images demonstrate that samples with thymol and limonene exhibited greater resistance compared to pure PHB.

The SEM images provide clear evidence that pure PHB has a higher susceptibility to degradation compared to the other samples, as shown by its significant biodeterioration. On the other hand, the sample containing 3% eucalyptol exhibited a relatively smooth surface, indicating a higher level of resistance to degradation than the other samples. Additionally, the sample that containing 3% thymol displayed better resistance to degradation than both the sample with limonene and the pure PHB, as depicted in Figure 8. These results suggest that the addition of eucalyptol and thymol can enhance the degradation resistance of the PHB polymer.

Figure 3 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 1 and 2 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 were 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.

In the next step, a comprehensive investigation will be conducted on the SEM pictures to prove the results of preliminary studies along with the burial test samples.

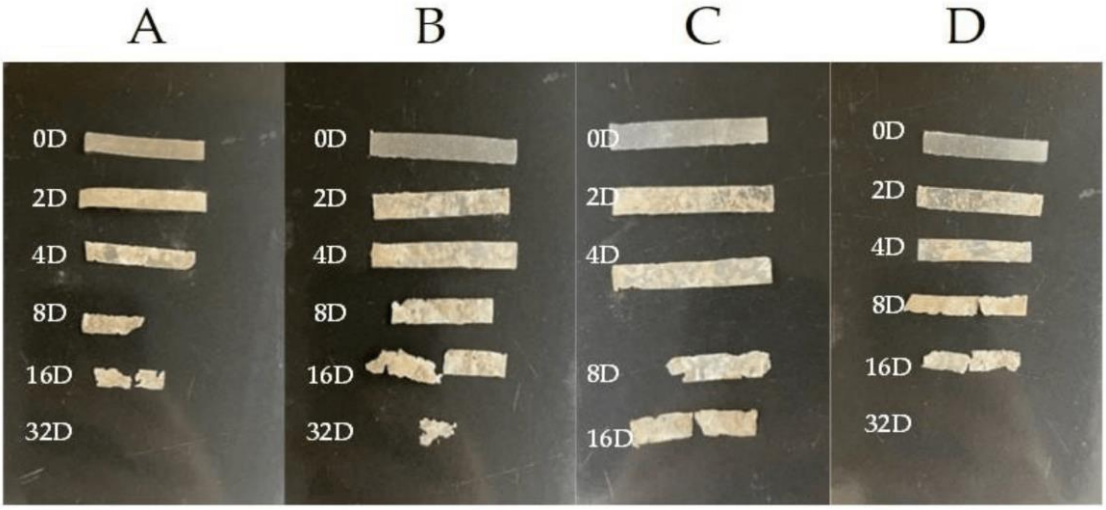

Figure 2. physical shapes of the samples with PHB and terpenoids during incubation

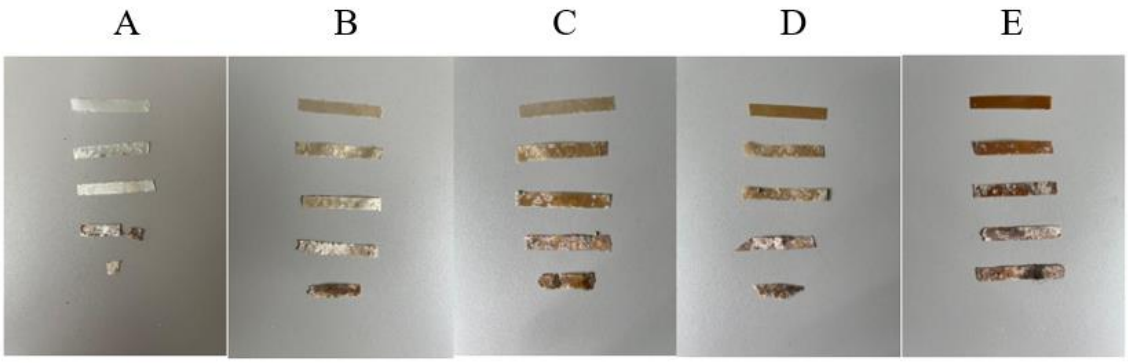

Figure 3. physical shapes of the samples with PHB and neutralized alkali lignin during incubation

4.3 Differential Scanning Calorimetry (DSC)

The influence of the material crystallinity on its biodegradation was also obtained from DSC data (Table 4). Initially, at the outset of the experiment and following 4 days of degradation, the crystallinity of the tested samples appeared comparable

(not more than 5% in comparison with pure PHB). However, after 8 days, the samples containing terpenoids showed increased crystallinity values compared to the samples of pure PHB. Most of the time, additives slightly enhanced the crystallinity of the matrix; however, some exceptions occurred in this research that could be due to some temperature differences in the storage room. As can be seen in Fig. 7, the samples started to degrade by microorganisms from the amorphous part, and crystalline parts remained. However, the DSC results in our research 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 [34] i.e. enzymatic degradation starts first in the amorphous phase, promoting the crystallinity of the samples.

Sample	Crystallinity (%)				
	0 day	4 days	8 days	16 days	32 days
Pure PHB	66.52	67.94	59.4	62.71	Degraded
Eucalyptol 3%	68.24	63.1	59	57.7	64.76
Limonene 3%	70.23	64.94	67.72	66.35	63.88
Thymol 3 %	63.08	64.57	63.1	62.25	Degraded

Table 4. The crystallinity of samples in different incubation time

Moreover, the other thermal parameters such as melting point, cold crystallization temperature and glass transition temperature have been performed by using differential scanning calorimetry (DSC). It is shown that the addition of the selected oils caused a slight T_g reduction (Table 5). The decrease in T_g values showed that eucalyptol, thymol, and limonene are miscible with PHB and increase the molecular mobility of the matrix in the amorphous phase [32]. Only minor enhancements in the first T_m were found in PHB modified by eucalyptol, suggesting that the addition of terpenoids did not significantly impact the T_m and crystallinity of PHB.

Following the introduction of the chosen compounds, the melting region of the PHB blends displayed two distinct melting transitions (Tm1 and Tm2), whereas pure PHB exhibited a single sharp peak at 172 °C (Tm2). Throughout partial biodegradation, the tested compositions consistently exhibited two melting

transition temperatures. This observation suggests that the prepared blends underwent melting and subsequent recrystallization of their subphases. Through biodegradation, the PHB modified with terpenoids experienced only slight alterations in the Tm, indicating minimal impact on its thermal behavior during the biodegradation process. However, limonene enhanced the melting point of the matrix more than other additives.

All the blends exhibited a notably low degree of cold crystallization (Tcc), as outlined in Table 2. Notably, the Tcc values displayed a marginal shift towards higher values with extended biodegradation time, with the maximum change being 3%. Interestingly, it appears that neither the presence of terpenoids nor the duration of degradation significantly influences the Tcc.

4.4 Dynamic mechanical analysis

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 [35]. The results of loss modulus are in progress and will be investigated and written in the next step of this research.

The storage modulus (E′) results for pure PHB and PHB blended with 3% limonene, thymol, and eucalyptol as a function of temperature are like the previous part, which will be investigated in the next step.

The last factor related to mechanical properties analysed 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 [36,37].

5. 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.

6. The importance of this research

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 a more eco-friendly 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.

Curriculum vitae

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Status Looking for a Job Position

Current position Researcher in Energy Consumption and Optimization at Montanuniversitaet Leoben, Austria

Research Interests Environmental Engineering, Air Pollution, Combustion improvement, Energy storage, Nano Technology, Mathematical modeling

Education

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

Project: Sealive , Horizon 2020

Expected Graduation: Febraury 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)**

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**. 2023. (Link)

Fayyazbakhsh, A.; BType equation here.ell, 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)

PUBLICATION

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)

Šašinková, D.; Serbruyns, L.; Julinová, M.; FayyazBakhsh, A.; De Wilde, B.; Koutný, M. **Evaluation of the Biodegradation of Polymeric Materials in the Freshwater Environment—An Attempt to Prolong and Accelerate the Biodegradation Experiment.** Polym. Degrad. Stab. 2022. (Link)

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)

Šerá, J.; Kadlečková, M.; Fayyazbakhsh, A.; Kučabová, V.; Koutný, M. **Occurrence and Analysis of Thermophilic Poly(Butylene Adipate-Co-Terephthalate)-Degrading Microorganisms in Temperate Zone Soils**. Int. J. Mol. Sci. 2020. (Link)

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)

References:

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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

Doctoral Thesis Summary

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