TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department’s title

COMPOSTING OF MODIFIED PHA AND PBS POLYMERS UNDER AEROBIC CONDITIONS

MODIFITSEERITUD PHA JA PBS POLÜMEERIDE KOMPOSTIMINE AEROOBSETES TINGIMUSTES

MASTER THESIS

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Tallinn 2021

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Thesis topic:

(in English) Composting of modified PHA and PBS polymers under aerobic conditions

(in Estonian) Modifitseeritud PHA ja PBS polümeeride kompostimine aeroobsetes tingimustes

Thesis main objectives:

1. Literature review
2. Propose a method to impelement ISO 14855 for modified PHA and PBS
3. Analysis of Co_2 evolution to calculate biodegradation degree

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Choosing thesis topic	1st Februarty
2.	Literature review	20th June
3.	Implementing the methodology	6th May
4.	Results analyzing	12th July
5.	Thesis finalization	20th July

Language: ………… **Deadline for submission of thesis:** "……."………20….a

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Table of Contents

PREFACE

This master thesis was motivated by the project BIO-PLASTICS EUROPE based "on the testing the biodegradability of modified plastic polymers Polyhydroxyalkanoates, and Polybutylene Succinate under the condition of ISO 14855-1". This testing took place at the Environmental laboratory of Tallinn technology university.

Polymers are usually modified to improve the properties, affecting biodegradability; therefore, it is crucial to run the test once after modification to ensure that it degrades under specific conditions. This project was necessary to determine carbon dioxide production to measure the amount of plastic's biodegradability.

This work was carried out under the supervision of Dr Viktoria Voronova and the co-supervision of PhD student Pavlo Lyshtva.

Keyword: BIOPLASTICS, BIODEGRADABILITY, COMPOSTING, MASTER THESIS

List of abbreviations and symbols

PVC - Polyvinyl chloride
PHA – Polyhydroxyalkanoates
PLA – Polylactic Acid
PHB - Polyhydroxy butyrate
PET – Polyethylene Terephthalate
HDPE – High-Density Polyethylene
LDPE – Low-Density Polyethylene
PP – Polypropylene
PE – Polyethylene
PS - polystyrene
CIS - Common wealth and Independent States
NAFTA - North American Free Trade Agreement
TPS - thermoplastic starch
PBS - Polybutylene Succinate
PCL -Polyglycolic acid
PGA - poly caprolactone
PHV - polyhydroxy valerate
PHBV- Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
O_2 – Oxygen
H_2S – Hydrogen sulfide
H_2O- water
S -sulfur
NO_2 – Nitrogen dioxide
SO_2 – sulfur dioxide
CH_4 – methane
NH_3 - Ammonia
H_2S- hydrogen sulfide
C-Carbon
PMs - Particulate matter
NOx - nitrogen oxides
CO - carbon monoxide
CO_2 - carbon dioxide
VOCs - Volatile organic compounds
TPS - thermoplastic starch
PCL - polycaprolactone

Kt - metric kilo tonnes

CA - cellulose acetate cellulose propionate

CP- cellulose propionate

CB - cellulose butyrate

PHV - polyhydroxy valerate

UV - ultraviolet

PHBV - Poly(3-hydroxybutyrate-co-3 hydroxy) valerate

FDA - food and drug administration

SA - succinic acid

BD - 1,4-butanediol

N_2 – Nitrogen gas

TOC – total organic carbon

NaOH - sodium hydroxide

KOH - potassium hydroxide

PUR – polyurethane

1 INTRODUCTION

The awareness of plastic's biodegradability has been growing in recent years because of problems the plastic industry has caused. The main problem is that non-degradable plastic has enclosed our planet, and plastic will maintain in the environment for centuries because of the non-decaying properties of the substance. Plastics are artificial, and when they enter the natural zone, the animals consume them which causes many defaults in our existing natural environment. Plastics that are discharged into the environment may end up on the plates of future generations.

Plastics, which are one of the world's leading issues, affected significant environmental problems. In 2015, the annual global production of plastics was more than 400 million metric tons, of which more than a third of the production was for the packaging sector. In the same year, the waste produced from global plastics production was about 300 million metric tons, of which half of the waste was from the packaging sector[1, 2].

Plastics are made through the polymerization process. Polymerization is the process of combining tiny molecules into long chains to make polymers. Nevertheless, sometimes, the chains can be unfinished, the additives and catalyst used to create the plastics material will be released from its surface. It leads to health and environmental problems if plastics are used as covers for foods. Additionally, it ends up in the marine environment and consumed by living organisms. Polyvinyl chloride (PVC) is the third most-produced plastic globally, and the monomer of PVC is carcinogenic. The plastics that finish up in the marine environment are consumed by the animals, which can cause pathological effect and inhibit reproduction[3].

Research has been done in order to decrease the problems of plastics all around the world. The research done in biodegradable and bio-based polymers is very likely to solve the environmental obstacles replacing the non-biodegradable plastic. The biodegradable and bio-based substances such as Polyhydroxyalkanoates (PHA), Polylactic Acid (PLA), Polybutylene Succinate (PBS) are suitable to produce comparable products like conventional plastics, which could replace the plastics markets in the future[3].

This thesis contains research on the biodegradation of modified PHA and PBS plastic under aerobic condition. The term biodegradable and compostable, which have caused confusion among the public, has been made clear by explaining the terms and differentiating them. The aerobic testing degradability was carried according to ISO

14855-1 determination of the ultimate aerobic of plastic materials under controlled composting conditions.

The aim of this thesis is give an overview of conventional plastic and bio-plastics, and propose a method to assess the degradability of modified PHA and PBs under aerobic condition for 60 days.

2 LITERATURE OVERVIEW

2.1 Overview of conventional plastics

Plastics are widely used in the world economy, with an annual production of 350 to 400 million tons. Each year plastic waste accumulate in terrestrial and marine settings due to inadequate recycling and low circular usage. Plastic has now been proven to negatively impact all ecosystems, with microplastics being a specific health risk. As a result, a current microbial study has looked at whether and how microbes might break down plastics in the environment[4]. Their properties cover flexible, mouldable, strong, durable, lightweight, and inexpensive, making them proper for the production of various products, including household items, product packaging, and shopping bags, which are primarily single-use products.

Carbon monoxide, dioxins, nitrogen oxides, and hydrogen cyanide, among other toxic gaseous compounds released during the plastic production process, represent a significant threat to the environment and human health[5].

Artificial plastics are manufactured using pure petroleum products where the synthetic polymers produced of carbon-carbon bonds are obtained in a controlled environment [6]. These conventional plastics made of heavy crude oil could commence fossil stock exhaustion, climate change, and greenhouse gas emissions [7]. There are two types of plastics:

- Thermoplastic: these plastic contain 92% of total conventional plastics like Polypropylene (PP), Low-Density Polyethylene (LDPE), Polyvinyl chloride (PVC), and High-Density Polyethylene (HDPE). The atoms in these plastics are chained in a long range, and each one is separated; the backbone is a carbon-carbon base that prevents them from degrading. The mentioned materials are usually used for packaging or to contain food and liquids[8].
- Thermoset: they only take 8% of the market share; these plastics have crossed links with smaller chains that make them sensible to degradation; they gained solid form after being melted, which is not reversible. Polyethylene terephthalate (PET) and polyurethane (PUR) are two of the most common thermosetting plastics [8].

The biodegradability of plastics depends on their chemical composition but not on the monomers' sources. For instance, ordinarily used plastics, polyethylene terephthalate (PET), PVC, HDPE, LDPE,polystyrene (PS), Polypropylene (PP), and miscellaneous plastics are non-degradable plastics; however, the origin monomers of polymers such as Polyethylene or polythene (PE), and PET could be gained from biological sources. These plastics are formed of high molecular weight due to their copies of small monomer units[9].

Invertebrates have recently been shown to be capable of degrading certain plastics. While these investigations showed that the insects crush and shred the plastics mechanically, it has been debated whether and to what degree the microbiomes associated with the various insects can really decompose the synthetic polymers[4].

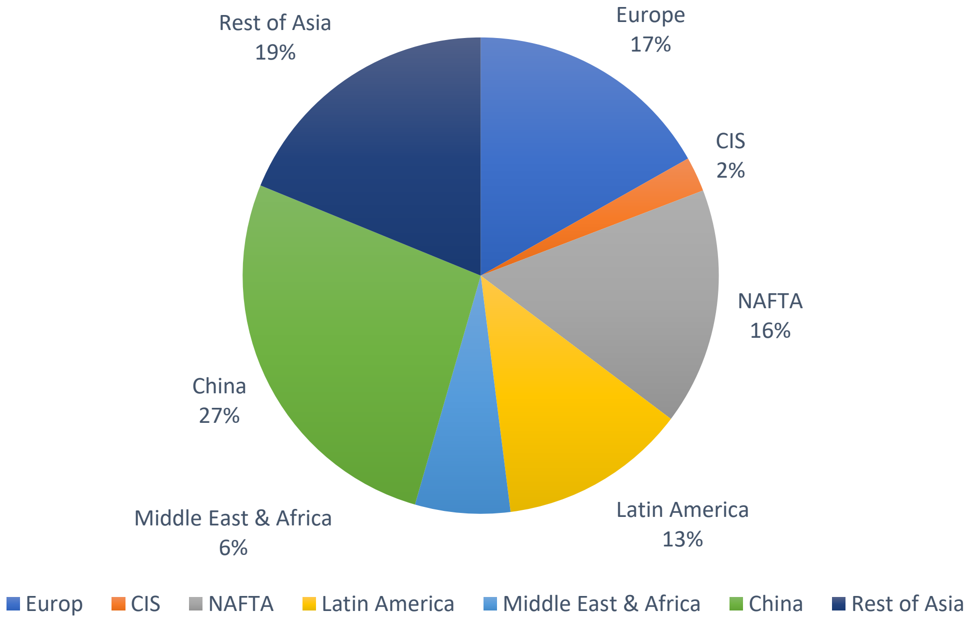


Figure2.1. Global production of plastics, (Common wealth and Independent States (CIS); North American Free Trade Agreement (NAFTA))[10].

2.2 Plastic waste treatment

According to the United Nations, about 453 million tons of plastic garbage will be created yearly since 2021, with output anticipated to quadruple by 2035 to 800 million tons and 1600 million tons by 2050[5].

Plastic has become far more single-use and 'throw-away' than prior synthetic artefacts due to its low cost, lightweight, and durability. Plastic waste is a significant concern to animals because it spreads non-native and potentially hazardous species, absorbs hazardous chemicals, and degrades into micro-plastics that they can eat. The number of potentially negative consequences of plastic waste has grown, and it is now recognized that these objects can transfer persistent organic pollutants and non-indigenous species.

Plastic source in marine:

- Plastics accumulate in the environment for various reasons, including direct littering and dumping on land or at sea, wind blowing from landfills, transportation losses, and accidents.

Plastic waste in a landfill:

- Many discarded plastics end up in landfills., including the considerable proportion used in single-use applications such as packaging. On the other hand, plastic endures in landfills and, if not adequately buried, might later reemerge as "debris." Plastic's durability assures that it does not 'go away' wherever it is; in other words, dumping plastics in landfills may simply be storing a problem for the future. Although the buildup of plastics on land is significant, little information on the volumes, rates, destiny, or effects is known[11].

Conventional techniques to handle plastic waste include:

- Primary method: re-introduce plastic piece in the heating cycle of plastic processing line itself for higher reproduction.
- Secondary method: mechanically re-extrude, process, and transforming plastic waste into new plastic outcomes mixed with virgin polymers for overall production cost minimization.
- Tertiary method: chemically or thermo-chemically change the polymer structure of plastic to apply it as monomer feedstock in industrial recycling circles [12].

These methods are essentially plastic recycling, but not all plastics can be recycled. For instance, there are two different types of plastics, thermoplastics and thermosetting polymers. The last contains polymers that cross-link to produce an irreversible chemical bond and cannot be re-melted into a new substance despite the amount of heat utilized [13]. In addition, recycling plastics is moderately inefficient and less cost-effective, where it declines the quality of the polymers yielded[14]. Therefore, biodegradation of plastic is an alternative practical, eco-friendly, and innovative method.

2.3 Microplastic

Microplastics are made through the fragmentation of bigger plastic items or created to be used in personal care products, medications, and industry.Beach litter, road runoff, sewage, and illegal dumping all contribute to the pollution of the waters. Microplastics are found in all types of marine environments, from deep ocean sediments to polar icecaps. Although plastic is called hazardous, legislation limiting the accumulation of marine trash is hampered by a lack of proof that it harms the environment[15].

Microplastics can be traced back to two primary sources:

- Direct runoff introduction
- Weathering breakdown of meso- and macro-plastics detritus.

Some microplastics which enter the oceans directly through runoff are produced from plastics used in consumer products. Micron-sized plastic particles, for example, are commonly employed in cosmetic compositions.

Plastic polymers break down to generate microplastics, which have a softer impact[16]. Microplastics are a source of concern since their size range coincides with the optimal particle size absorbed by animals at the bottom of the marine food web. [15].

2.4 Ecological impacts of plastic waste

2.4.1 Marine impact

Plastic garbage in water bodies disrupts natural flow, restricts fish reproduction, and kills essential creatures. At the same time, polymers in the oceans may contribute to global warming by forming a darkened canopy that prevents plankton from growing [5].

2.4.2 Soil impact

In terms of soil pollution, many forms of plastic wastes pollute the soil by settling on the surface or infiltrating the soil layers in various ways, including sludge, fertilizers, wastewater irrigation, landfilling, biosolids, and other sources. Temperature and photo-oxidation contribute to the fragmentation of plastics into microplastics on the soil surface. Plants and soil creatures can move broken microplastics deeper into the soil, polluting groundwater, and degrading soil characteristics [5].

2.4.3 Incineration impact

The incineration of plastic garbage emits various toxins into the sky, making it one of today's significant contributors to air pollution. Particulate matter (PMs), metals, methane (CH_4), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), volatile organic compounds (VOCs), and other substances such as solid material are among the most common pollutants released by incineration, which raises levels of heavy metals, inorganic salts, and organic compounds in the environment [5].

2.4.4 Human impact

Inhalation and digestion of plastic can have a substantial influence on human health, either directly or indirectly. Inflammation, genotoxicity, apoptosis, oxidative stress, and necrosis are some of the biological responses that microplastics can cause, while chronic exposure can result in tissue damage, fibrosis, and carcinogenesis. The leaching of unbound compounds or leftover monomers may have a range of chemical consequences, resulting in human health degradation[5].

Plastic waste's pervasiveness makes it impossible to eliminate it from the marine ecosystem, as contamination will always surpass this threshold level, making the ocean the final resting place for most poorly managed plastics[17].A comprehensive mainstream media describes collapsed beached whales, turtles, and seabirds with stomachs plentiful of plastic waste, showing the severity of how these wastes have affected marine organisms. These charismatic marine species preserve a significant contribution to society. If these crises were not overcome, future ages might never have a chance to watch the existence of these marine animals [18].

Other literal outcomes caused by the presence of plastic wastes include a variety of unexpected damages (e.g., sharp debris, entangled in nets and exposure to unsanitary items),which are harmful to physical and mental wellbeing (e.g., social interaction, family bonds and physical activity[19].

2.5 Public awareness on plastics and the environment

The anticipated importance of the environmental risks generated by plastic pollution has developed in society in the past two decades due to its growing and uncontrolled appearance in the environment [20]. However, because of social practices, the use and production of plastic still predominate among producers and consumers. It has been reviewed the studies of the public on the plastic obstacle and summarized that people admire and use plastic, despite it is likely harmful to the environment [21].

2.6 Impacts of plastic wastes' accumulation

The plastic production method releases many toxic gaseous elements into the air, including carbon monoxide, dioxins, nitrogen oxides, and hydrogen cyanide, which act as a severe menace to the environment and human health.

Concerning plastic disposal, between 1950 and 2018, 6.3 billion metric tons of worldwide plastic product was dumped, and before disposal, more than 4 billion tons of material were used only once[1]. Moreover, approximately 4.5 billion tons of plastic trash are disposed in landfills or released into the environment, affecting the soil's microbial balance in a negative way. Since more than 500 years are necessary for complete decomposition, landfilling results in soil unproductiveness [22], while toxins are also released as a result of plastic breakdown[23].Several microorganisms hasten biodegradation in landfills, including bacteria like Pseudomonas sp., nylon-eating bacteria, and flavobacteria, which split nylon throughout the action of the nylon’s enzyme [24].

2.7 Overview of bioplastics

2.7.1 Description

Within the title of bioplastics, it can be identified:

- biobased.
- Biodegradable plastics.

Bioplastic can additionally fulfil both of these criteria. Bio-based plastics are typically constructed from renewable sources by the activity of living organisms. They can be polysaccharides (e.g., starches, like TPS); cellulose, such as reformed cellulose; (pectin, and chitin), proteins (e.g., wheat gluten, wool, silk, casein, and gelatine),lipids(e.g., animal fats, plant oils), or outputs of microorganisms (e.g.,PHA such as PHB). Besides, bio-based plastics can also be chemically synthesized from bio-derived stocks (e.g., PLA, PBS). Furthermore, there is another share of plastics that are bio-based but not biodegradable that is described as "drop-ins" (e.g., bio-PET, bio- Polyethylene (PE), bio-PP) with equal characteristics as their petrochemical ancestors. Besides, biodegradable plastics with a specific degree of biodegradability can also be manufactured from petrochemical sources, such as poly glycolic acid (PGA), polycaprolactone) (PCL). Many biodegradable bioplastics are already on sale and provided by different companies under different trade names. The order of different bioplastics is illustrated in Figure2.2[25].

Biodegradable polymers are becoming increasingly popular, such as polylactic acid, cellulose-based thermoplastics, and other polysaccharide-based plastics, which helps to reduce pollution [26].

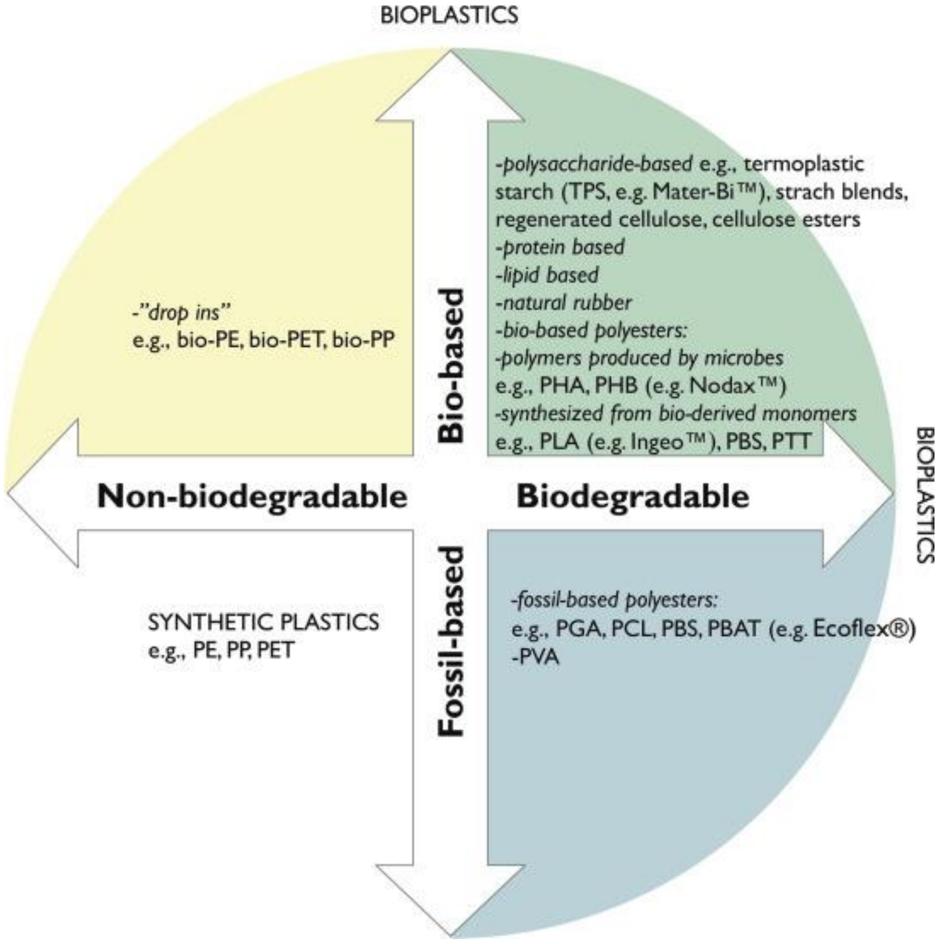


Figure 2.2. Biodegradable and bio-based plastics[25].

2.7.2 Biobased material

The term biobased refers to a product that is created entirely or partially from basic renewable resources. On the other hand, renewable raw resources are organic resources derived from agricultural and forestry output and utilized for purposes other than food and feed.

Experts examine two potential techniques for identifying biobased content. The first, just the carbon content of the product is taken into account, with the biobased component stated as a proportion of total carbon. The alternative method compares non-biobased material to the overall biobased mass fraction, including biobased oxygen, hydrogen, and nitrogen[27].

2.7.3 Modified natural polymers

Thermoplastic starch

Destructing starch granules make TPS by an extrusion method. The starch must be exposed to sufficient mechanical force and heat in the presence of so-called plasticisers or softening chemicals to be destroyed, i.e. to lose its granular structure and crystallinity. Water, glycerine, and sorbitol are examples of suitable plasticizers[27].

Cellulose-based plastics

Cellulose regenerates cellulose that has been chemically dissolved and rebuilt into fibres or films. Viscose, viscose silk, rayon, lyocell or artificial silk, and a few more fibres and textiles are the most well-known members of this category of materials. In 2018, cellulose produced fibres had a world share of 9.2% (6.8 million tons).

In terms of industrial applications, cellulose derivatives are crucial. There are two types of cellulose ethers:

Cellulose ethers
Cellulose esters

Cellulose was made from 75 percent cellulose nitrate (obtained from nitric acid and cellulose) and 25 percent camphor and is the most significant category of cellulose esters. In essence, cellulose esters are made by esterifying cellulose with organic acids. From a technological standpoint, essential cellulose esters are cellulose acetate (CA), cellulose propionate (CP), and cellulose butyrate (CB), with CA having the highest market importance[27].

Cellulose is the primary ingredient of cell walls in all higher plant life structures. Therefore, it is the most frequent organic mixture and the most common polysaccharide (multi-sugar). Cellulose consists of many hundred glucose molecules (in a glucosidic bond) or cellobiose pieces. The cellulose molecules join together with more powerful compositions that often have a static function as tear-resistant fibres in plants [28].

Protein-based plastics

Another combination of bioplastics that originated from animal or plant proteins is casein. Casein is one of the bioplastics produced from animal protein and was a meaningful player at the plastics' lifetime commencement. The primary casein, taken from skimmed milk and plasticized, is processed to build a cross-linked plastic by formaldehyde and water elimination to produce a casein plastic. A different kind of protein-based plastic is gelatine. In addition to the well-known purposes, it is used as a nutritional supplement and as a necessary agent or capsule for pharmaceutical pills. In most cases, gelatine is manufactured from collagen[28].

Polyhydroxy alkenoates

Starch and other substances that supply carbonates can also be switched into bioplastics by fermentation and the activity of micro-organisms. Examples are PHA or polyhydroxy fatty acids, a group of polyesters. Appropriate bacteria can create these molecules as intracellular resources. By "farming" this type of bacteria and maintaining them on sugar or starch, or at times on plant oils or other nutrients rich in carbonates, it is possible to receive PHS's on an industrial order. The family of polyhydroxyalkanoates includes PHB and polyhydroxy valerate (PHV)[28].

2.7.4 Synthesised biobased polymers

Biobased polyesters Polylactic acid (PLA)

PLA is the most well-known bioplastic on the market today. PLA is made up of lactic acid and is produced primarily through the fermentation of sugar or starch with the help of microorganisms. The United States began production of the world's first large PLA generation unit, with a capacity of 140,000 tonnes per year. PLA manufacturing plants can now be found in the Netherlands, Japan, and China.[28].

Polyethylene terephthalate (PET)

PET, from the second half of the 20th century, has been a mass-produced plastic. Real growth began in 1975 with its application by the big North American soft drinks companies to make “easy-to-grip” and “unbreakable” beverage bottles.

PET is a thermoplastic polyester manufactured by polycondensation of mono ethylene glycol and terephthalic acid dimethyl terephthalate. Since 2010 the primary beverage bottles have been provided partially from biobased PET [29]. Terephthalic acid as the second component of PET adopting renewable resources was too extensive and costly. However, there are straightforward ways to the economical creation of biobased terephthalic acid [29].

2.8 Polyhydroxy alkenoates

2.8.1 Advantage and disadvantage

Small pore size with high recycling potential, high volume to surface ratio, biodegradability, and biocompatibility are vital advantages of PHA. PHA has lately attracted interest due to various beneficial qualities such as ease of processing, ultraviolet (UV) resistance, and water insolubility, among others.

These beneficial features make them a viable replacement for non-biodegradable bio-based materials such as polyethylene terephthalate, bio-polyamide, and other non-biodegradable bio-based materials used in agriculture, food, and medicine[30].

Despite their commercial potential, most PHA-based biomaterials, particularly crystalline short chain length PHA with higher monomeric compositions of 3-hydroxybutyric acid such as poly (3-hydroxybutyrate) (PHB), are highly hydrophobic, have a low heat distortion temperature, and have poor gas barrier properties. Because of these drawbacks, they degrade slowly.Compared to other bio-based polymers, the cost of producing PHA is substantially higher. As a result, these biopolymers fall short of meeting industrial expectations[31].

2.8.2 Modification

By changing the biopolymers, several ways are designed to improve the PHA's physical and chemical characteristics to overcome these drawbacks. PHAs are changed physically, chemically, or biologically to broaden their applicability in diverse industries. Chemically modified PHA with folic acid, for example, might be an effective cancer medication carrier. The changes to PHA can also speed up the breakdown of these polymers[32].

A PHA's structure can be changed physically, chemically, or biologically to create a new polymer with predictable function and molecular weight changes. These alterations may change their mechanical capabilities, amphiphilic character, surface structure, and degradation rate to meet the demands of their various uses[33].

2.8.3 Structure and properties of PHA

The monomer units of (R)-hydroxy fatty acid make up a PHA molecule. Figure 2.3 depicts the fundamental structure of PHA. Ester bonds bind the monomeric units to one another. A side chain R group, such as a saturated alkyl group or an unsaturated alkyl group, is present in each monomeric unit[34].

PHAs are classified into distinct categories based on the length of their structural chains:

- Short-chain length PHA: They are made up of monomeric 3–5 carbon building pieces.
- Medium-chain length PHA: They are made up of monomeric units of 6–14 carbon atoms.
- Long-chain length PHA: They are made up of monomer building units with 15 or more carbons[35, 36].

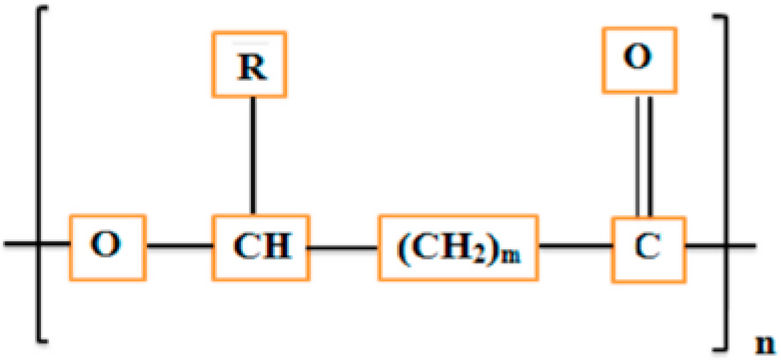


Figure 2.3 PHA structure[37]

PHA shares many of the same qualities as petroleum-based polymers. Insolubility in water, UV resistance, rigidity, high degree of polymerization, biodegradability, and thermoplasticity are some of the physical features of PHA[37].

Table2.1 Modified PHA properties[38].

Properties	**Method**	**Unit**	**Value**
Optical properties			Opaque
Melt temperature	ISO 527	°C	170 – 176
Tensile strength at yield	ISO 527	MPa	41
Tensile elongation at yield	ISO 527	%	2.7
Tensile maximal strength	ISO 527	MPa	40
Tensile elongation at maximal strength	ISO 527	%	2.7
Tensile strength at break	ISO 527	MPa	5200
Young's Modulus	ISO 527	MPa	7

2.8.4 Applications of PHA

The biodegradable nature of polyhydroxyalkanoates and other qualities like high-temperature stability, reduced surface porosity, increased toughness, elasticity, and so on lead to their use in a variety of disciplines such as medicine and agriculture. The following are some PHA applications[37].

Medical applications

- Drug delivery: The main purpose of the drug delivery system is to increase the efficacy of the pharmaceuticals by delivering them in a controlled and targeted way. As a result of their natural origins, PHA is employed as a raw material for producing tablets, nanoparticles, and other products [39].
- Tissue engineering: PHA, with just a few alterations, makes a significant contribution to tissue engineering. PHA may be utilized to make scaffolds that provide nourishment to cells and have better mechanical strength. Pins, films, sutures, and other scaffolding materials are available[40].
- Dressings: Wound dressing is done with the use of PHA-based volatile solutions. To avoid contamination, these materials form a thin layer over the wound. Swabs, fleece, lint, and other dressings made of nonwoven fibrous material can be used as swabs, fleece, and lint. Soft-tissue regeneration, nerve restoration, cardiovascular therapies, and other medical uses of these polymers are just a few[40].
- Biomedical Implant Materials: Only some PHA, including PHB, and Poly(3-hydroxybutyrate-co-3 hydroxy valerate (PHBV) are available in adequate amounts for purpose research[41]. Therefore, much of the application research, including tissue engineering and managed drug release, is based on the PHA mentioned above. PHA and its composites have been utilized to enhance sutures, suture fasteners, meniscus repair devices, rivets, tacks, staples, bone plates and

bone plating systems, surgical mesh, slings, orthopaedic pins, and adhesion barriers during the last 20 years[42].

Agricultural applications

PHA has a wide range of applications in agriculture. PHA improves the nutritional quality and shelf life of plants under severe environments. One of the specialists' uses in agriculture is the controlled discharge of herbicides and insecticides. PHA can be used to make biodegradable plastic sheets for crop protection, seed encapsulation, fertilizer encapsulation, and other agricultural applications[43].

Market applications

PHA bioplastics have features that make them acceptable substitutes for many current applications covered by petroleum-based plastics, opening up a vast market. PHA's adaptability allows for a wide range of applications in the industry. PHA is mainly used in packaging and food service due to its degradability, non-solubility, non-permeability, and flexibility [44]. PHA is a kind of packaging film that is used to make shopping bags, paper coatings, cups, diapers, and carpets, among other things. Many items, such as PHA-coated boxes, paper, sheets, and boards, are now available[37].The figure 2.4 represents some applications as a summary and the structure of PHA.

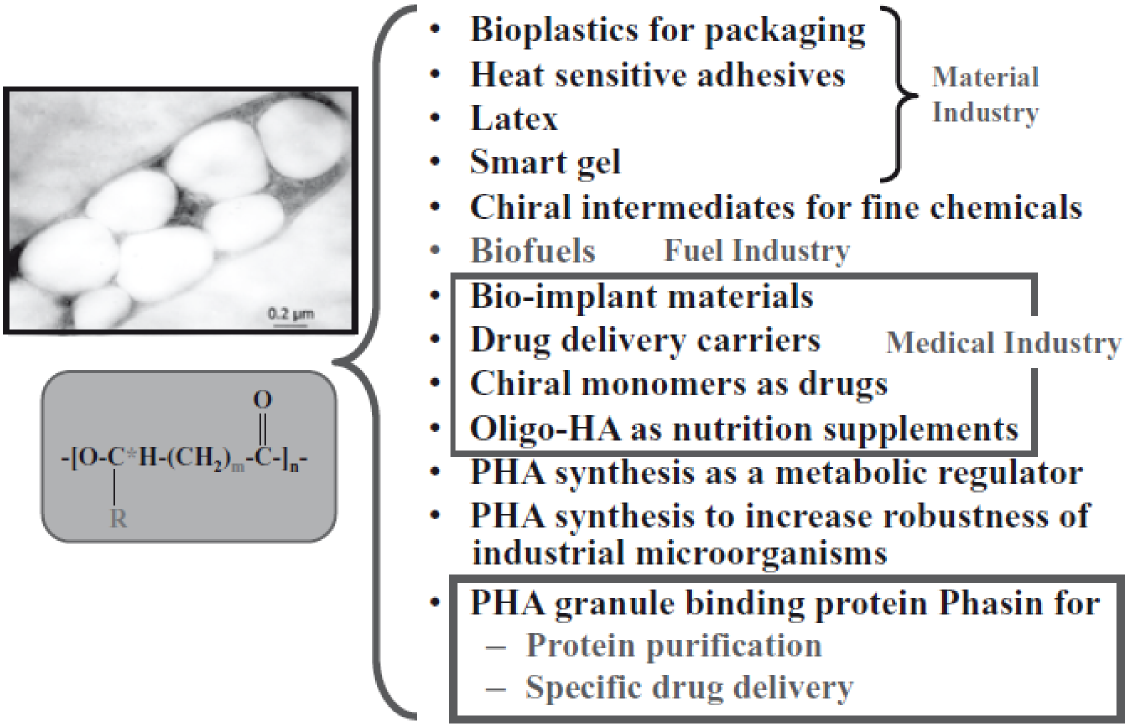


Figure 2.4. application of Polyhydroxyalkanoates [45].

2.8.5 Cost-cutting strategies for PHA manufacture

PHA's high cost is due to the substrates, which account for 30–40% of overall manufacturing costs. PHA can be made from inexpensive materials such as sucrose, glucose, and lignin[46].

2.8.6 Biodegradability

The biodegradation of bacterial plastics advances actively under various soil conditions according to their different characteristics. PHA is one of the natural plastics. Microorganisms that can create and store PHA under nutrient-limited conditions can usually degrade and metabolize when carbon or energy origin is limited[47]. The degradable PHA monomers are water-soluble and small enough to diffuse through the cell wall passively. They can furthermore be metabolized by b-oxidation and the tricarboxylic acid cycle of several organisms to generate carbon dioxide and water under aerobic circumstances [48].

2.8.7 Future perspective

The evolution of PHA into a category of the bulk chemical industry will address at least three problems:

- A shortage of petroleum for plastic substances,
- Mitigation of CO_2 emissions
- Environmental protection

It is similar to the sustainable development of the chemical and material industries. The recently developed PHA-based biofuels open up a new development area that avoids discussions on food versus fuel. However, much more effort is needed to decrease PHA production costs so that PHA-based biofuel could be added to the existing bio-based fuels, including ethanol, propanol, butanol, biodiesel, hydrogen, and methane gas High-value-added PHA demands should be developed simultaneously, especially the implant biomaterials that have begun to be acclaimed by the food and drug administration(FDA)[45].

2.9 Polybutylene Succinate

Showa-Denko manufactures it under the BionolleTM brand name, while Mitsubishi Chemical Corporation manufactures it under the GS PlaTM brand name. Mulching films, biodegradable bags, nonwoven sheets and textiles, catering items, and foams are some of its most common applications[49]. This bioplastic manufacturing accounts for between 25% and 30% of the entire plastics market worldwide[50].

The monomers used in the PBS synthesis are succinic acid (SA) and 1,4-butanediol (BD), both easily accessible on the market and may be derived from fossil resources. Both SA and BD may be created not just from oil but also through fermentation. Succinic acid is produced by microorganisms fermenting renewable feedstocks like glucose and starch. Corn-derived glucose is fermented to succinic acid, which is then purified by electrodialysis before being catalytically reduced to BD[51]. Several microorganisms have been screened and tested for the generation of succinic acid by biotechnological techniques in recent years, with promising results. The SA produced in this way can then be hydrogenated to produce BD. This would result in a fully bio-based PBS[49].

2.9.1 Properties and characteristics

PBS is a commercially available biodegradable polymer with some appealing characteristics, including strong mechanical properties, melt processing, biodegradability, and compostability[52]. When mixed with other materials, PBS is very easy to handle and process. PBS is stronger but somewhat more brittle than other plastics since it is manufactured from petroleum-based components, and has high heat stability and mechanical characteristics[53].

PBS is a highly crystalline polyester with a melting point of 115 degrees Celsius and a heat distortion temperature of 97 degrees Celsius. Unoriented specimens have tensile yield strength of 30–35 MPa. PBS has Young's modulus of 300–500 MPa, depending on crystallinity, low manufacturing cost, and mechanical qualities similar to polypropylene. PBS is projected to be a potential alternative to conventional plastics[51, 54].

- Physical Properties: Due to the inclusion of other materials like reinforcement, additive, or filler, the physical characteristics of PBS were somewhat altered. Many studies that employed PBS found that the physical characteristics of the composite improved. The brittleness of PBS can be addressed by adding a plasticizer, such as glycerol, which can also enhance the elongation of the PBS for future use[55].

- Mechanical Properties: When it comes to assessing the industrial application of freshly synthesized polymers, the mechanical characteristics of PBS are the most critical consideration. The mechanical characteristics of the PBS copolymer were altered when the block length was reduced to lessen the elastic modulus, tension at break and increase the elongation at break. Increased PBS content in blends with other polymers has been shown to cause a reduction in Young's modulus and tensile strength, resulting in strain hardening[56].

Table2.2 Modified PBS properties[38].

Properties	**Method**	**Unit**	**Value**
Biobased carbon content	ASTM D6866	%	51
Melt temperature		°C	115
Optical properties			Translucent
Tensile maximal strength	ISO 527	MPa	40
Tensile elongation at maximal strength	ISO 527	%	22
Tensile strength at break	ISO 527	MPa	30
Young's Modulus	ISO 527	MPa	720

2.9.2 Advantage and disadvantage

PBS is a commercially available biodegradable aliphatic polyester that is susceptible to microbial attack and conversion to carbon dioxide and water due to the fragile ester linkages found in its major chains. Due to its superior melt processability and chemical resistance, PBS has the potential to be used in a variety of circumstances, including food packaging, personal care, cosmetics, medical devices, and automotive components[57].Compared to the fossil counterpart, the use of SA and BD from renewable resources decreases PBS carbon footprint, with greenhouse gas emissions falling by 50% to 80%[58].

Due to the high expense of PBS, several researchers have substituted alternative materials, such as natural fibers, for a part of it. Oil palm fibre is utilized as a reinforcing element in PBS-based products to reduce the amount of PBS utilized and manufacture costs. Reinforcement materials also help to increase the material's tensile strength. Furthermore, combining biodegradable polymers lowers the material's total cost while simultaneously altering the required attributes and degradation rates[59].

2.9.3 Structure

PBS possesses physical qualities that are similar to polyethylene terephthalate, high elongation capabilities, and the ability to be used in various applications. When PBS is exposed to water, an ester group in its chemical structure degrades into low molecular weight polymers. The rate of PBS depletion increases as the temperature rises. The repeat unit's chemical structure is–[O–(CH2)m–O–CO–(CH2)n–CO]N, as shown in Figure 1.5 m and n were discovered to be 4 and 2, respectively.

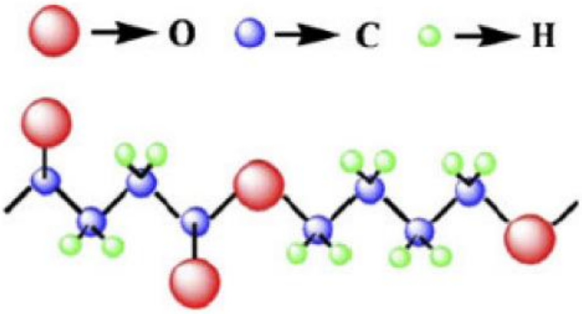
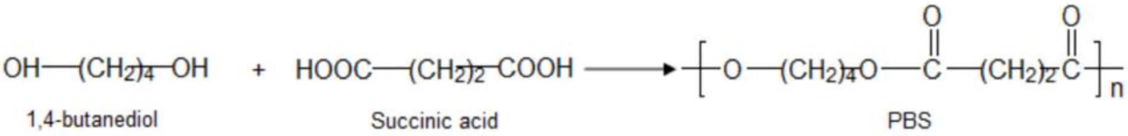


Figure 2.5 Polybutylene succinate's chemical structure[60].

2.9.4 Synthesis

PBS may be made in various methods, such as by polycondensing SA and BD, with the monomers coming from either fossil or renewable sources. This synthesis technique has the advantage of improving thermal, mechanical, and thermoplastic processability. Catalytic hydrogenation of maleic acid or its anhydrite is the most widely used way of producing petrochemical succinic acid[51].



$$OH-(CH_2)_4-OH + HOOC-(CH_2)_2-COOH \longrightarrow \left[O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}\right]_n$$

Figure 2.6 Synthesis of PBS[60].

2.9.5 Application

PBS is suited for extrusion, injection molding, thermoforming, fibre spinning, and film blowing and has a wide processing/temperature window. PBS is utilized in various areas, including electronics, food packaging, agricultural mulch films, hygiene goods, thanks to these traditional processing techniques. Because of its high thermo-mechanical characteristics, biocompatibility, and biodegradability, PBS has shown to be a promising material for both biomedical and environmental applications, such as controlled drug release systems and tissue engineering supports[58].

- Biomedical: PBS has much potential for generating stem cells in the bone marrow. PBS can be used to stimulate new tissue growth in bone tissue engineering. However, because PBS is susceptible to bacterial infection, developing tissue engineering presents certain obstacles[49].
- Food Packaging: PBS is a biodegradable substance used to safeguard the environment and food quality in food packaging. Because of its great flexibility, superior durability, high elongation at break, and good biodegradability, PBS is ideal for food packaging. Its applications are restricted because of its low molecular weight, low melting temperature, and low stiffness and power. Blending PBS with PLA increased the substance's characteristics for use in food packaging[61, 62].

2.9.6 Biodegradation

The biodegradability of plastics is strongly linked to their composition, and the chemical and physical features of plastics impact the biodegradation process. The surface conditions of polymers, such as surface area, hydrophilic and hydrophobic characteristics, play a strong impact in the biodegradation process. PBS, on the other hand, is more expensive than petrochemical-based plastics. The cost of processing, which includes electrochemical processing and the condensation of SA and BD, is higher[49].

The molecular weight, water permeability, pH, temperature, purity, crystallinity, and catalytically active additions, including bacteria, enzymes, or inorganic fillers, all affect PBS breakdown[63].

PBS and its copolymers are degraded more quickly by enzymes than by hydrolysis at neutral PH. In lipase solution, soil burial, water, activated sludge, and compost, PBS and its copolymers are biodegradable. PBS copolymer biodegradation rates vary depending on the chemical structure, condensed state structures, and biodegradation environment[51]. The degree of crystallinity and wettability of a material can have a significant impact on its biodegradation rate. The lower the hydrolytic and enzymatic degradation rate, the higher the degree of crystallinity since the less ordered and packed amorphous domains are more easily attacked[49]. PBS's biodegradability, which allows it to decompose at high rates in a short amount of time, is an appealing feature for single-use food packaging as well[64].

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PBS outperforms other aliphatic polyesters regarding biodegradability, thermal characteristics, melt processability, and chemical resistance. It is a potential plastic material in the industry because of these characteristics. It has been used to make injection-moulded objects, fibres, and films[65].

2.9.7 Economic challenges of PBS

PBS production has the potential to have a significant influence on the global plastic output. As a result, the technological and economic challenges must be addressed before successfully replacing present synthetic plastics and serving as a future benchmark. The cost and availability of the product should be the most critical factors to evaluate. PBS must first meet its economic and technological goals in the lab before being scaled up to an industrial scale with defined parameters throughout the entire system. Aside from the costs, the revenues generated by the process will determine whether the industry makes a profit or loses money. To make a profit, the unit price of the plastic sold must be higher than the unit price of manufacture. As a result, it is contingent on the number of plastics sold in a given year. Aside from that, in order to make stiff items out of PBS, the material requires specific modification and additives that can overcome PBS's fragility.

To take full advantage of biodegradable plastics, they must be adopted on a large enough scale to make a difference. Improper or fragmented policies and regulations should be recognized, revised, or eliminated first[66].

Temperatures in landfills have been reported to reach about 100°C, accelerating decomposition rates if there is enough moisture and oxygen available for the thermal-oxidative and hydrolytic processes. The disorderliness in the polymeric structure caused by the rise in atom kinetic energy leads to molecular scission of the components of the long-chain backbones[67].

2.10 Degradation mechanisms

The polymer matrix's degradation mechanism is described by changes in polymer formation caused by chemical, physical or biological effects, which commence chaining cut and the development of new functional groups. These changes may be displayed in the optical, mechanical, and electrical features [68].

Degradation of polymers may be developed by different mechanisms started by environmental factors and their combination. According to initiators, two ways of degradation are founded:

- Abiotic
- Biotic.

2.10.1 Abiotic degradation

Two determinants may cause abiotic degradation:

- Physical
- Chemical

Nevertheless, these processes are often in close synergy, and only one factor occurs. Several environmental factors can begin the degradation, e.g., moisture, light, temperature, and pH. Generally, abiotic degradation is based on deformity without microorganisms present.

Physical degradation

Physical mechanisms of abiotic degradation are considered processes where the decomposition is based on an action causing only physical changes in the polymer composition, such as melting, dissolution, swelling. Physical transitions can be induced by water, mechanical charging (compression, tension, shear force), or rising temperature. The degradation may generally lead to reduced end-use properties of products shape changes, surface erosion, weight loss[69].

Chemical degradation

The mechanism of chemical degradation is based on processes where chemical changes in the polymer structure occur. These changes can be characterized by the reduction of Molecular weight and conversion of chemical composition due to chain cut. Chemical degradation may be triggered by exposure to electromagnetic irradiation, heat, and atmospheric pattern of oxygen and particular chemicals. Nevertheless, the effects of radiation, heat, and oxygen are often in close synergy. Hence, the degradation by radiation and heat often happens with oxygen assistance, and photooxidation is suggested to be the principal mechanism throughout the degradations.

2.10.2 Biotic degradation

Biodegradation is described as the decomposition of organic matters by the progress of microorganisms. Mainly two types of microorganisms engage in the degradation of polymers:

- bacteria
- fungi

Their progress leads to polymer mineralization with main end-products, including new biomass, water, carbon dioxide, and methane[70].

Fungi have the potential to play a significant role in the biodegradation of plastics and other polymeric materials because they can generate extracellular enzymes including lignin peroxidase, manganese peroxidase, versatile peroxidase, and multicopper oxidase laccase, which breakdown lignin and convert it to CO_2 and H_2O[5].

Aerobic degradation

Aerobic biodegradation regularly expresses composting within industrial composting conditions. In a high-oxygen environment (not less than 6%) [71], microorganisms employ the polymer as a carbon and energy source and deliver carbon dioxide and water as the main degradation by-products in addition to the remaining part, which is described as compost. Industrially composting is conducted in a warm (approximately 60–70°C) and moist (approximately 60%) environment under controlled conditions(pH 8.5) [25]:

$$\text{Organic matter} + S + O2 = CO2 + H2O + NO2 + SO2 + \text{Heat} + \text{Compost}[25] \qquad (2.1)$$

2.10.3 Mechanism of microbial plastic degradation

Microbes use biochemical transformation to break down complex substances into simpler forms. Changes in the physical properties of plastic polymers, particularly molecular weight reduction, mechanical strength loss, and changes in plastic surface properties, are all signs of biodegradation[72]. The conversion of resistant wastes to non-toxic lower molecular mass molecules that can be recycled into the biogeochemical cycle is the goal of plastic biodegradation. Biodeterioration, biofragmentation, assimilation, and mineralisation are the different biochemical degradative routes involved in plastic biodegradation, and all of these processes are carried out via diverse enzyme activity and bond cleavage[73].

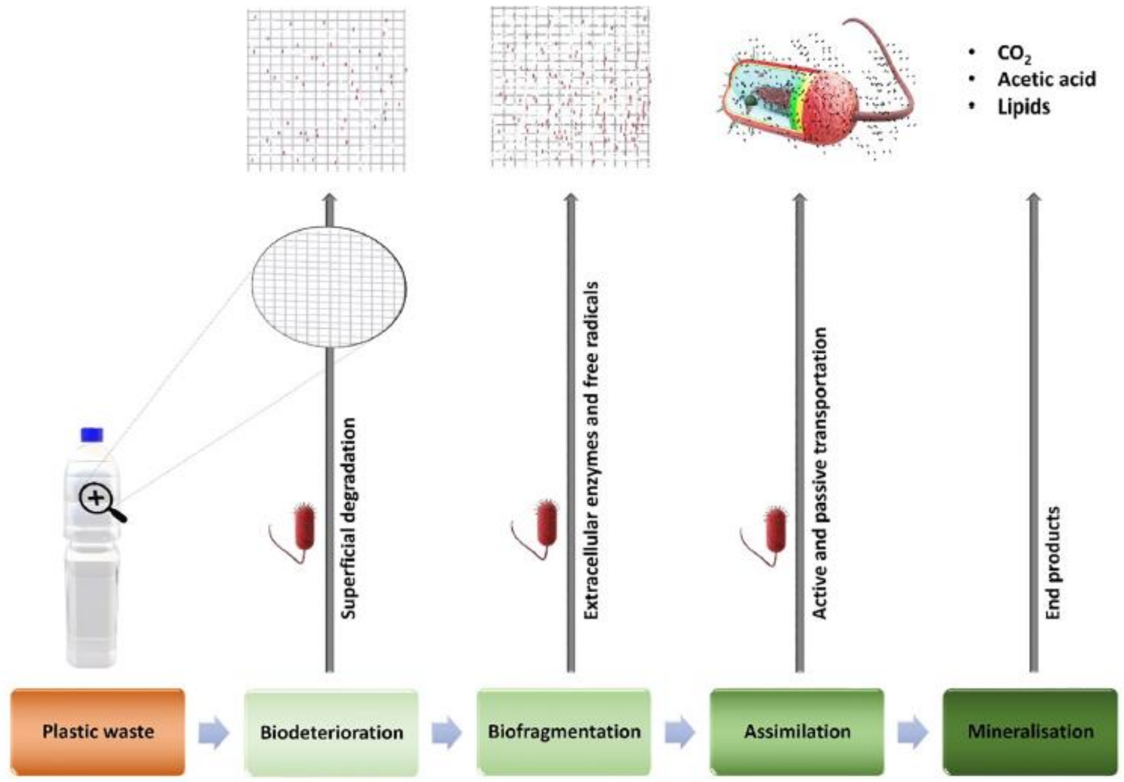

Figure 1.7 Steps in the biodegradation of plastic[74].

Biodeterioration

The chemical and physical actions of bacteria, or other biological agents, produce biodeterioration, which results in the superficial breakdown of the plastic polymer and changes in its chemical, mechanical, and physical properties[74].

Bio fragmentation

The bio fragmentation process is thought to feature two main reactions:

- polymer molecular weight reduction
- oxidation of lower weight molecules

These reactions are required to allow microbial enzymatic systems to target lower molecular weight molecules.

Assimilation

At the assimilation stage, the lower molecular weight molecules formed during bio fragmentation are carried into the cytoplasm of the microorganism.

Mineralization

Once these plastic derivatives have been successfully delivered into the cells, they are subjected to a series of enzymatic reactions that result in their total breakdown into oxidized metabolites such as CO_2, nitrogen gas(N_2), CH_4, and H_2O. The mineralisation process can be aerobic or anaerobic in origin[74].

2.11 Factors impacting plastic biodegradation by microbes

Microbial biodegradation of plastic polymers in nature and under controlled settings is influenced by several elements that can be classified into three categories:

- Polymer properties
- Environmental factors
- Chemical factors

These variables essentially assist subsequent microbial action by increasing surface area, hydrophilicity, and molecular weight reduction[74].

2.11.1 Polymer characteristics

As polymers must be carried across the cellular membrane to be metabolized, the rate of microbial breakdown has been seen to decrease with increasing molecular weight. As a result, smaller polymer units such as monomers, dimers, and oligomers are more easily destroyed[75]. The morphology of the polymer, which involves the degree of branching, crystallinity, and physical form, has a significant impact on the rate of degradation of plastic polymers. The microbial breakdown is less effective in plastic polymers with a higher fraction of side chains and enhanced branching[76].

The rate of microbial breakdown is highly influenced by the melting temperature of the specific polymer. It has been discovered that the temperature and biodegradation rates have an inverse connection[75].

2.11.2 Environmental factors

In a dry atmosphere, humid air, a landfill, compost, a sea environment, the rate of microbial action will differ. Bond scission has been discovered to be enhanced by factors like light, heat, moisture, pH, and biological activity[77].

The presence of moisture in the environment will aid in the shrinking of plastic polymers by increasing their solubility and the rate of hydrolysis. These, in turn, will lead to more chain scission and, finally, increased microbial action sites on polymer chains for improved biodegradation. Degradation in the marine environment is substantially higher than on land, even when all other conditions are held equal[22, 78].

2.11.3 Chemical reagents and additives

By influencing the functional groups, chemical reagents in polymeric structures or the surrounding environment can either activate, stop, or promote the biodegradative process[79]. Additives have recently been applied to polymers to act as flame retardants, and pro-degradants, among other things. Some additives have been demonstrated in studies to reduce plastic recalcitrance during future reprocessing or degradation[80].

Furthermore, microbial action on plastics is affected by an alternative and simpler carbon source in the environment.The degradation of a polyethylene derivative increased by 80%, when glucose was removed from the media. The addition of biodegradable additives such as starch and palmitic acid, which served as a nutrient source for microbes, improved biodegradation[81].

3 Methodology

3.1 ISO14855-1

To measure the biodegradability of bioplastic, ISO 14855-1 was applied. This method is designed to simulate normal aerobic composting conditions. The primary method specified in this part of ISO 14855 standard uses a solid-phase respirometric test system with mature compost as the foundation, the origin of nutrients, and an inoculum mellow in thermophilic microorganisms.

3.2 Scope

The standard ISO 14855 specifies a method for determining the final aerobic biodegradability of plastics based on organic mixtures under recommended composting conditions by measuring the amount of carbon dioxide produced and the plastic's progressive disintegration at the end of the test. For the organic component of solid mixed municipal garbage, this approach simulates standard aerobic composting periods. An inoculum made from compost is used to test the material. Temperature, aeration, and humidity are all carefully monitored and managed during the composting process. The goal of the test technique is to determine the proportion of carbon in the test material converted to grown carbon dioxide, as well as the percentage of conversion.

3.3 Principal

Carbon dioxide, water, and new microbial cellular components are the ultimate biodegradation products during aerobic biodegradation of the test material. To estimate the total carbon dioxide production, the carbon dioxide produced is constantly monitored or measured at regular intervals in test and empty containers. The ratio of carbon dioxide generated by the test substance to the maximum theoretical quantity of carbon dioxide produced by the test material determines the percentage of biodegradation. The measured whole organic carbon (TOC) concentration determines the maximum quantity of carbon dioxide produced.

According to Figure 3.1, the air is supplied from line 1 to solution 6, sodium hydroxide (NaOH), to remove CO_2 from the air; since the solution of NaOH content water, the air will be humidified too. The air from line 2 blows to the bottom of the sample and aerate the compost then it discharges from line 3 which includes gas like carbon dioxide oxygen nitrogen and biogas, the gas will experience a moisture trap in another bottle and then flows to carbon dioxide trap solution which is potassium hydroxide (KOH) solution in bottle 9. The CO_2 percentage was measured from the determination sample exhaust, and it was less than 0.1%; however, the feed gas had almost 2.7% of carbon dioxide, which shows the high efficiency of this process.

Incubation may be in the gloom or diffused light, in a room reserved at a steady temperature of 58 °C ± 2 °C and free from vapours inhibitory to microorganisms.

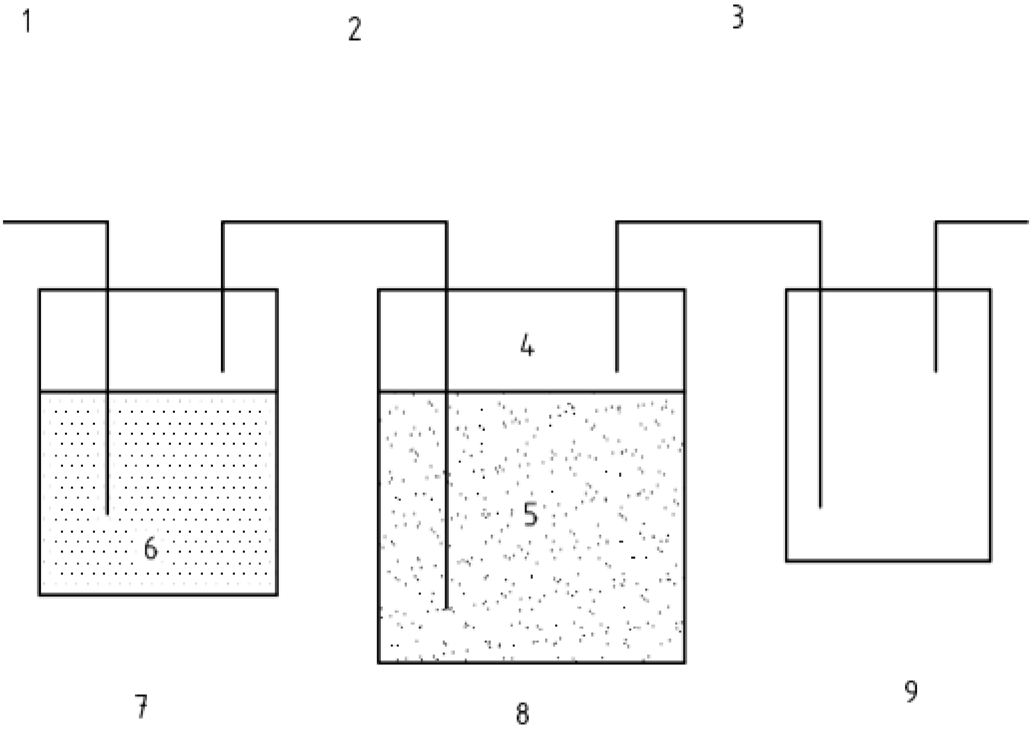

Figure 3.1. Layout of test system[82].

3.4 Equipment and materials

3.4.1 Composting vessel,air supply,bottles,tube network

A glass flask containing compost with plastic samples and a tube to feed air into compost from the bottom of the flask and an existing on the cap discharges the gas to the second container to remove moisture from the gas.

One air pump was used to blow air into two vessels to feed the compost with air and maintain the oxygen percentage in the vessel over 6%.

Three kinds of bottle were applied for each test sample to run this process: first, one with NaOH solution to remove CO_2 from the air, second one from sample to remove moisture from gas, a third one to determine CO_2 from gas, including KOH solution.

To connect air supply to bottle series, from air supply to air CO_2 removal, then compost sample and moisture removal and at last CO_2 determination of gas sample.

3.4.2 Heating bath

A heating bath is needed to maintain a steady temperature inside the composting containers.Selecta BATH "PRECISTERM" 20l was chosen for it. This machine has a capacity of 20l, can heat up to 110 °C. Moreover, it is corrosion-resistant, has a control panel, and can place 6 composting containers inside.

Figure 2.2. Heating bath Selecta "PRECISTERM" 20l [83].

3.4.3 Gas detection device

Gas Analyzer GFM 406 was chosen to measure carbon dioxide and oxygen from the upcoming air and gas outlet from the CO_2 determination bottle. The equipment can measure up to 6 gasses, including O_2, CO, H_2S, H_2, CH_4, and hydrocarbons.

Figure 2.3. Gas Analyzer GFM 406[84].

3.4.4 Muffle furnace, balance,PH meter

This equipment is used to evaporate the water content of compost at 105 °C to find total dry solids and on the next round at 550 °C to measure total volatile solids.

Balance was used to measure the weight of compost samples and cups, this balance has been applied, and a PH meter was used to measure the PH level of the compost sample during the process. The PH should be between 7 up to 9.

3.4.5 Small flask, Pipette, Methyl and phenol phthalein(indicators)

Flasks were used to take samples from CO_2 determination bottles into 3 flasks for titration, and the pipette was applied to take out a sample from determination CO_2 bottles for titration. Indicators were used to identify the CO_2 determination solution PH when it reaches 7 and 4.

3.5 Procedure

3.5.1 Preparation of inoculum

The inoculum should be well-aerated humus from an aerobic composting plant that is working well. There should be no vast inactive things in the inoculum, such as glass, stones, or metal bits. The compost was sieved on a screen of about 0,5 cm to 1 cm. After that, the total dry solids and the inoculum's volatile solids content was measured by using a muffle furnace. The total dry solids content shall be between 50 % and 55 % of the wet solids, and the volatile solids no more than about 15 % of the wet or 30 % of the dry solids. The water content was controlled by adding water to mixture to adjust moisture.

3.5.2 Start-up of the test

Set up was done by these vessels:

a) three vessels for the test material(plastic with compost)
b) three vessels for the reference material(cellulose with compost)

c) three vessels for the blank(compost)

The inoculum's dry mass ratio to the dry mass of the test material shall be about 6:1. Inert material is not examined in this association. About three-quarters of the composting vessel's volume with the test mixture to have some free space for shaking the bottles. The volume of bottles is 1 litre and left some free space for shaking the mixture. After filling the bottles with sample and compost, it was connected to the air supply. The CO_2 in the air was removed by NaOH solution supply, and then it was blown to the sample from below of bottles to aerate compost well. Then the gas was discharged from the top of the bottle to the second bottle line to remove the moisture of gas; after that, the gas was discharged to the third bottle line, the CO_2 determination solution, which was filled by 0.2 or .03 molar KOH. The oxygen percentage was under monitor (more than 6%) by the gas analyzer, PH (between 7 to 9), and (30 to 50 percent)moisture content of the sample over time to adjust to as it was desired. Oxygen levels were monitored during the first week closely by measuring at least twice daily.

3.5.3 Incubation period

This period should not last more than six months, the overall first week, on lag phase the amount of CO_2 will not be at low level, after day 8 to 30, the sample enters degradation phase, the higher rate of evolved CO_2 occurs in this period and after that enters plateau phase which the rate is steady.

3.5.4 CO_2 determination

To remove CO_2 from the air, it was passed through a 0.48 mol/l sodium hydroxide (NaOH) solution. Each bioreactor's air was separated and passed via tubes at a flow rate of 30 to 50 mL/min. The CO_2 from the bioreactors was trapped in a 1000ml 0.3 molar KOH solution, and the amount of CO_2 in the solution was quantified using acid–base titration.

When the CO_2 deposit reached a particular level, the KOH solution was changed. To determine the amount of CO_2 in solution, 20 milliliter aliquots of the 1000 ml trapping KOH solution were withdrawn and titrated with 0.2 molar hydrochloric acid (HCl) solution. The CO_2 concentration in the 20 mL solution was compared to the CO_2 concentration in the 1000 mL solution, and the real CO_2 amount was calculated. The

CO_2 trapping reaction was carried as stated in ISO 19679 determination of aerobic biodegradation of non-floating plastic materials in a seawater, and discussed further below:

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \text{[85]} \quad (3.1)$$

The solution, which contains K_2CO_3 and KOH can be titrated with HCL until it becomes neutral as:

$$K_2CO_3 + HCI \rightarrow KHCO_3 + KCI, \text{ at pH 8,5 [82]} \quad (3.2)$$

$$KOH + HCI \rightarrow KCI + H_2O, \text{ at pH 7 [82]} \quad (3.3)$$

$$KHCO_3 + HCI \rightarrow H_2CO_3 + KCL \text{ at pH 4 [82]} \quad (3.4)$$

A few drops of phenolphthalein indicator were first added to the 20 ml KOH aliquot, which was then titrated until the color changed from pink to colorless.K_2CO_3 is transformed to $KHCO_3$ and KCl at this step. Some drops of methyl orange indicator were added next, and the solution was titrated until it went from orange to red. $KHCO_3$ combined with HCl to produce KCl and H_2CO_3.

As a result, the amount of HCl used in the reaction 3.4 can be used to calculate CO_2 concentration in solution using Formula 3.5:

$$\text{mmol } CO_2 = VHCl(4) * [HCl] \quad (3.5)$$

Where

VHCl(4) is the volume of HCl (expressed in ml) consumed in Formula 3.4

[HCI] is the concentration of the HCI (0.2 mol/L)

The amount of CO_2 expressed in mg is finally obtained using Formula 3.6:

$$\text{mg } CO_2 = \text{mmol } CO_2 * 44 \quad (3.6)$$

Where

44 is the molecular weight (g/mol) of CO_2

3.5.5 Calculation of the theoretical amount of CO_2

The theoretical amount of carbon dioxide $ThCO_2$ can be estimated in grams per vessel, which can be generated by the test material using Formula (3.7):

$$ThCO_2 = MTOT * CTOT * (44/12) \text{ [82]} \quad (3.7)$$

Where:
MTOT is the total dry solids, in grams, in the test substance introduced into the composting vessels at the start of the test.

CTOT is the proportion of total organic carbon in the total dry solids in the test substance, in grams per gram; the plastic supplier provides this amount.
12 and 44 are the molecular mass of carbon and the atomic mass of carbon dioxide.

3.5.6 Calculation of the percentage of biodegradation

From the total amounts of carbon dioxide released, determine the percentage biodegradation Dt of the test material for each measurement period using Formula (3.8):

$$D_t = \frac{(CO2)T-(CO2)B}{ThCO2} * 100 \text{ [82]} \tag{3.8}$$

Where:
$(CO_2)_T$ is the cumulative amount of carbon dioxide developed in each composting vessel, including test material, in grams per vessel;
$(CO_2)_B$ is the aggregate amount of carbon dioxide evolved in the blank vessels, in grams per vessel;
$ThCO_2$ is the theoretical amount of carbon dioxide generated by the test material in grams per vessel.

3.5.7 Measurement of dry solids, fixed solids and volatile solids

In the inception, the research material is placed in the cup, which has fixed weight. The dry and fixed solids are defined by the gravimetric method, so it was measured by balance after two heating process at 105°C and 550°C in a muffle furnace.
The dry solids define the content in substances when the moisture content is zero, and all of the water has been evaporated at temperature 105C.

$$X = \frac{A-B}{m} \tag{3.9}$$

X=total dry solid
A=mass of the cup and test material after keeping in the furnace at 105°C
B=mass of the empty cup
m= mass of test material

The fixed solids give a piece of relative knowledge on the mineral composition of the sample; when the dried sample is put at 550°C it lose the volatile compound, which is an indicator of the organic compound.

$$Y=\frac{C-B}{m} \tag{3.10}$$

Y= total fixed solid
C= mass of cup and test material after keeping in the furnace at 550°C
B= mass of the empty cup
m= mass of test material
Volatile solids are calculated as a difference between dry solids and fixed solids:

$$Z=X-Y \tag{3.11}$$

According to the ISO 14855-1, dry solids of the compost should be on the scale from 50% to 55%, and volatile solids have to be more than 15% from the wet substance or 30% from dry material.

4 DATA ANALYSIS

4.1 Modified Polyhydroxyalkanoates

4.1.1 Daily CO_2 generation

The carbon dioxide generated from each sample was determined by titration with hydrogen chloric acid. Table 4.1 shows the amount of total dry solids by material and compost in the mixture in each sample.

Table 4.1 modified PHA and compost content in each sample

Mass(g)	**sample 1**	**sample 2**	**sample 3**
Modified PHA	45.04	45.04	45.04
Compost	272.05	266.85	269.7
Compost / PHA ratio	6.04:1	5.92:1	5.99:1

The figure below(figure 4.1) illustrates the amount of CO_2 evolution in 3 samples during 60 days. Figure 4.1 shows that during the first 10 days of the period, CO_2 evolution is less than the next 30 days, which could be the result of degradation of modified PHA, which has started after 10 days. There are some fluctuations in this figure; for instance, in sample 2 on day 20 there is a sharp rise in CO_2 evolution; there was no gas flow in this sample from day 14 to 17, and it was deposited there for 6 days. The airflow rate and compost composition affected CO_2 generation in samples.

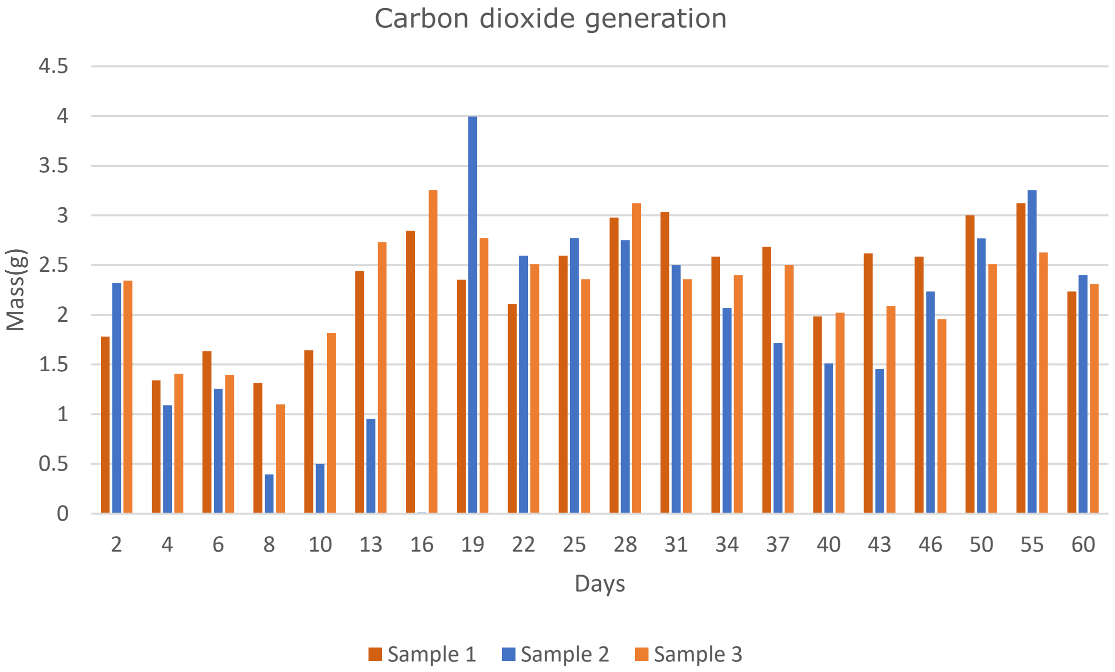

Figure 4.1 Daily carbon dioxide generation of modified PHA

4.1.2 Cumulative CO_2 generation

Figure 4.2 shows the average amount of cumulative CO_2. During the first 10 days of the process, this rate is low, but then it commences to rise, which shows the activity of microorganisms that are consuming compost and plastic materials. After 2 months, the total amount of CO_2 for samples are 46.9,38.5, and 45.6 grams.

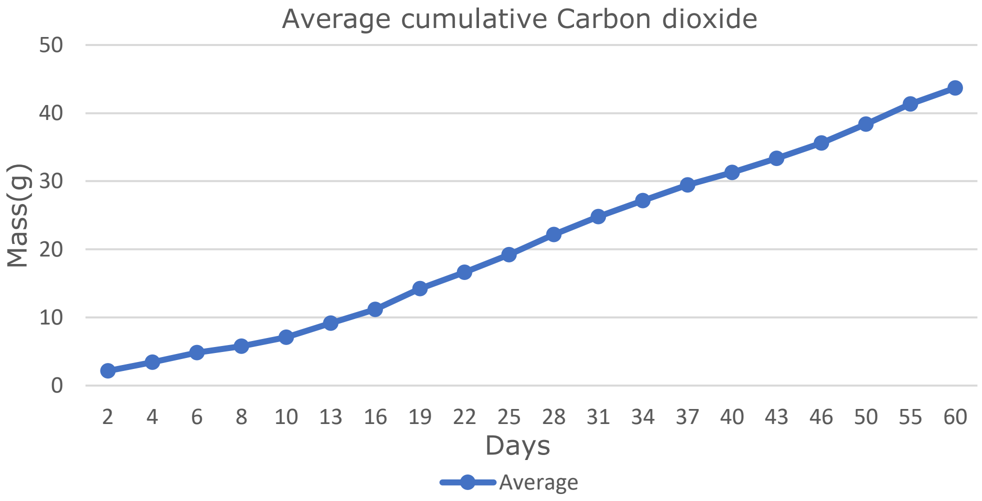

Figure 4.2 Cumulative CO_2 evolution for modified PHA

4.1.3 Biodegradation degree

Figure 4.3 illustrates the average biodegradation degree for modified PHA. After 11 days, the plastic has started to degrade by the microorganism, and after 2 months this degree has reached 23.98%.

Since the compost wasn’t homogeneous, CO_2 generation in blank samples was more than material samples, therefore, the biodegradation degree fell below 0 during first 11 days.After that by plastic degradation this amount has increased.

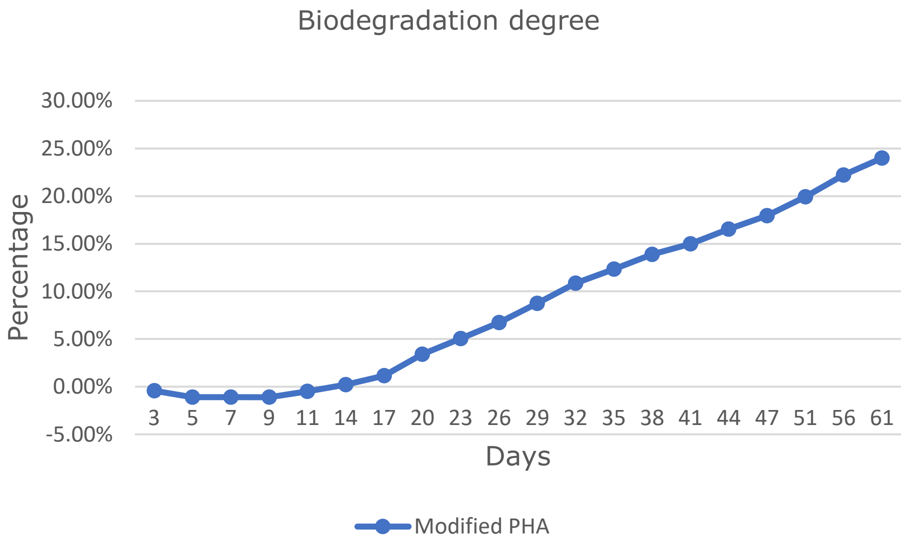

Figure 4.3 Biodegradation degree of modified PHA

4.1.4 Comparison of biodegradation degree between PHA and modified PHA

PHA began to deteriorate after 5 days of induction. After 70 days, the biodegradation curves of PHA tended to level out. The average degree of biodegradation of PHA was 86 percent[86].

In comparison to PHA, the biodegradation degree of modified one has experienced less degradation by 23.98% after 60 days, which shows this type of modified PHA is less likely to degrade in comparison to neat one.

4.2 Modified Polybutylene Succinate

4.2.1 Daily CO_2 generation

Figure 4.4 shows the amount of CO_2 evolution by 3 samples for 2 months. Each sample included a mixture of plastic material and compost. Table 4.2 shows the amount of total dry solid by plastic material and compost composition in each sample.

According to figure 4.4, CO_2 evolution has a steady trend except for sample 3 on day 14. The reason was that the flow rate before that day was too low, and after adjusting the flow rate, CO_2 rate increased sharply to 4.26 g.

Table 4.2 modified PBS and compost content in each sample

Mass(g)	sample 1	sample 2	sample 3
material	44.99	44.99	44.99
compost	270.75	269.25	269.6
Compost / PBS ratio	6.02	5.98	5.99

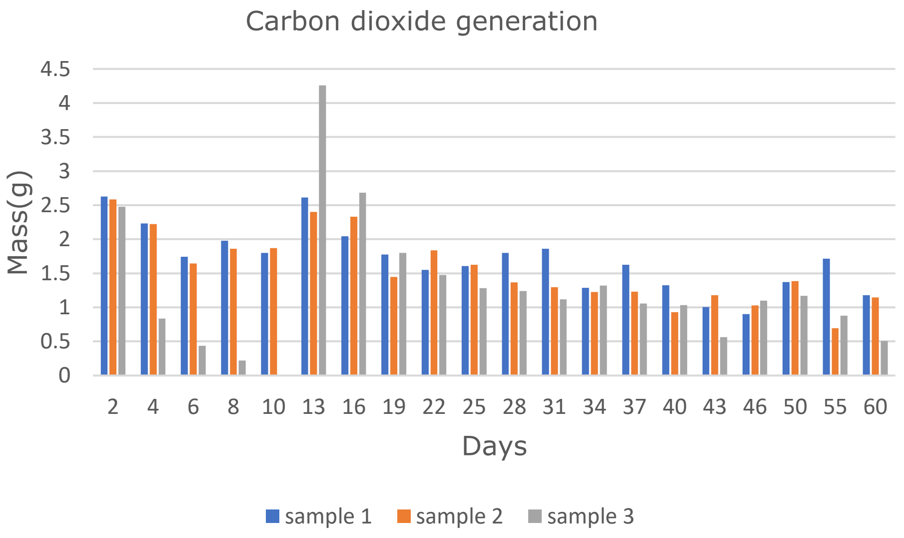

Figure 4.4 Daily carbon dioxide generation of modified PBS

4.2.2 Cumulative CO_2 generation

Figure 4.5 represents the cumulative amount of CO_2 in 3 samples for 2 months. After 10 days, total CO_2 generation initiated to rise, and after 2 months, it reached 34.0,31.3, and 25.4 for 3 separate samples.

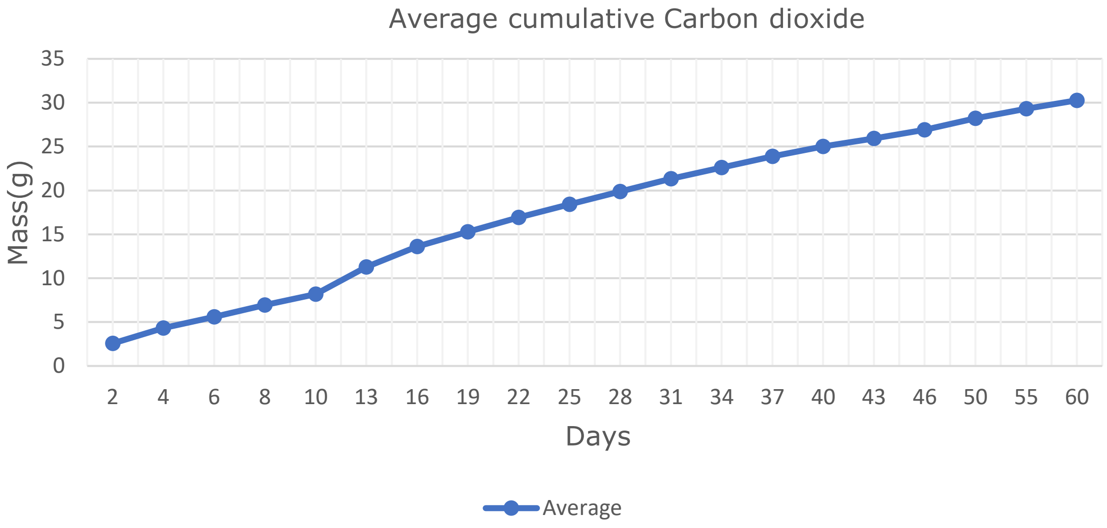

Figure 4.5 Cumulative CO_2 evolution for modified PBS

4.2.3 Biodegradation degree

Figure 4.6 shows the average biodegradation degree for modified PBS. After 9 days, the plastic has started to degrade by the microorganism, and after 2 months this degree has reached 11.18%.

Since the compost wasn't homogeneous, CO_2 generation in blank samples was more than material samples, therefore, the biodegradation degree fell below 0 during first 9 days.After that by plastic degradation this amount has increased.

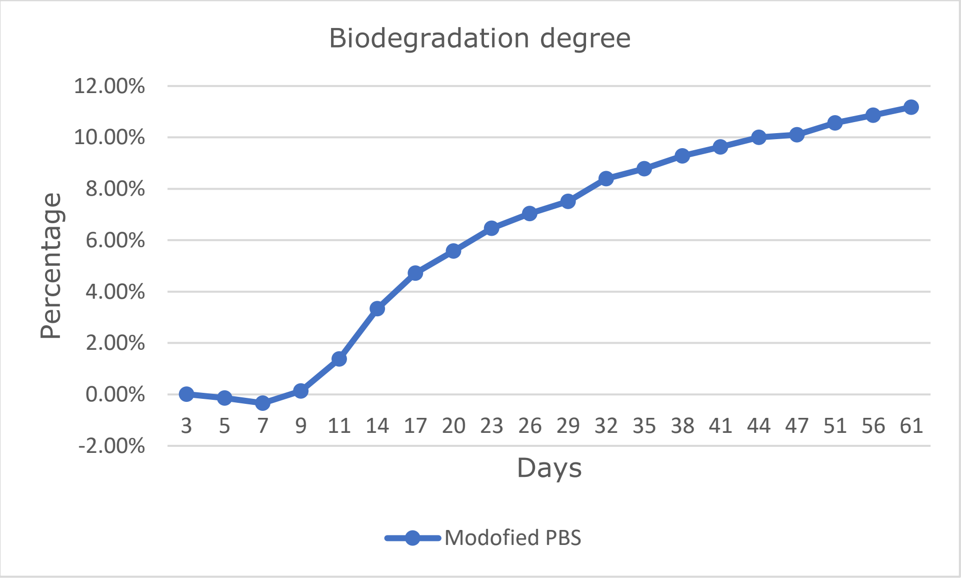

Figure 4.6 Biodegradation degree of modified PBS

4.2.4 Comparison of biodegradation degree between PBS and modified PBS

PBS has entered to degradation phase after 7 days and reached up to 58% of biodegradation in 60 days and after 80 days moved into the plateau phase[87].

In comparison to the project results,modified PBS moved into degradation phase after 8 days and it reached 11.18% of biodegradation by 60 days which shows a sharp decrease in comparison to PBS.

5 CONCLUSIONS

This project was implemented based on ISO1485-1 to determine the biodegradation degree of modified PHA and PBS.

According to the standard, this experiment should continue for 6 months to reach maximum degradation, some conclusions can be done under 60 days period:

1)Under aerobic conditions during 60 days, modified PHA has degraded more than PBS.

2) For polymers with a slow biodegradation rate, such as PBS, the biodegradation evaluation methods in a controlled compost could be applied. The powder shape, which has a larger surface area, should be employed to demonstrate complete biodegradation for these types of slow biodegradable polymers.

3) These results are produced under standard conditions; it is expected that this rate can fall in nature because of temperature, light, moisture and oxygen presence.

In comparison to PHA the modified one degrade less which could be because of the structure or chemical content to improve the properties of PHA,the trend is the same for modified PBS in comparison to PBS, it has degraded less during the same period of time.

To achieve maximum biodegradation degree, the process should maintain for 6 months; moreover, for a future project, it is better to try a different method to prevent further use of chemicals which will turn to waste.

6 SUMMARY

Conventional plastics are a major concern to the environment; here are some issues that should be noticed:

- Microplastics in the marine environment which can be consumed by aquatic and transferred into the food web
- Accumulation of plastic in landfill which will result in land use and toxic materials in leachate
- Low efficiency on recycling
- Toxic substances which release to the air by incineration

To solve these environmental impacts, bio-plastic is proposed. Bioplastics divide into two subgroups, bio-based plastic, which is made of sustainable bioproduct and biodegradable plastics. These plastics can degrade in the environment and convert into non-toxic substances.

Bioplastics suffer some disadvantages like melting point and brittleness; therefore, to improve these properties, they are modified, which can affect biodegradability as well. For that reason, the new modified plastics should be tested for the biodegradation process.

The purpose of this thesis :

- Provide an overview of conventional plastic and a full picture of PHA and PBS
- Propose a method to determine the biodegradation degree of modified bioplastics

A variety of ISO standards have been developed to determine the ultimate aerobic biodegradability of plastic materials. ISO 14855-1, is a widely used test method for determining the amount of carbon dioxide released utilizing techniques such as continuous infrared analysis, gas chromatography, and titration.

According to results, the biodegradation degree of modified PHA has reached up to 23.98% and for modified PBS up to 11.18% during 60 days. However, gas leaks and human error affected the results.

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