BIOPLASTICS: THE SUSTAINABLE SOLUTION OF FUTURE

M.Sc. Dissertation
by

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APRIL 2022

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DISSERTATION

Submitted in partial fulfilment of
The degree of M.Sc. (Inorganic Chemistry)

By

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To

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DECLARATION

I hereby declare that the work embodied in this report entitled “BIOPLASTICS: THE SUSTAINABLE SOLUTION OF FUTURE” was carried out by me during the year 2021-2022 under the guidance of Dr. Kedar Umakant Narvekar. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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ACKNOWLEDGMENTS

First and foremost, I would like to thank God who has given me the power to believe in myself and pursue my dreams. His unending showers of blessings helped me to complete work successfully.

I take immense pleasure to express my sincere and deep sense of gratitude to my supervising guide Dr. Kedar Umakant Narvekar for his sustained enthusiasm and positivity throughout the course of my project work. It was a great privilege and honour to work and study under his guidance.

I wish to thank Dr. Vidhyadatta Verenker, Dean of School of Chemical Sciences, Goa University.

I wish to express my hearty thanks to my friends. I am extremely grateful to my parents and my sister for their love, prayers, caring and sacrifices for educating and preparing me for my future.

RAHUL T V

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CHAPTER 1

INTRODUCTION

Petroleum-based plastics have received a lot of scrutiny in the last decade because of the features that made them so popular: their durability and disposable nature. The industrial era's exploitation of such characteristics has now culminated in the huge environmental challenge of plastic pollution. Recent advancements in environmental sciences, microbiology, genetics, and toxicology have made it possible to study the occurrence and potential impacts of microplastics at various trophic levels and in the ecosystem.[1] Microplastics ingestion by organisms not only causes physical injury and inflammation, but also provides a viable route for the introduction of various environmental contaminants into the food web (endogenous plastic additives, metals, dichlorodiphenyltrichloroethane, polychlorinated biphenyls, and pathogenic microorganisms).[2] Microplastics' lipophilic nature allows them to adsorb persistent organic pollutants found in contaminated areas, potentially increasing their negative impact once digested by organisms.[3] Microplastics have been linked to a variety of harmful effects, including disruption of biological processes, gastrointestinal discomfort, microbiota modification, lipid metabolism, and oxidative stress.[4] These findings raise concerns since the ingestion, inhalation, and cutaneous sorption of harmful compounds by MPs results in their eventual bioaccumulation and biomagnification, posing a risk to human health. Bioplastics are being examined as an environmentally beneficial approach to address this problem. However, not all materials in this category are the same, which has led to a number of misunderstandings about the commodity and its after-life processing. The Great Garbage Patches in the oceans have resulted from quick industrial breakthroughs, the fossil fuel crises, and a plethora of loopholes in environmental rules exploited by multinational corporations, aggravating the issue of rapid climate change. As a result, several countries and corporations are looking into bioplastics to replace traditional plastics, as many of them are said to be biodegradable and so can be a solution to plastic pollution.[5]

1.1 Definition

Although there is no universally acknowledged definition for a bioplastic, the most frequently accepted definition is a polymer that is either biobased or biodegradable, or both. This highlights the fact that not all bioplastics are biodegradable, i.e., biobased does not imply biodegradable, and that some non-biobased polymers, such as PBAT, are biodegradable. Even common plastics, such as low-molecular-weight polyolefins, can be converted into low-molecular-weight compounds that microorganisms can use through abiotic processes including photodegradation and heat breakdown. Significant biodegradation over a realistic time frame necessitates a molecular weight of less than 5000 Da. During deterioration, a drop in the amount of carbonyl groups is a good sign of microbial development. Water and carbon dioxide are the end products of the breakdown of these smaller polyolefins. Metal salts and other pro-degradant additives are commonly used to speed up the rate of degradation of these polymers. Bioplastics of more recent provenance, such as Bio-PET, are called bioplastics mainly because the monomers are made from maize, but the polymerization process is chemical, and the final polymer has the same qualities as ordinary PET, making it non-degradable.[6]

1.2 Types of bioplastics

(i) Starch-Based Bioplastics - Starch-based bioplastics are polymers that contain native or modified starch moieties. This category also includes natural or manufactured plastics containing starch, as well as polymers derived from starch fermentation. This accounts for over half of the global bioplastics business, and many of the thermoplastics in use today are made from it. Bio-PET, for example, and thermoplastic starch (TPS).[7]

(ii) Cellulose-Based Bioplastics - Bioplastics made from cellulose esters or other cellulose derivatives are called cellulose-based bioplastics. Cellulose contains glucose molecules linked together by a (1,4) linkage, which explains why ruminants require specific symbiotic microbes to digest it.[8] E.g., cellulose acetate, methyl cellulose

(iii) Aliphatic Polyesters - Include materials that are more resistant to hydrolytic degradation. E.g., PHA and PLA

(iv) Protein-Based Bioplastics - Made from milk, wheat gluten, and other protein-rich sources. It's very similar to the process of creating cheese. Casein bioplastics, for example.

(v) Lignin-Based Bioplastics - Although lignin has long been obtained as a byproduct of cellulose production, it is only recently that this polymer has gained importance as a result of biorefinery projects.[9] Blends of PP and lignin polymers, PHA and lignin polymer blends, and so forth.

(vi) Chitin-Based Bioplastics - Chitin is the second most abundant biopolymer after cellulose and is made up of Nacetyl-D-glucosamine units linked by (1,4) linkages. Although chitin can be found in the cell walls of yeast and fungi, as well as in the exoskeletons of arthropods, it is extracted mostly from the shells of crustaceans such as crabs, prawns, and shrimp. E.g., ., Chitosan based bioplastics, chitin blends with PP, etc

1.3. Production

In terms of production, bioplastics may be broadly grouped into three types: (i) polymers directly extracted from biomass, (ii) polymers produced from bio-derived intermediates, and (iii) polymers produced by microorganisms.

Bioplastics made from biomass include polymers made from lignin, cellulose, starch, chitin, and even milk. Intermediates such as lignin, cellulose, and starch-based polymers are frequently used to build blends with other plastics. The biomass resources obtained from byproducts of the timber industry and agricultural areas appear to be the largest in the world. Furthermore, lignocellulose accounts for 90% of this plant's biomass, and cellulose accounts for roughly half of the carbon in this lignocellulosic substance. Processes such as acylation, acetylation, and esterification with other components such as carboxylic acids and their derivatives can be used to make cellulose-based polymers including cellulose acetate, cellulose nitrate, and methyl cellulose. The Kraft method, Caustic Soda processing, and the Sulfite method are the most prevalent cellulose extraction processes. To cleave the links between hemicelluloses and lignin to cellulose, all three procedures use a mixture of wood chips and chemicals ranging from sodium hydroxide to sodium sulfite. The Kraft method can be used to extract lignin in the same way as it can be used to extract cellulose. However, due to the strong chemicals used in this procedure, the polymer's backbone is cleaved, and new functional groups may be introduced into the polymer. When compared to lignin produced by other industrial methods, organic solvents can be utilised to solubilize degraded forms of lignins and are structurally most comparable to natural lignins. The major drawback is that the amounts of lignin produced by these processes are extremely low as compared to the amount of solvent required and the disposal of these solvents also provide an environmental hazard.

Because there is no shortage of chitin resources as a result of increased fishing and aquaculture systems, chitin-based polymers could be considered a viable alternative to conventional plastics. However, in regard to the polymers made from it, extraction, yield, and final product quality are some issues of concern. Whether chemical or biological, chitin extraction follows the same steps: demineralization and deproteinization. The chemical approach uses dilute hydrochloric acid for demineralization, sodium hydroxide for deproteinization, and organic solvents for lipid removal. The usage of large amounts of toxic solvents and the loss of mass after processing are two key disadvantages of this technology. The biological method of extraction, on the other hand, employs microbes such as lactic-acid bacteria and proteolytic enzymes.

Starch is a useful filler for conventional plastics since it is biodegradable and has sufficient thermal stability to avoid interfering with the polymer's melt flow processing. However, because it is a hydrophilic molecule, it loses mechanical characteristics and provides low adhesion because ordinary plastics are hydrophobic, resulting in poor starch-polymer interface development.

Microorganisms create polymers such as PHA and, in some situations, extracellular polymeric compounds such as alginate. Microorganisms can be cultivated on carbon-rich sources like glucose or oil, and the carbon is accumulated as polymers by the organisms.

1.4 Properties of bioplastics

(i) Biodegradability- Biodegradation is the process by which materials can be broken down by microbes and used as a food source.

(ii) Compostability- A compostable material can be broken down into nutrient-rich biomass in three months or less under composting conditions.

(iii) Ecotoxicity due to polymer breakdown- When conventional plastics are left in the soil, they can break down into minute microparticles, releasing additives like Bisphenol A. These particles and chemicals can then enter our food chain through the water we drink, causing biomagnifications in people at the top of the food chain. In reality, BPA is a known hormone disruptor in vertebrates and has been linked to gene expression alterations. Metals were added to oxy-degradable polymers to speed up the decomposition process, and these metals can leak into the soil, changing the nutritional composition or potentially affecting the water table. Similarly, if not properly disposed of, the byproducts of some, but not all, bioplastics can cause debilitating damage to the surrounding ecosystems and the food web it holds.

1.5 Uses

Bioplastics such as PHA are biodegradable and can be made without the need of fossil fuels because they are mostly made from biomass, implying possible carbon neutrality. As a result, there has been a surge in the use of these materials in the form of blends or composites with degradable or non-degradable synthetic polymers. This isn't a new concept; corn and soybean oil were historically used to make parts for machines like the Ford Model T. Bioplastics are currently most commonly used in single-use goods such as food packaging, utensils, film wrap, another advantage of bioplastics' biodegradability is that the end products can be recycled as raw materials, removing the requirement for virgin raw materials and providing the product with several end-of-life alternatives.

Food packaging, hygiene-related goods such as toothpicks, food service ware, and planting pots are just a few of the applications for starch polymers. Bioplastics made from a combination of starch-based polymers and other biodegradable plastics are both biodegradable and compostable, and can be used to construct starch-based films for recycling bags, mulching films, and compostable packaging.and other similar items.

Because chitin-based polymers are biodegradable and biocompatible, they can be employed in a variety of fields, including biomedicine, food technology, textiles, nanoparticle production, and agriculture.

The aromatic rings of lignin-based polymers give them stiffness, while the hydroxyl groups in its phenolic moieties and aliphatic chains allow them to be utilised as chemical handles. The ability of lignins to adsorb heavy metals has been demonstrated, and their use as an adsorbent material for wastewater purification is being considered. Lignins have also been found as a possible precursor for the production of carbon fibres, which have high strength and stiffness requirements. Lignin has also been proposed as a potential fire retardant.

Cellulose has been used to make Cellulose Nanofibres (CNFs) and Cellulose Nanocrystals (CNCs) because cellulose nanomaterials have physical properties such as high tensile strength and elastic modulus, low density, and large specific surface areas, all of which are important from an application standpoint. Cellulose is also being investigated as an alternative to petroleum-based plastics in single-use packaging. It is utilised as an edible covering for various food items to extend their shelf life. Because of its biodegradability, renewability, and non-toxic nature, cellulose can be used in a variety of applications. Furthermore, because cellulose is soluble in a wide range of liquids and mediums and because the process is reversible, the generation of regenerated cellulose is being investigated. This process includes the addition of solubilizing agents like carbon sulfide or ionic liquids which can then be removed to obtain the fibres once more. This process is often used to obtain artificial silk and for the production of artificial membranes for medical devices.

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Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or P(3HB-co-3HV) and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) or P(3HB-co-3HHx) are two PHA copolymers that are employed as biodegradable packaging materials [69]. As a pharmaceutically active chemical, PHAs have a wide range of medical applications, including the treatment of HIV and various malignancies. They've also been utilised to make nanoparticles for drug delivery to treat ailments including respiratory disorders. PHA can also be utilised in agriculture as mulch films to maintain soil structure and moisture retention, as well as agricultural nets and grow sacks for nursery plant rearing.

CHAPTER 2

LITERATURE REVIEW

Akshaya Krishnamurthy *et al.* aimed to develop bioplastic films using combination of jackfruit waste four and sago as a low-cost starch source. Three composite bioplastic films were developed using starch mix with lemon extract and water but with different cross-linkers: (1) PV (polylactic acid and crude palm oil), (2) AV (glycerol and crude palm oil), (3) PAV (polylactic acid, glycerol and crude palm oil). The formulated films' physical, chemical, mechanical and biological parameters were characterized. PV film showed the best tensile strength (TS) of 5.24 MPa and least elongation at break (EAB) of 3.49%, while PAV film had the least TS of 0.78 MPa with a maximum EAB (73.38%). FTIR analysis of films showed peak at 1736.3–1743.3 cm^{-1} indicating strong interaction of triglycerides (C=O stretching). In thermogravimetric analysis (TGA), all the films displayed gradual desorption occurring between 150 and 220 °C where the volatile compounds started to evaporate and around 300 °C the lower molecular weight compounds like plasticizer, cross-linker and other additives started to release out; pyrolysis of carbonated compounds occurred above 500 °C. PAV film displayed best thermal stability with half decomposition at 330 °C. Biodegradability of films was demonstrated through soil burial method and culturing of pure cultures of microorganisms in minimal media by providing the film as carbon source. Bioplastic films developed in this study using low-cost plant starch sources have displayed properties with potential application in food packaging industry.[10]

Figure 1 Bioplastic films[10]

Nurul Aino Ismaila *et al.* extracted starch from chosen tubers with high content of starch namely potato and yam have been used as raw materials for bioplastics. The chemical, mechanical, and thermal properties of the products were analyzed using Fourier transform infrared (FTIR), tensile strength tester and Thermogravimetric analysis (TGA). The FTIR spectra of the product displayed the presence of O-H, C-H, C=O and C-O absorption peaks, which indicate the formation of bioplastic has already occured. The tensile strength obtained for potato and yam starch-based bioplastic were 0.6 MPa and 1.9 MPa, respectively. The results gained from TGA showed that 50% weight loss was occurred at 250°C for potato and 310°C for yam-based plastic. The highly biodegradability of plastic was proven using soil burial test, which observed through percentage of soil biodegradation for potato and yam-based bioplastic in 1 week duration were 43% and 26%, respectively. These bio-based plastics have exhibited good thermal and mechanical properties with high biodegradability that makes them a suitable alternative for the existing conventional plastics.

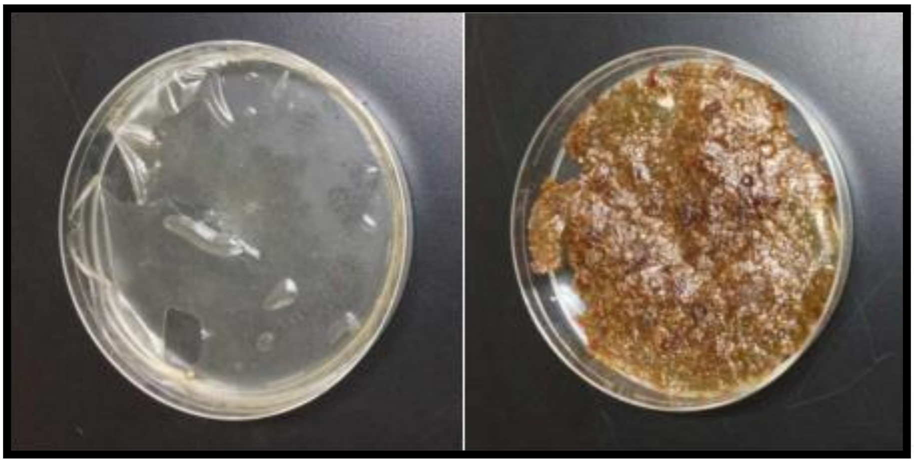


Figure 2 The starch based polyester synthesized from potato and yam tubers[11]

From this study, it is concluded that starch-based bioplastic synthesized from potato and yam tubers have exceptionally high biodegradable properties with decent thermal and mechanical properties and make them a suitable alternative for the existing conventional plastics. Furthermore, starch is a renewable resource, cheap and can be easily modified.[11]

Malin Brodin *et al.* worked on utilized non-food crops, such as lignocellulosics, for production of drop-in polymers or new dedicated bioplastics. Lignocellulosic resources have a potential to replace plastics and materials, which have been traditionally based on fossil resources. The intention of their work was to review the current advances that have been made during the years within fractionation and purification of lignocelluloses and the processes that may feasible for production of bioplastics, based on wood components. Bioplastics production from lignocellulosic materials involves processes as pre-treatment, saccharification, detoxification of liquids, fermentation, conversion, separation, and purification. They have considered the production of conventional bioplastics such as PLA, PHA, BioPE and discussed its production in relation to the potential production from forestry biomass. One aspect considered was the production of novel and dedicated bioplastics instead of focusing on drop-in polymers. Additionally, wood-based platform molecules such as HMF are another example of a platform chemical that can be produced from carbohydrates. HMF can be the basis for various bioplastics such as BioPET, BioPA and BioPCL. However, a viable utilization of HMF as a platform molecule requires processes to convert cellulose into HMF at good yields and thus avoiding the challenging processing step of hydrolyzing cellulose into glucose. Some advances have been reported in this respect.[12]

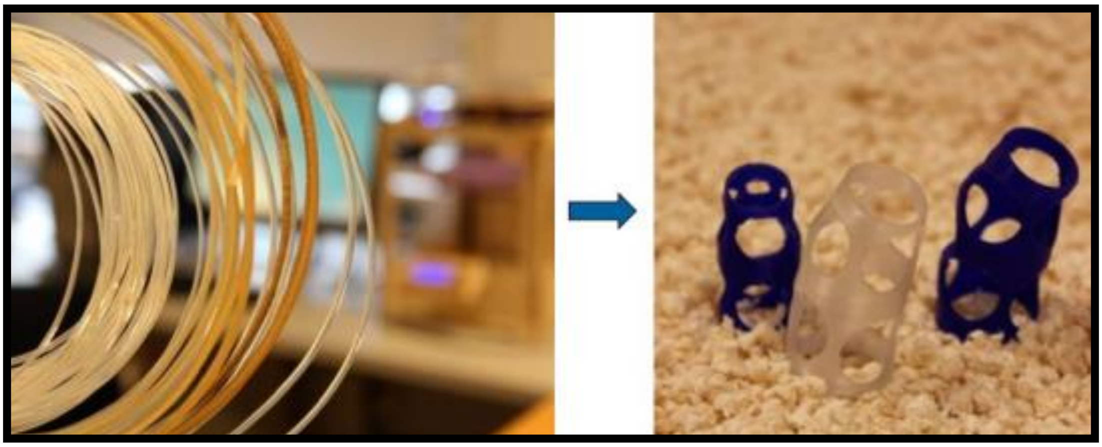


Figure 3 PLA-based filaments containing wood fibers for 3D printing by fused deposition modeling (left). PLA-based 3D printed finger orthosis (right)[12]

Nanou Peelman *et al.* gave information on the performance of bioplastics 33 materials, focusing on food packaging. It gives an overview of the main materials used for 34 producing biobased films, their limitations, solutions thereof, possible applications and a 35 state of the art on bioplastics already used as a food packaging material. the inventory of films 629 show a wide variety in properties, which could make them also applicable as a packaging 630 material for other food products with stricter conditions, like MAP packaging. Storage tests 631 and tests on the industrial packaging machines should be performed to make sure that these 632 films can be used commercially.[13]

Fabio M. Lamberti *et al.* studied the most promising biopolymers PLA, PGA, PHA and bio-versions of conventional petro-plastics bio-PET, bio-PE. The most optimal recycling routes after reuse and mechanical recycling are: alcoholysis, biodegradation, biological recycling, glycolysis and pyrolysis respectively.

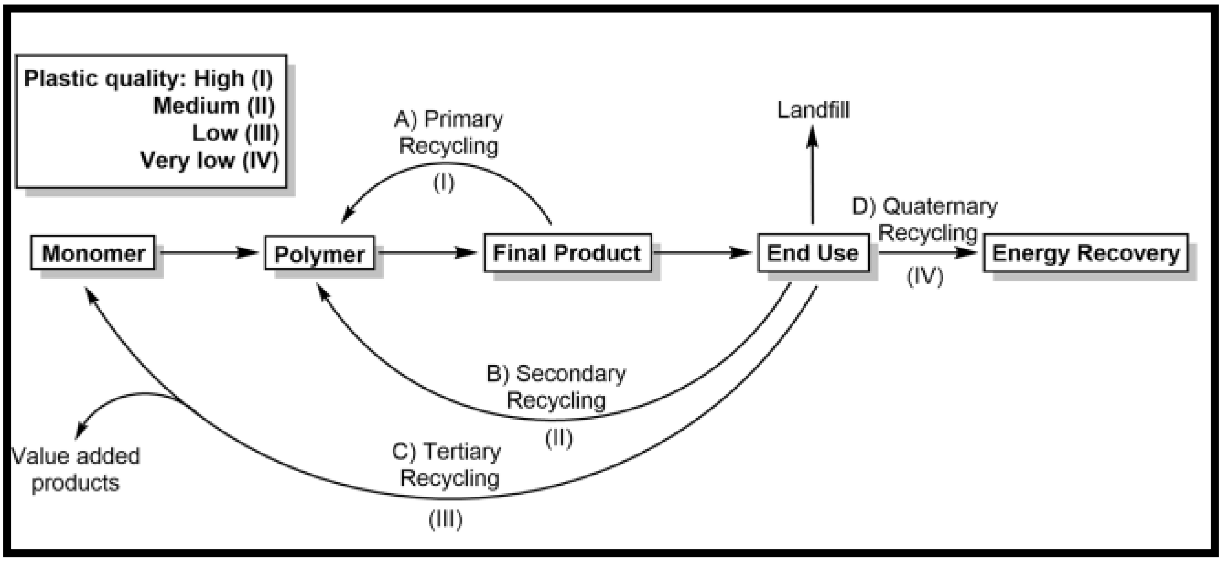


Figure 4 (a) Different plastic waste treatment options and associated plastic quality (b) Circular route for PLA production[14]

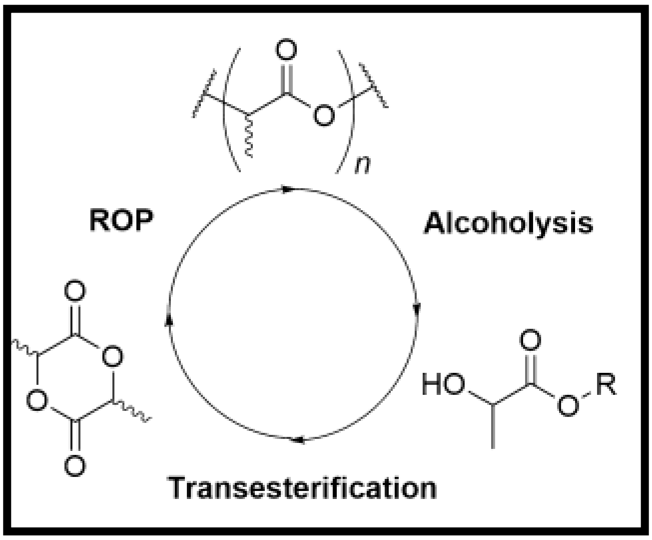


Figure 5 One possible circular route for PLA production[14]

Bioplastics should be synthesized from second generation biomass instead of first generation and should then replace petro-plastics in as many applications as possible due to their inherit lower carbon footprint. In applications that require the superior properties of petro-plastics, instead of replacing them with a mechanically inferior bioplastic the petro-plastic itself should be derived from a renewable resource. This review mentioned two such cases, the commodity plastics PE and PET are conventionally derived from fossil fuels even though bioversions of both can be synthesized that match the mechanical ability just at a fraction of the carbon footprint. The optimal recycling route for each of the mentioned polymers should first be reuse, after which the polymers should be mechanically recycled for as long as possible until they become low grade. Bio-PET and bio-PE both maintain their mechanical properties for a decent number of recycles. Once the polymers become low grade their monomers should be recovered via a chemical route, the monomers can then be repolymerised resulting in a circular production economy. Each biopolymer has an optimum route with the lowest activation energy. PLA should be recycled via alcoholysis since it generates a value-added product. Similarly, bio-PET should be recycled via glycolysis since it also generates a value-added product. Bio-PE has strong solvent resistance so it can only be recycled via pyrolysis. PGA has a small amount in circulation and is only used in medical applications where it fully biodegrades. PHA should be biologically recycled as it reduces the need for antibiotics and decreases the cost of animal feed. Undigested PHA in fecal matter is an ideal medium for MMC fermentation to generate new PHA.[14]

S. Mehdi Emadian *et al.* highlighted the recent findings attributed to the biodegradation of bioplastics in various environments, environmental conditions, degree of biodegradation, including the identified bioplastic-degrading microorganisms from different microbial communities.

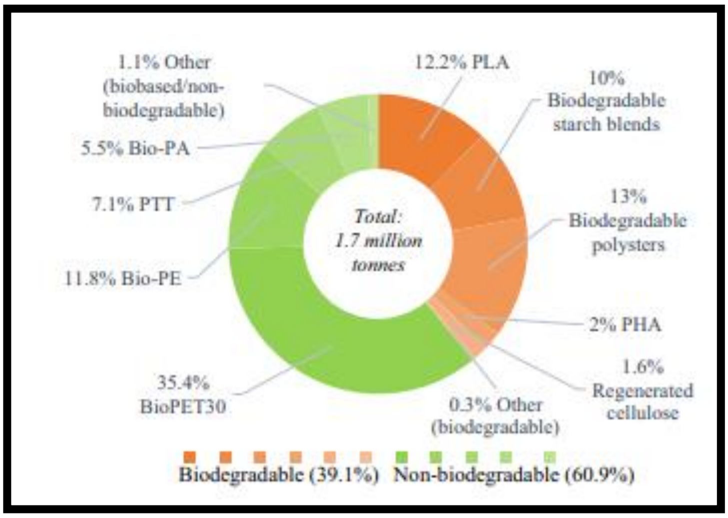


Figure 6 Global production of bioplastics 2014[15]

Microorganisms are responsible for the biodegradation of bioplastics in different ecosystems. In fact, microorganisms catalyze the biodegradation of biopolymers through responsible enzymes. Fungal and bacterial species were isolated from soil, compost, marine water, river water and other environments, which were capable of utilizing the bioplastics to end products. Among the actinomyces or actinobacteria, Amycolatopsis and Streptomyces species, bacterial species such as Paenibacillus, Pseudomonas, Bacillus and Bulkholderia species and Aspergillus, Fusarium and Penicillium species as fungal species were the most commonly isolated microorganisms from different environments. In this paper, the biodegradation of bioplastics was extensively investigated in soil and compost environments. Bioplastics mainly showed high degradability in these environments. However, a large amount of these plastics do find their ways to the water bodies and to marine systems. Subsequently, they may eventually cause unavoidable impacts on fresh water and marine ecosystems, affecting different species of plant and animals adversely. It is well known that a huge amount of plastic waste is available in the marine environment either by direct disposing of solid wastes into oceans or by wastewater discharge. Moreover, instead of disposing bio-based bioplastics into the landfills, alternative management techniques such as composting should be considered as an important recovery option within the integrated waste management approach due to their acceptable degradation properties. Disposal of bioplastics in landfills, contributes to more management problems in landfills rather than offering a sustainable solution. Management of bioplastics in developing regions, along with conventional plastic wastes, is another challenging area, where further study seems to be required.[15]

Alberto Di Bartolo *et al.* discussed the field of bioplastics, including standards and life cycle assessment studies, and discuss some of the challenges that can be currently identified with the adoption of these materials.

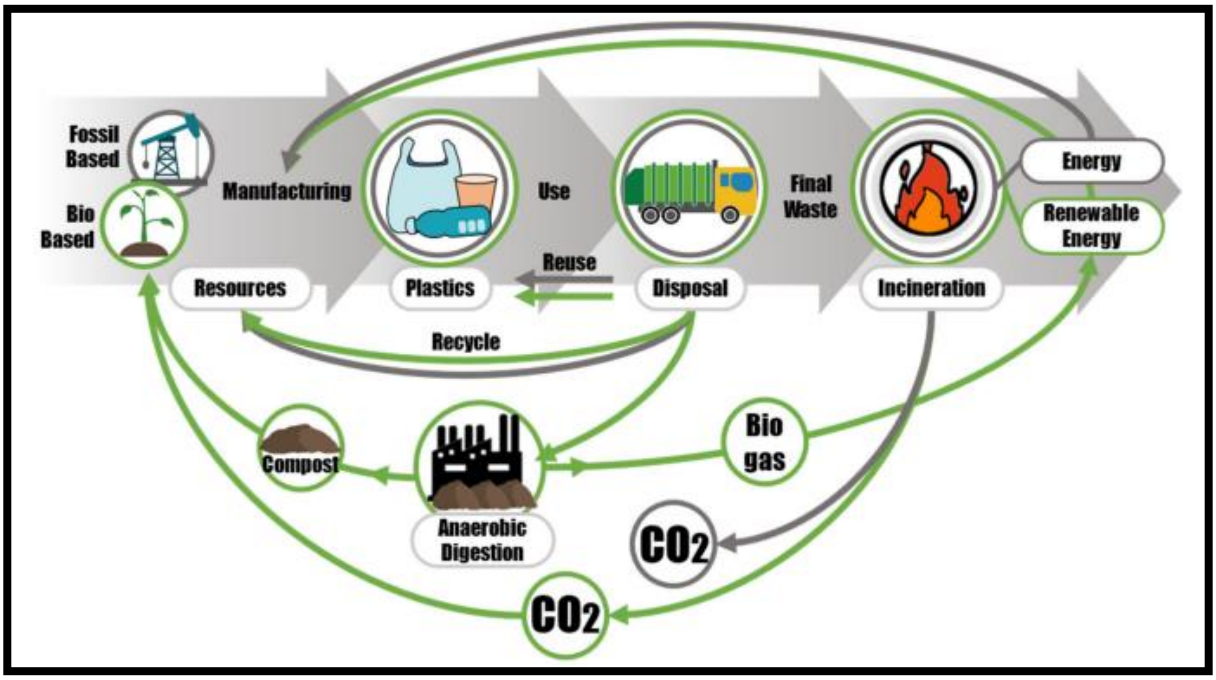


Figure 7 A simplified infographic representing the main steps in linear economy (straight arrows) and the additional steps introduced by circular economy with a focus on bioplastics (green arrows), considering anaerobic digestion as EOL option for compostable plastics, reuse and recycling for durable bio-based plastics and incineration as final disposal of any plastic that is no longer recyclable nor reusable.[16]

The adoption of bio-based plastics might surely come with risks (use of fertilizers, social risks, etc.) as well as advantages. Materials should be designed to ensure effective degradation without causing technological issues while retaining their mechanical properties.[16]

Sangwoo Kim *et al.* crystallized Lactobacillus jensenii (Ljd-LDH), a key enzyme for the production of the d-form of lactic acid from pyruvate concomitant with the oxidation of NADH to NAD^+ using the hanging-drop vapour-diffusion method in the presence of 28%(w/v) polyethylene glycol 400, 100 mM Tris–HCl pH 9, 200 mM magnesium sulfate at 295 K. The polymers of lactic acid are used as biodegradable bioplastics. X-ray diffraction data were collected to a maximum resolution of 2.1 A˚. The crystal belonged to space group $P3_121$, with unit-cell parameters a = b = 90.5, c = 157.8 A˚ . With two molecules per asymmetric unit, the crystal volume per unit protein weight (VM) is 2.58 A˚ 3 Da^{-1} , which corresponds to a solvent content of approximately 52.3%. The structure was solved by single wavelength anomalous dispersion using a selenomethionine derivative.[17]

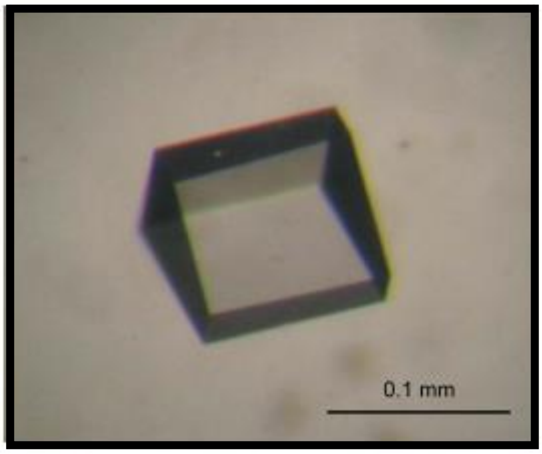


Figure 8 Hexagonal crystals of Ljd-LDH[17]

Minglian Zhao *et al.* crystallised Aeromonas hydrophila strain 4AK4 using the hanging-drop vapour-diffusion method. Single crystals were cryocooled for X-ray diffraction analysis. The phasin crystals belonged to space group P212121, with unit-cell parameters a = 80.8, b = 108.9, c = 134.4 A˚. Polyhydroxyalkanoates (PHAs) are accumulated as water-insoluble granules in the bacterial cytoplasm as intracellular carbon-storage and energy-storage materials in a large variety of bacteria under conditions where a carbon source is provided in excess quantity or any other essential nutrient is limited. These biopolymers have attracted increasing attention owing to their interesting properties, which include biodegradability, biocompatibility and piezoelectricity. PHAs have potential for use as bioplastics to replace environmentally unfriendly petroleum-derived thermoplastics.[18]

Figure 9 Rod-shaped monocrystals of recombinant granule-associated phasin PhaPAh with high diffraction quality[18]

Ezgi Bezirhan Arikan *et al.* looked at aspects of the bioplastics from the perspective of sustainability, advantages/disadvantages and standards. In this review they focus that The global bioplastics market is thought to be growing at a rate of 20%~25% per year. They have some advantages such as lower carbon footprint, independence, energy efficiency, and eco-safety. However, they have some disadvantages such as high cost, recycling, reducing raw materials, misused of terms and lack of legislation. For the sustainability, recycling systems and production technology may be developed for bioplastics and by-product should be used for their production. Also, there is much standardization about them. It is important to have comparable international standard methods. Therefore, there is an urgent need to standardize all details. A new guide and standard for just bioplastics should be developed for production, usage and bioplastic waste management for every country in the world.[19]

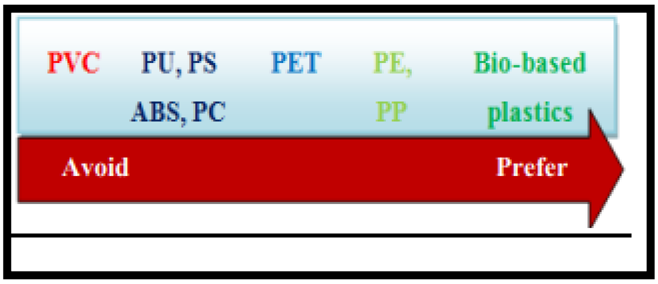


Figure 10 Plastics spectrum[19]

B. S. Saharan *et al.* highlights the applications, production, types, challenges, sustainability, fermentation, process development and use of cheap substrates for bioplastics. These substances have been increasingly spotlighted as means to saving fossil fuels, reducing CO2 emission and plastic wastes. Biodegradability of Bioplastics has been widely publicized in society and the demand for packaging is rapidly increasing among retailers and the food industry at large scale. The plastic which is available in market is very dangerous as it is non-biodegradable. Therefore, it is the demand of the day that biodegradable plastics should be produced and used.

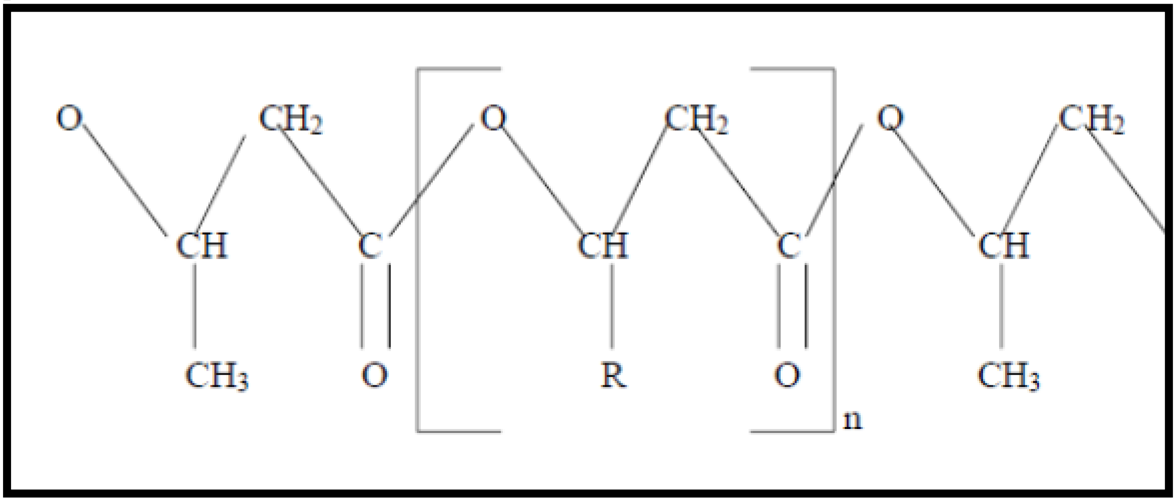


Figure 11 Structure of PHA[20]

The renewable nature and biodegradability of PHAs make them appropriate resources to substitute synthetic plastics in many applications. Currently their production is expensive, but these plastics are only in their first stage of commercial development. Further research on recombinant microbial strains, mixed cultures, efficient fermentations, recovery ⁄ purification and the use of inexpensive substrates can substantially reduce the production cost. Therefore, the future of bioplastics depends on the efforts towards fulfilling price as well as performance requirement. Microbial synthesis of PHA seems to be an inexhaustible game; we can either make homopolymers with diversified monomers, or copolymers or block copolymers of various combinations. Because of their special characteristics and broad biotechnological applications, PHAs have an extremely promising future.[20]

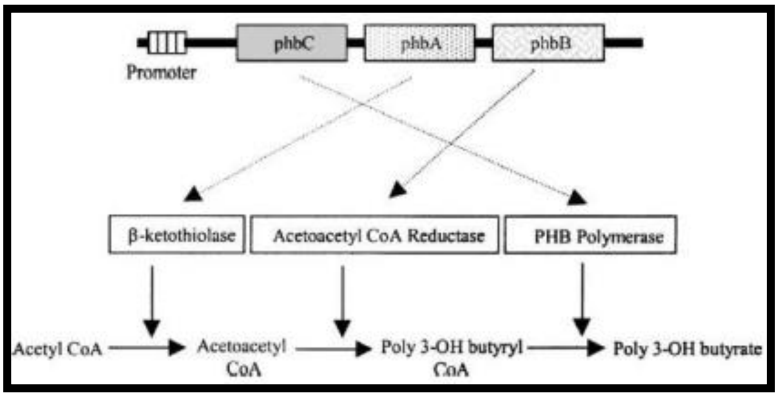


Figure 12 Genes and enzymes involved in PHA synthesis[20]

Jan-Georg Rosenboom *et al.* assessed the advantages and challenges of bioplastics in transitioning towards a circular economy. Compared with fossil-based plastics, bio-based plastics can have a lower carbon footprint and exhibit advantageous materials properties;

moreover, they can be compatible with existing recycling streams and some offer biodegradation as an EOL scenario if performed in controlled or predictable environments. However, these benefits can have trade-offs, including negative agricultural impacts, competition with food production, unclear EOL management and higher costs. Emerging chemical and biological methods can enable the ‘upcycling’ of increasing volumes of heterogeneous plastic and bioplastic waste into higher-quality materials. To guide converters and consumers in their purchasing choices, existing (bio)plastic identification standards and life cycle assessment guidelines need revision and homogenization. Furthermore, clear regulation and financial incentives remain essential to scale from niche polymers to large-scale bioplastic market applications with truly sustainable impact.

The plastics industry has traditionally been based on linear life cycles (Figure 13). Crude oil is cracked and refined into monomers and polymer products using fossil energy, which, at their end of life, are either disposed of (~80%) with potential environmental leakage, incinerated (~10%) or, in the minority of cases (10% globally), mechanically recycled into lower-grade products, which also end up landfilled. In a ‘circular plastic economy’, plastic waste becomes raw material for a recycling process at its end of life, and all production and recycling processes are supplied with renewable energy. Renewable resources (lignocellulosic biomass and pyrolysis oils) are the starting materials for polymer products, which all have a defined circular end-of-life scenario. CO_2 generated through bioplastic incineration, aerobic composting or incineration of CH_4 from anaerobic composting is a net-zero addition to the carbon cycle, as it is captured by photosynthesis into new biomass. Advanced recycling routes enable upcycling of plastic waste: polymers with functional backbones (such as polyesters or polyamides) can be depolymerized biologically or chemically, and the subsequent monomers are polymerized into tailored high-quality or virgin-quality product. Polymers with non-functional backbones such as polyolefins (including polyethylene (PE), bio-based PE, polypropylene (PP) and polystyrene) are better suited for cracking into hydrocarbon oil and gas by thermolysis and can then follow a similar upcycling path. PEF, polyethylene furanoate; PET, polyethylene terephthalate; PHA, polyhydroxyalkanoate; PLA, polylactic acid.

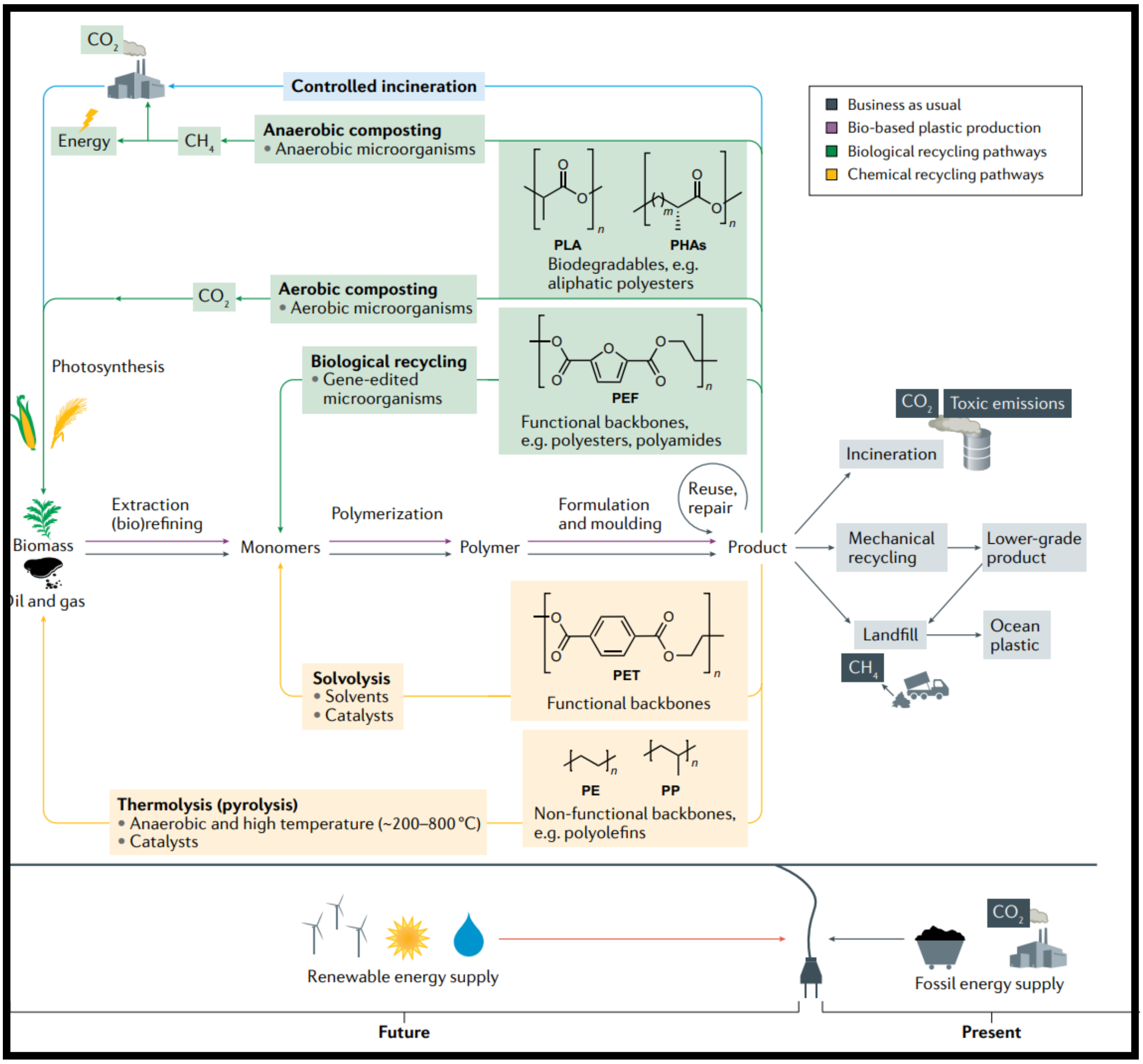


Figure 13 The circular plastic economy[21]

Petrochemical feedstocks are the traditional resources for most commercial monomers and polymers for durable and single-use applications (such as polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC) and polyethylene terephthalate (PET)), as well as for several fossil-based biodegradable polymers (such as polybutylene adipate-co-terephthalate (PBAT) and polyvinyl alcohol (PVA)). Several plastic families, such as polyamides, are not included here for reasons of space and complexity. Using renewable raw materials, biorefineries upgrade first-generation and second-generation biomass (that is, edible plant products and non-edible biowastes, respectively) into the same building blocks as those derived from petroleum, as well as others. These monomers can be polymerized into several durable drop-in polymers (such as bioPE and bioPET), new durable polymers (such as polyethylene furanoate (PEF)), as well as biodegradable ones (such as polylactic acid (PLA) and bio-polybutylene succinate (bioPBS). Polyhydroxyalkanoates (PHAs) are biosynthesized in microorganisms from various feedstocks. Advanced catalysis unlocks captured CO_2, which, together with plant-oil-derived terpenes and epoxides, can be used to synthesize polycarbonates (PCs)85,86. Bio-based non-isocyanate polyurethanes (PUs) can be made from plant-oil-based polyols93. Separated lignin is often incinerated for energy recovery but its phenolic network can also be converted into useful chemicals. Polysaccharides can be extracted from plant biomass and converted chemically into plasticized starch and cellulose-based products. BPA, bisphenol A; EG, ethylene glycol; FDCA, 2,5-furandicarboxylic acid; HMF, 5-hydroxymethylfurfural; PS, polystyrene; TA, terephthalic acid.[21]

Tanja Narancic *et al.* summarised the advances in drug delivery systems, specifically design of nanoparticles based on the biodegradable polymers. They also discussed the research performed in the area of biophotonics and challenges and opportunities brought by the design and application of biodegradable polymers in tissue engineering. They discussed state-of-the-art research in the design and application of biodegradable polymers in packaging and emphasise the advances in smart packaging development and provided an overview of the biodegradation of these polymers and composites in managed and unmanaged environments.

Polymers originating from fossil fuels (polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), polypropylene (PP)), or from renewable resource(s) (polybutylene succinate (PBS), polybutylene adipate (PBA), polycaprolactone (PCL)) can either be recycled or biodegraded. Biobased polyethylene terephthalate bio-PET and biobased polyethylene bio-PE are made from renewable resources and are recyclable. Polylactic acid, PLA; polyhydroxyalkanoates, PHA; biobased polybutylene succinate Bio-PBS are made from renewable resources and are biodegradable.[22]

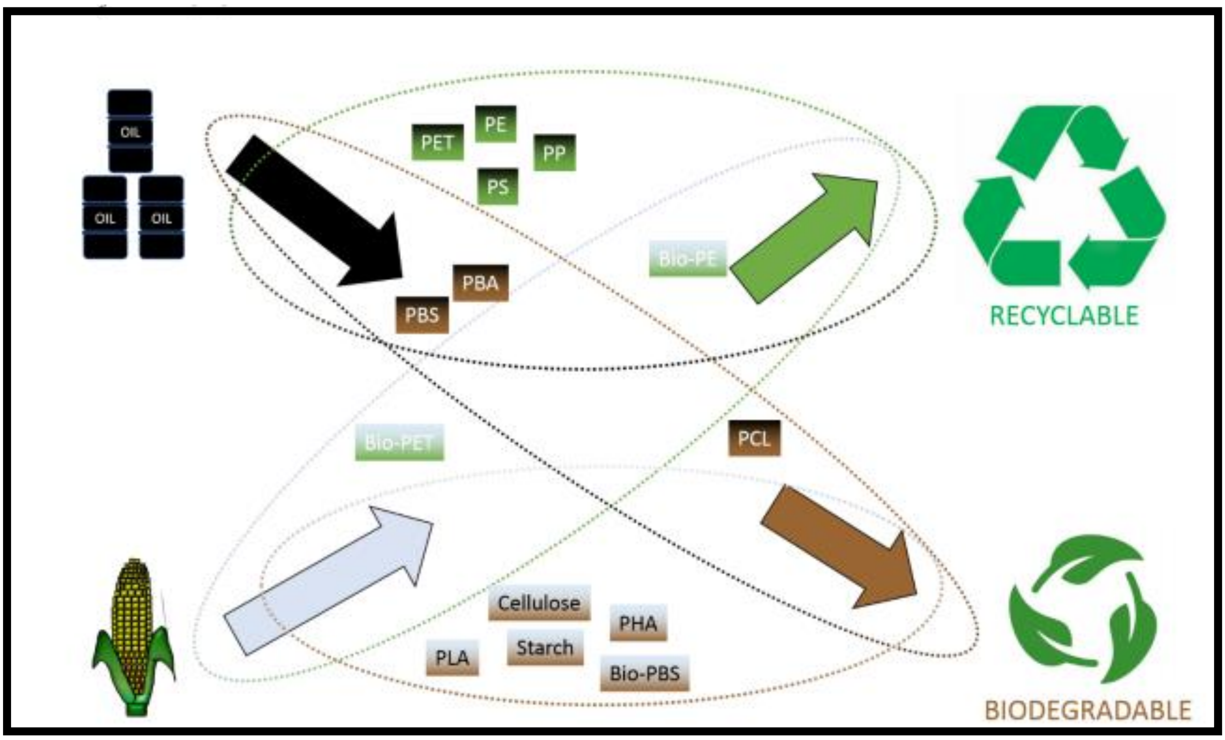


Figure 14 Four-way diagram of origin vs. end-of-life management for different polymers[22]

Kjeld W. Meereboer *et al.* summarized recent advances and opportunities to utilize polyhydroxyalkanoates (PHAs) as a biodegradable substitute in some applications where non-biodegradable and petroleum-based plastics are currently used. PHAs are a well-known family of bacteria-based biodegradable plastics and offer an approach to carbon neutrality and support a more sustainable industry. PHAs such as poly(3- hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) show biodegradable behaviour in all aerobic and anaerobic environments defined by ASTM standards, and can be used to make completely compostable, and soil and marine biodegradable products – a strong positive compared to the negativity associated with the landfilling of plastics. However, PHAs are relatively expensive compared to petroleum-based alternatives. To reduce the cost, PHAs can be used in biocomposite materials, where bio-based agro-residues are incorporated, while maintaining the performance in certain applications. Organic fillers and fibres composed of cellulosic material can improve the properties of polymers, however, their effect on the marine biodegradable properties of the composite matrix remains an unexplored area. When used in biocomposites with PHAs, they improve biodegradation rates in all environments. In addition to cellulose, other bio-based fillers such as proteins (i.e. distillers dried grains with solubles) and starch have been reported to significantly improve soil and marine biodegradability rates compared to other fibres and fillers. Other components that affect biodegradability are additives (i.e. chain extenders) and compatibilizers (i.e. maleic anhydride etc.) that are added to optimize the service life properties, but are reported to inhibit the biodegradation properties by impacting the hydrophilicity of the polymer and enzyme activity. The multitude of possible combinations of polymers and fillers and fibres, and their effect on the biodegradation of PHA-based biocomposites are a largely unexplored frontier. The potential benefits of PHA-based biocomposites make a strong case for further research into this area.

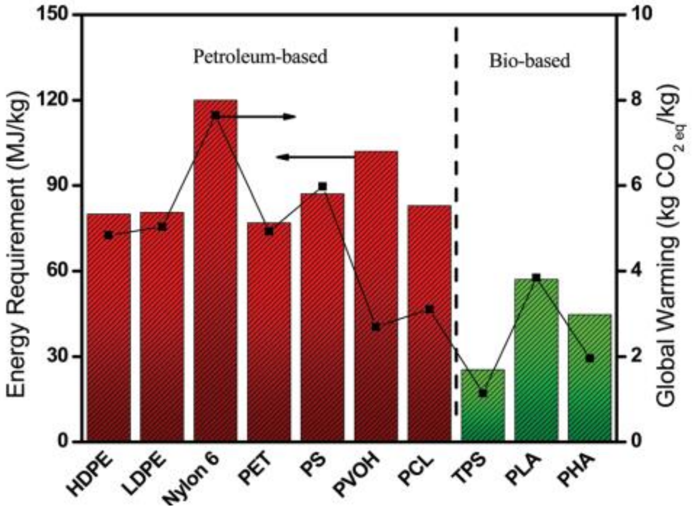


Figure 15 Production energy and CO_2 emissions of petroleum-based and bio-based polymers[23]

Several factors affect the biodegradation of PHAs in the natural environment (non-laboratory) including location, temperature, nutrients, microorganisms present, UV light exposure, dissolved oxygen and salinity. In lab scale studies, optimal temperature, moisture content, pH and higher amorphous content consistently promote enzymatic depolymerization of PHAs in all types of aerobic and anaerobic biodegradation. Combined with abiotic factors, the optimal conditions for PHA degradation can be derived.

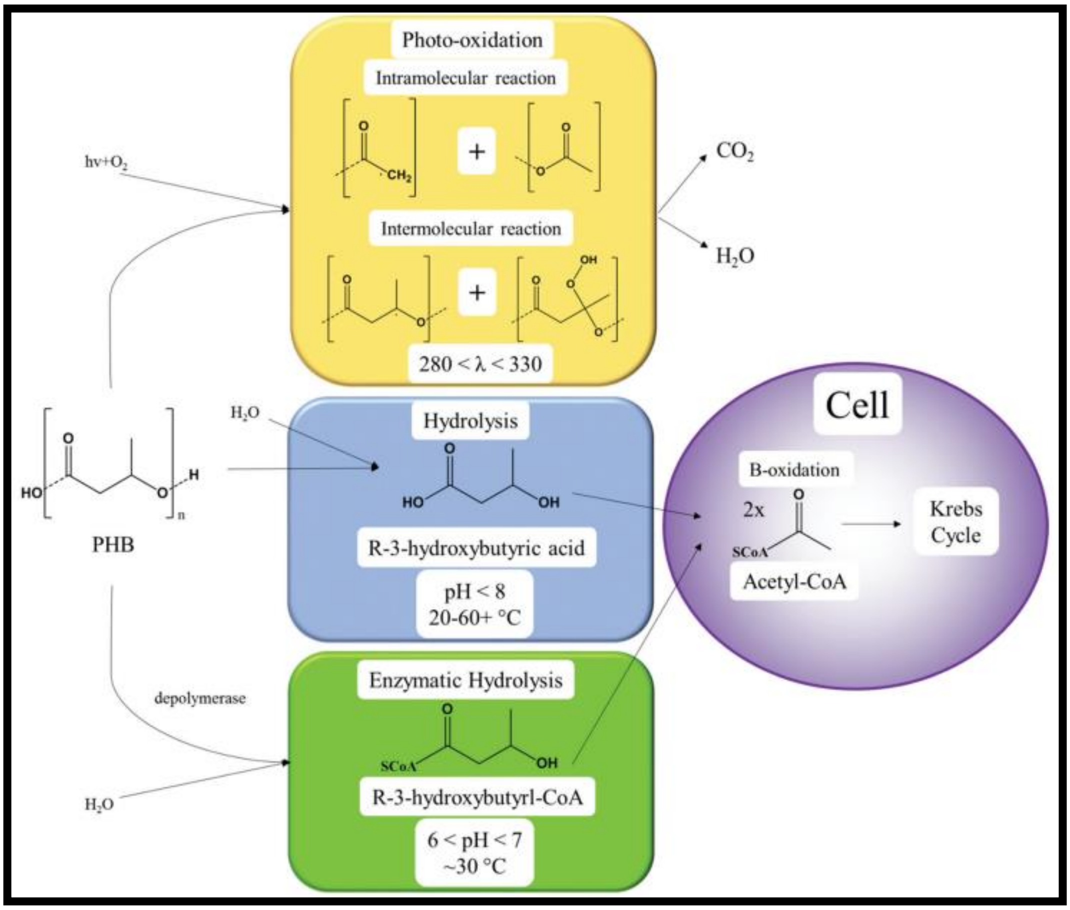


Figure 16 Simplified main pathways and optimal conditions for PHB degradation and bioassimilation in natural environments.[23]

Other polymers may include factors such as their Tg (i.e. PLA), due to the transition from a glassy to rubbery state resulting in an increased free volume around biodegradation temperatures that may impact hydrolytic and enzymatic degradation. Small chain PHAs also do not suffer from thermal degradation under 60 °C.252 Under composting conditions, PHAs would undergo some thermal degradation; however, the conditions become thermophilic and the thermophilic enzymes used are more stable in this environment, becoming the major driving force for PHA degradation. The bio-assimilation of PHAs mainly depends on the complexity of the polymer, where less complex polymers are more easily assimilated, but at the same time are limited by their high crystallinity (that limits the degradation rate). Furthermore, the presence of other organic matter can either promote the bio-assimilation of PHA to produce specific products (methane) or can repress the bio-assimilation of PHA in favour of more easily accessible carbon sources (e.g. cellulose, starch, glucose etc.). Mesophilic temperatures are reported to be most favourable for PHAs compared to other biodegradable polymers (i.e. PLA), in both aerobic and anaerobic biodegradation. The effect of additives and blends of PHAs are important to consider since virgin PHAs are not usually used in industry. Chain extenders, antifouling agents and the synthetically produced plasticizers TBC and glycerol inhibit the biodegradation of PHAs, despite reducing the crystallinity, either by inhibiting the enzymatic action, reducing hydrophilicity or inhibiting the microbial growth. In such cases these can delay the onset of biodegradation for tuneable attributes if so desired. Inoculum sources provide a significant added diversity of microorganism consortia that is responsible for the variability of PHA biodegradation between studies. In high solid content studies, such as soil biodegradation, marine biodegradation and landfill biodegradation, a high moisture content allows for the microorganisms to have an increased diversity and population that can enhance the biodegradation rate. Therefore, to ensure that biodegradation studies are applicable in research, they should follow ASTM/ISO standards, and also have inoculum sources that are comparable to either a natural environment or comparable inoculum sources that are readily available such as those from waste water treatment plants.[23]

V.C. Shruti *et al*. highlighted current knowledge of microplastics to incorporate biodegradable MPs in the ongoing researches. Recent studies have identified that some biodegradable MPs exhibit same effect as conventional type MPs. Furthermore, we performed a simple degradation experiment and found that polyhydroxyalkanoate films formed MPs in water environment alike other biodegradable and conventional plastics sharing common research interests. In an effort to promote investigations, we recommend the knowledge gaps identified on bioplastics MPs: understanding the timeframe of disintegration and degradation of developing bioplastics; ensuring degradability and less persistence; promoting toxicity tests and potential effects on a wide variety of organisms; promoting attempts to assess the impacts on ecosystems; evaluating the interaction of microorganisms and MPs; working towards identifying novel disposal and collection methods from public to ease recycling and degradation processes.[24]

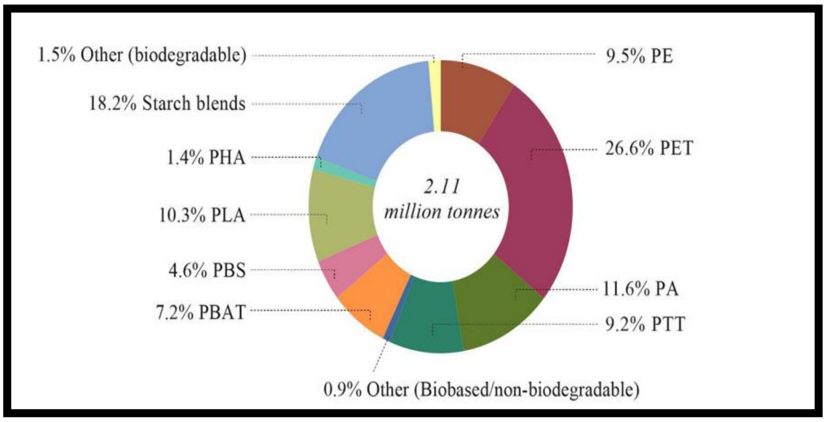


Figure 17 Global production capacities of biodegradable plastics in 2018[24]

Jose´ M Luengo *et al*. discuss the occurrence, biosynthesis, catabolism and biotechnological applications of poly 3-hydroxyalkanoates.

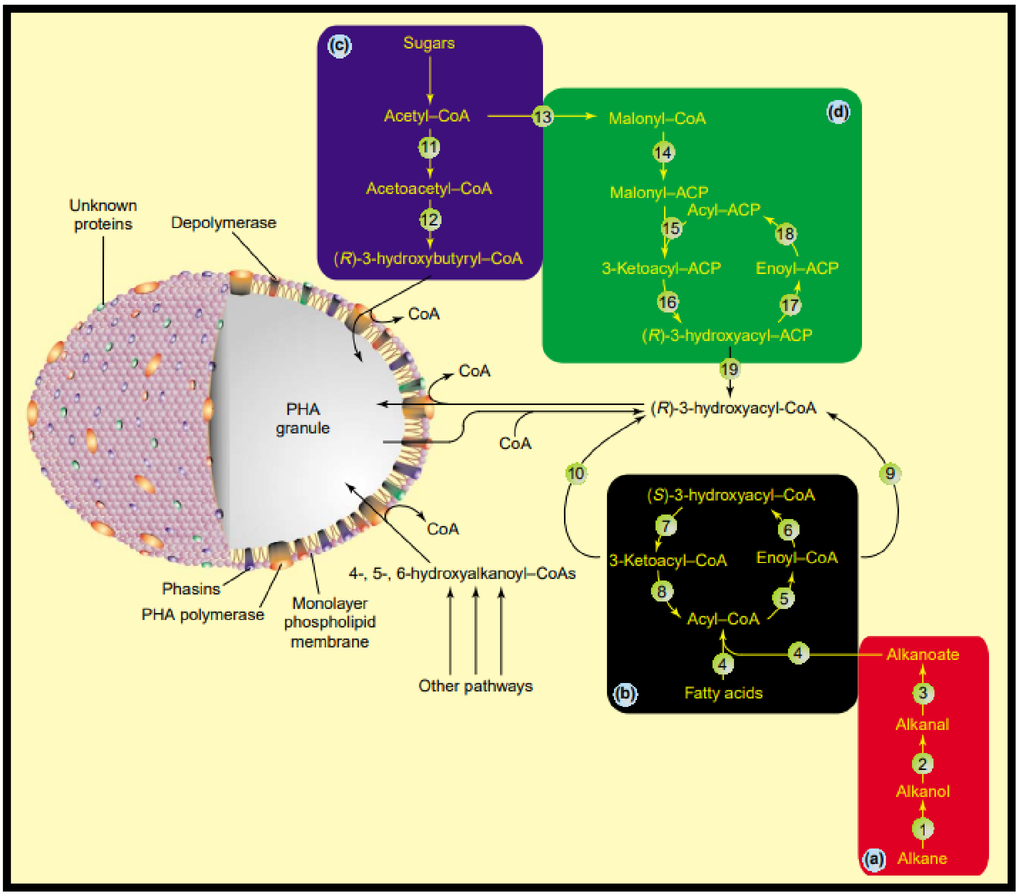


Figure 18 Structural organisation of a PHA granule and metabolic interconnections between the different pathways involved in the biosynthesis and catabolism of PHBs and PHAs.[25]

Atomic force microscopy and confocal Raman spectroscopy are techniques currently used for poly(3-hydroxyalkanoate) (PHA)-granule analysis. Bioplastics can be isolated by centrifugation (cell-free extracts) or by solvent extraction (dried intact bacteria) with chloroform, trifluoroethanol, dichloroethane, propylene carbonate, methylene chloride or dichloroacetic acid. Their molecular weights (ranging from 50 000 to 1 000 000 Da) have been established by light scattering, gel permeation chromatography, sedimentation analysis and intrinsic viscosity measurements and their monomer compositions have been determined by gas chromatography (GC), mass spectroscopy (MS) and nuclear magnetic resonance (NMR) analyses. Other physical properties, such as crystal structure, polydispersity, melting temperature, enthalpy of fusion, glass transition temperature and mechanical properties were established using different procedures.

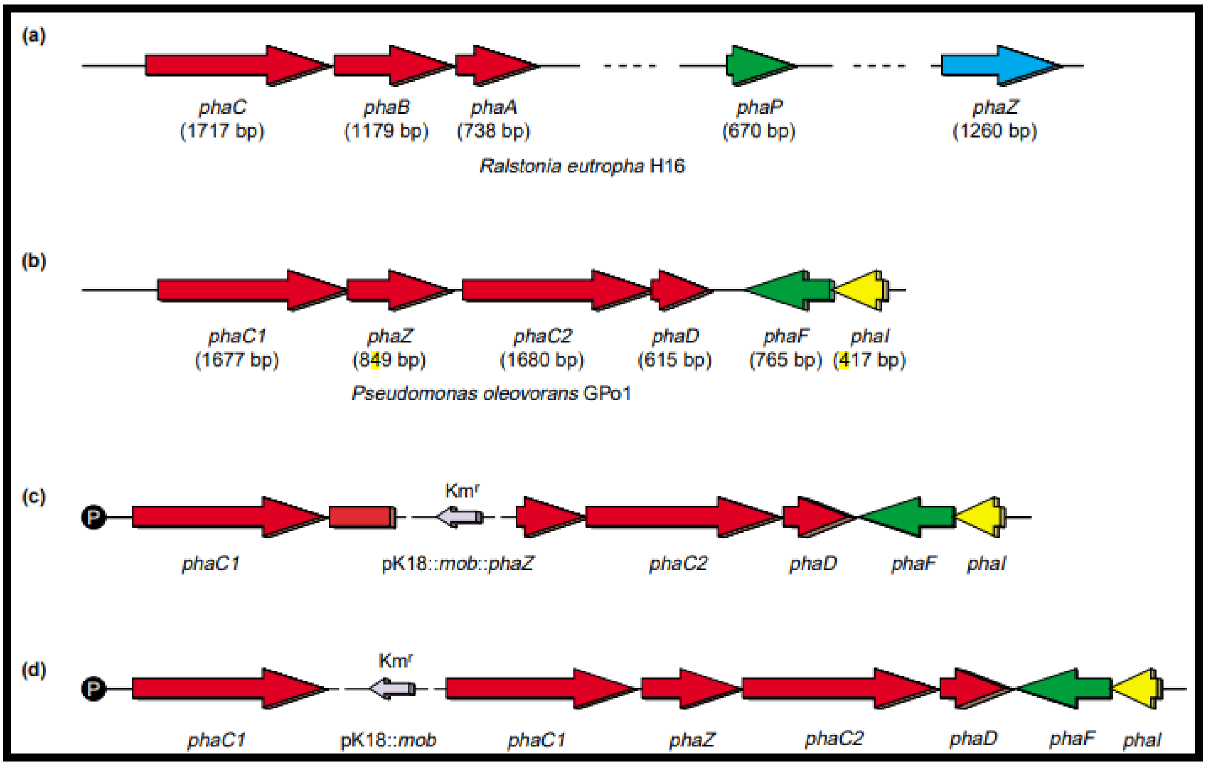
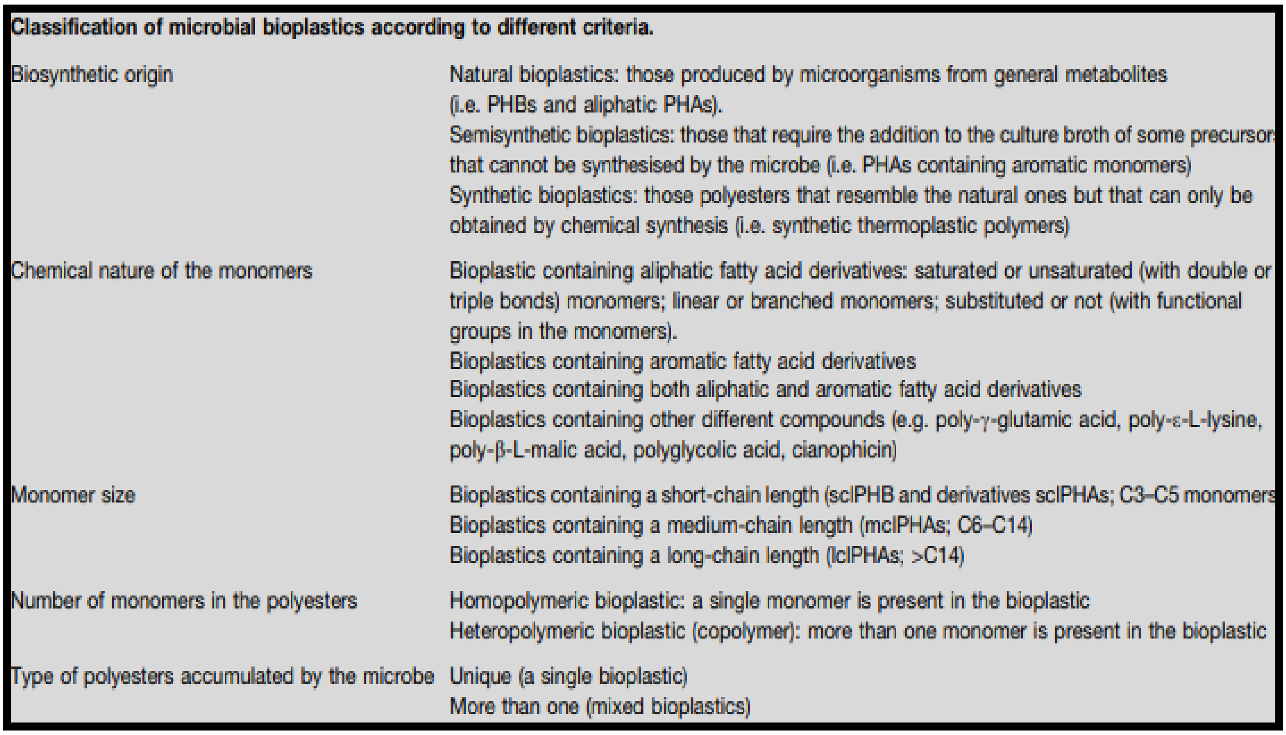


Figure 19 Organisation of the genes and enzymes involved in the biosynthesis of bioplastics. (a) Biosynthesis of PHBs in Ralstonia eutropha (b) PHAs in Pseudomonas oleovorans (c,d) PHAs in different mutants of P. putida U designed to prove the existence of promoters downstream from phaC1 (c) P. putida U mutant disrupted by the insertion of the integrative plasmid pK18::mob into the depolymerase gene (d) P. putida U mutant in which the phaC1 gene has been duplicated and a new cluster phaC1ZC2DFI, without the promoter region (P1) located upstream from phaC1, has been generated.[25]



Classification of microbial bioplastics according to different criteria.

Biosynthetic origin	Natural bioplastics: those produced by microorganisms from general metabolites (i.e. PHBs and aliphatic PHAs). Semisynthetic bioplastics: those that require the addition to the culture broth of some precursor that cannot be synthesised by the microbe (i.e. PHAs containing aromatic monomers) Synthetic bioplastics: those polyesters that resemble the natural ones but that can only be obtained by chemical synthesis (i.e. synthetic thermoplastic polymers)
Chemical nature of the monomers	Bioplastic containing aliphatic fatty acid derivatives: saturated or unsaturated (with double or triple bonds) monomers; linear or branched monomers; substituted or not (with functional groups in the monomers). Bioplastics containing aromatic fatty acid derivatives Bioplastics containing both aliphatic and aromatic fatty acid derivatives Bioplastics containing other different compounds (e.g. poly-γ-glutamic acid, poly-ε-L-lysine, poly-β-L-malic acid, polyglycolic acid, cianophicin)
Monomer size	Bioplastics containing a short-chain length (sclPHB and derivatives sclPHAs; C3–C5 monomers Bioplastics containing a medium-chain length (mclPHAs; C6–C14) Bioplastics containing a long-chain length (lclPHAs; >C14)
Number of monomers in the polyesters	Homopolymeric bioplastic: a single monomer is present in the bioplastic Heteropolymeric bioplastic (copolymer): more than one monomer is present in the bioplastic
Type of polyesters accumulated by the microbe	Unique (a single bioplastic) More than one (mixed bioplastics)

Figure 20 Classification of microbial bioplastics[25]

PHAs are polyesters containing monomers of mediumchain length or long-chain length. Although PHAs are structurally related to PHBs, the microbes that synthesise PHBs usually fail to make PHAs.[25]

Jet Yin Boey *et al*. highlighted the current synthesis process and application of PHAs and PLA and its composites for food packaging materials and coatings. These biopolymers can be further ameliorated to enhance their applicability and are discussed by including the current commercially available packaging products. Factors influencing biodegradation are outlined in the latter part of this review. The review article aimed to organize the scattered available information on various aspects of PHAs and PLA, and its composites for packaging application purposes. It is evident from a literature survey of about 140 recently published papers from the past 15 years that PLA and PHA show excellent physical properties as potential food packaging material.[26]

Lisa Zimmermann *et al.* extracted 43 everyday bio-based and/or biodegradable products as well as their precursors, covering mostly food contact materials made of nine material types, and characterized these extracts using in vitro bioassays and non-target high-resolution mass spectrometry. Two-third (67%) of the samples induced baseline toxicity, 42% oxidative stress, 23% antiandrogenicity and one sample estrogenicity. In total, they detected 41,395 chemical features with 186–20,965 features present in the individual samples. 80% of the extracts contained > 1000 features, most of them unique to one sample. They tentatively identified 343 priority compounds including monomers, oligomers, plastic additives, lubricants and non-intentionally added substances. Extracts from cellulose- and starch-based materials generally triggered a strong in vitro toxicity and contained most chemical features. The toxicological and chemical signatures of polyethylene (Bio-PE), polyethylene terephthalate (Bio-PET), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), polylactic acid (PLA), polyhydroxyalkanoates (PHA) and bamboo-based materials varied with the respective product rather than the material. Toxicity was less prevalent and potent in raw materials than in final products. A comparison with conventional plastics indicates that bioplastics and plant-based materials are similarly toxic. This highlights the need to focus more on aspects of chemical safety when designing truly “better” plastic alternatives.

They combined in vitro bioassays with high resolution non-target mass spectrometry to characterize the toxicity and chemical composition of bio-based and biodegradable materials. Results indicated that the majority (67%) of bioplastics and plant-based products contain toxic chemicals as well as a large number and diversity of compounds (> 1000 chemical features each in 80% of the samples). They applied solvent extraction in order to analyze the intrinsic chemical toxicity present in the products. The study demonstrates that bio-based and/or biodegradable materials available on the market are just as toxic as conventional plastics with regards to the chemicals they contain. This highlighted that the positive connotation of “biological” or “sustainable” materials does not extend to chemical hazards. Their findings imply that in order to develop bio-based/biodegradable materials that indeed outperform conventional plastics, sustainability and chemical safety aspects must be addressed alike. One way to promote this is to integrate chemical toxicity into the life cycle assessment of materials. On a positive note, they showed that safer products are already at the market that can be used as best practice examples. Additionally, the chemical safety of materials can be further optimized using green chemistry to “design out” toxicity during the development of new biobased and biodegradable materials. Besides these human health aspects, the carbon, energy, water and land footprints need to be minimized to create truly better plastics or plastic alternatives and avoid regrettable substitutions.[27]

Nor Izaida Ibrahim *et al.* presented an overview of the introduction of bioplastic materials and classifications, and a comprehensive review of their drawbacks and areas of importance, including basic and applied research, as well as biopolymer mixtures and biocomposites developed in the last decade. At the same time, this article provides insights into the development of bioplastics research to meet the needs of many industries, especially in the packaging industry in Malaysia. This review paper also focuses generally on bioplastic packaging applications such as food and beverage, healthcare, cosmetics, etc

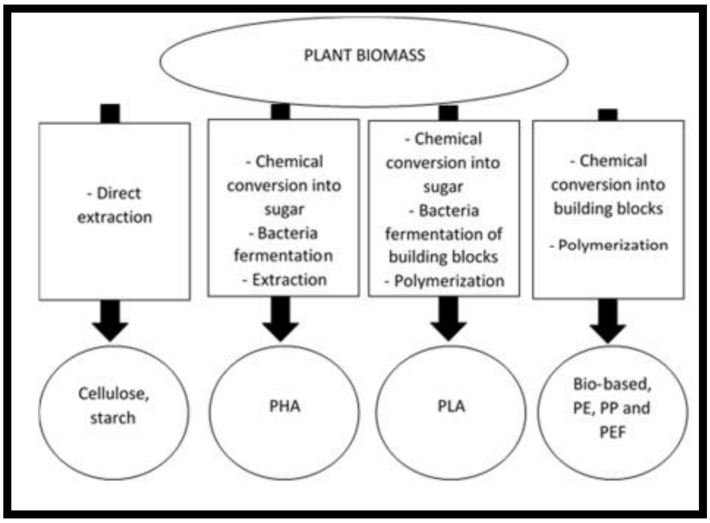


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Figure 21 Bioplastic processing routes dependent on plant biomass[28]

Plant biomass can also be transformed chemically or biocatalytically into building blocks for other polymers (e.g., polylactide (PLA) and polyolefins). Biobased products, on the other hand, do not have to be made entirely of renewable sources; they can also incorporate fossil fuel-based raw materials. Carbohydrate-rich food crops, such as corn or sugar cane, are widely used to make biobased polymers. Non-food crops, such as lignocellulosic material, can be converted into chemical building blocks that can be used to make a range of bioplastics.

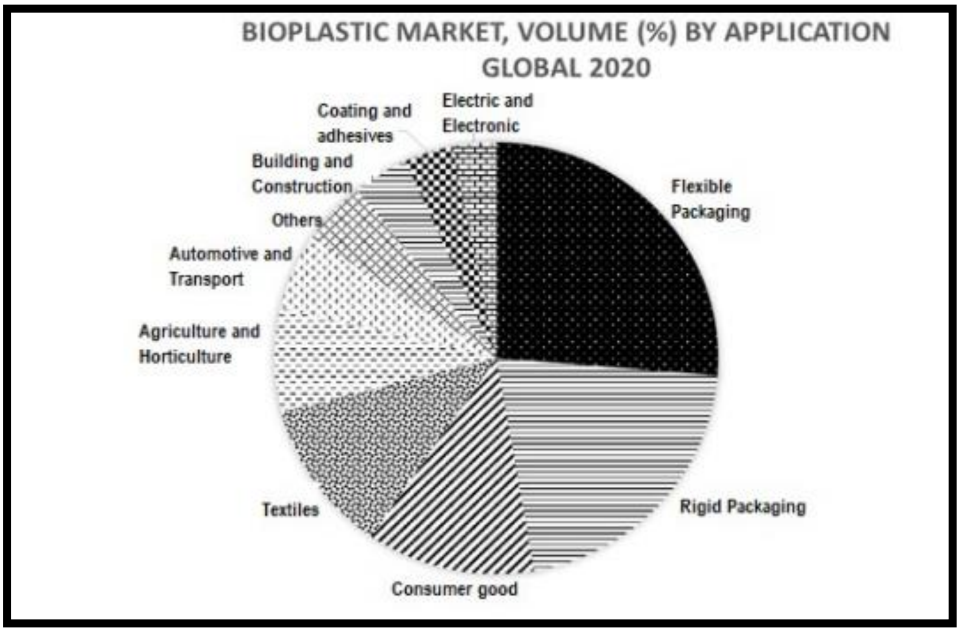


Figure 22 Composition of bioplastic market worldwide, 2020[28]

The figure shows that the bioplastic materials used in packaging applications are supposed to work by protecting products from the environment and preserving the quality of products. In bioplastic packaging applications such as food and beverage, healthcare, cosmetics, etc., most packaging is produced by the food processing sector. Food packaging is a combination of the art, science and technology of containment of a commodity in order to ensure the secure and low-cost transport and the supply of the products to customers in good condition.[28]

Harsini Venkatachalam *et al*. highlighted some aspects of bio plastics, its production, application, recycling, and recent development in bio plastic. Every country desperately needs to develop bio plastic usage and its proper waste management for a pollution free world.

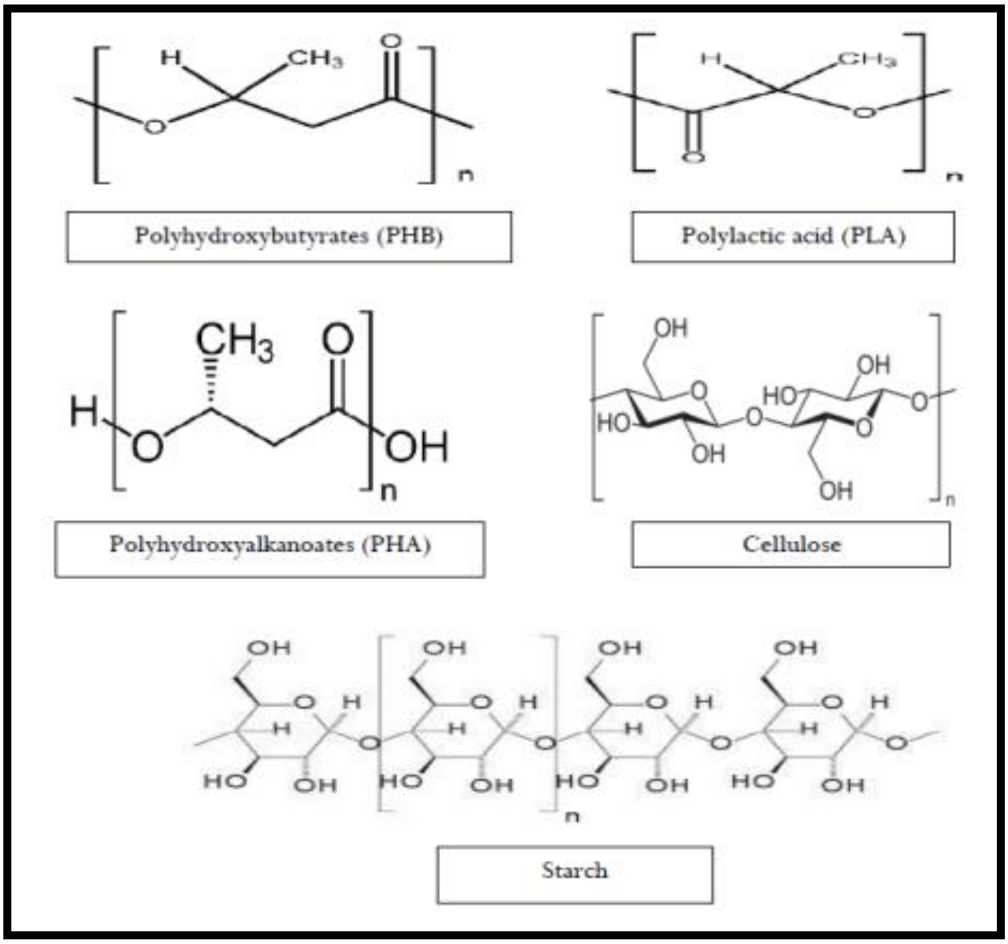


Figure 23 Chemical structure of polymers[29]

The fossil fuels derived plastic disrupts the natural cycle and accelerate the release of carbon dioxide into atmosphere and lead to greenhouse effect. The plants grow by taking in carbon dioxide and when it biodegrades, it releases the carbon dioxide back into the earth. These natural resources undergo different processes to form polymers. Polymers are further processed to bio-plastics. During bio plastic degradation carbon dioxide is released back to the atmosphere. Therefore, carbon dioxide which is taken from the environment is cycled back to the atmosphere by passing through different stages and forming a closed cycle. Many bio-plastics are 100% compostable and typically biodegrade in 180 or less days when disposed of in a municipal composting facility and it is absorbed back into the earth as nutrient for the soil.

Bio-plastics have two thirds less harmful greenhouse gas emissions and can save up to 35% energy.

Asia produces around 50 % of bio plastic around the world. Europe has second place in production capacity of bio plastics. New biopolymers like PLA (Poly lactic acid) and PHAs (Polyhydroxyalkanoates) are 100 % bio-based and biodegradable and help the economy of bio based and biodegradable to grow. Approximately 10 % – 15 % bio plastics of the total plastic market will increase its market share to 25%-30% by 2020, and it will be over 10 billion by 2020.[29]

M. Selvamurugan *et al.* traces the different types of bioplastics and provides an overview of its development and waste management. This paper also makes out a case for an accelerated shift from traditional petrochemical plastics to bioplastics. Polylactic acid (PLA), polylactide plastics are today’s most important bioplastics on the market.31 PLA is based on lactic acid and is mainly produced by the process of microbial fermentation of starch obtained from the maize, cassava, potato, sugarcane and sugar beet. The problems identified in the starch substituted bioplastics can be overcome through these PLA bioplastics. Polyhydroxyalkanoates (PHA) based plastics are produced from the plant based starch by the processes of microbial fermentation. These PHA based plastics are having the physical and chemical properties very similar to polyesters, polyethylene and polypropylene.34 In the presence of excessive carbon sources, several natural microorganisms form PHAs granules intercellularly.

The continuous research and developmental activities towards bioplastics and growing awareness towards environmental conservation have led to a remarkable growth of the overall bioplastics market.72 Further, the stringent regulatory reforms by the several governments towards the reduction of plastic usage have augmented the demand for bioplastics. At present, the contribution of bioplastics products in the total plastics market is around only 1 per cent. However, the results of European Bioplastics’ annual market data update, presented at 12th European Bioplastics Conference held on 29 November 2017 in Berlin, confirmed that steady growth of the global bioplastics industry. The capacity of the global bioplastics production is 2.05 million tonnes in 2017 and it is expected to be increased to 2.44 million tonnes in 2022. 73 The growth rate of bioplastics is around 20-25 per cent per year but the growth rate for conventional plastics is only 4-9 per cent per year.74 The European bio-plastics market reported that the global bioplastics market is to be growing at more than 20% per year.75 The only disadvantage of the global bioplastics market is high production cost over conventional plastics,76 however, it can be overcome by the technology advancement. Moreover, the increasing price of crude oil has also boosted the manufacturer towards the production of bioplastics over petroleum based plastics.20,60 The developing countries like India, China, etc., also promoting the bioplastics. by providing incentives coupled with contract manufacturing which is also further expected to contribute to the growth of the bioplastics market. At present, the drop-ins bioplastics are dominant in the bioplastics market. Around 56 per cent of the global bioplastics production is only the drop-in bio-based plastics viz., bio-PET, bio-PA and bio-PE.67 While considering the individual types, the drop-in biobased PET is dominating in the bioplastics market over other types of bioplastics, which is followed by the starch-based bioplastics. However, the PLA and PHA based plastics production are expected to increase in the bioplastics market due to its superior quality and valid end-of-life options. In terms of application, the global biodegradable plastics market is segmented into packaging, textile, agriculture, electronic, medical, building construction, injection moulding and a number of other segments. Among them, the packaging industry is the largest field which contributes to 60 per cent of global bioplastics production.[30]

CHAPTER 3

POLYLACTIC ACID AS A BIOPLASTIC

PLA is a poly(a-ester), well-known in terms of its disposable and hydrolytically degradable nature that stems from its labile ester bonds in its backbone. The polymer has a repeating ester unit of (C3H4O2)n. PLA was first synthesized by condensation of lactic acid by Théophile-Jules Pelouze in early 1845, and then in 1932, when Carothers et al. reported the use of lactide as a monomer. Initially, however, PLA was limited in use due to its low molar mass and high cost. Cargill Inc. established a commercial ring opening process for lactide to high molar mass PLA, and it is now more widely used. Since 2010, Nature Works LLC in the United States, Evonik Industries (Germany), PURAC Biomaterials (The Netherlands), Synbra Technology BV (The Netherlands), and several other manufacturers produce PLA. PLA is now used in many fields, such as biodegradable packaging, woven and nonwoven textiles, together with biomedical devices and electronics. The environmental concern over conventional plastic packaging has increased worldwide demand for biodegradable materials such as PLA.[31]

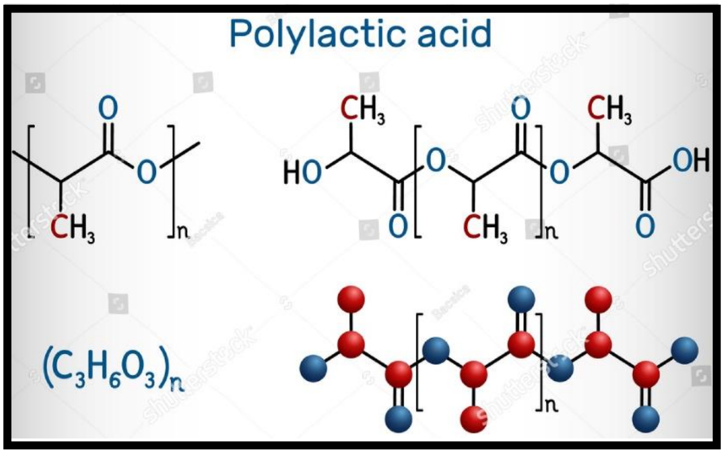


Figure 24 PLA[32]

3.1 PLA PRODUCTION

Lactic acid is a major PLA building element that can be made via a petrochemical pathway or fermentation of carbohydrates from sugarcane, cassava, corn, and tapioca. L-lactic acid and D-lactic acid are the stereo-regular forms of lactic acid. D,L-lactic acid is produced by the petrochemical route, whereas L-lactic acid is virtually entirely produced by the fermentation of starch from various renewable resources. Polycondensation, azeotropic dehydration condensation, and ring-opening polymerization are all methods that can be utilised to make PLA. Lactic acid polymerization via direct condensation produces low molar mass, brittle polymers that are mostly useless unless external coupling agents are used to extend the chain length. The hydroxyl and carboxylic groups of lactic acid react to create PLA when it is directly condensed. A variation of this reaction is the azeotropic dehydration condensation of lactic acid, which can yield high molar mass PLA. However, the most effective route to high molar mass PLA is the ROP of lactide, the cyclic dimer of lactic acid. Several catalysts have been utilized in the production of PLA by ROP, most are alkoxides of stannous tin (Sn), but aluminum (Al), copper (Cu), and zinc (Zn) are also used. Among these types of catalysts, stannous octanoate (Sn(Oct)2)dthat is tin (II) 2-ethylhexanoatedis the most widely used due to various reasons, for example: ready solubility in organic solvents and the molten bulk lactide, good stability during storage, and excellence in catalytic activity.[33]

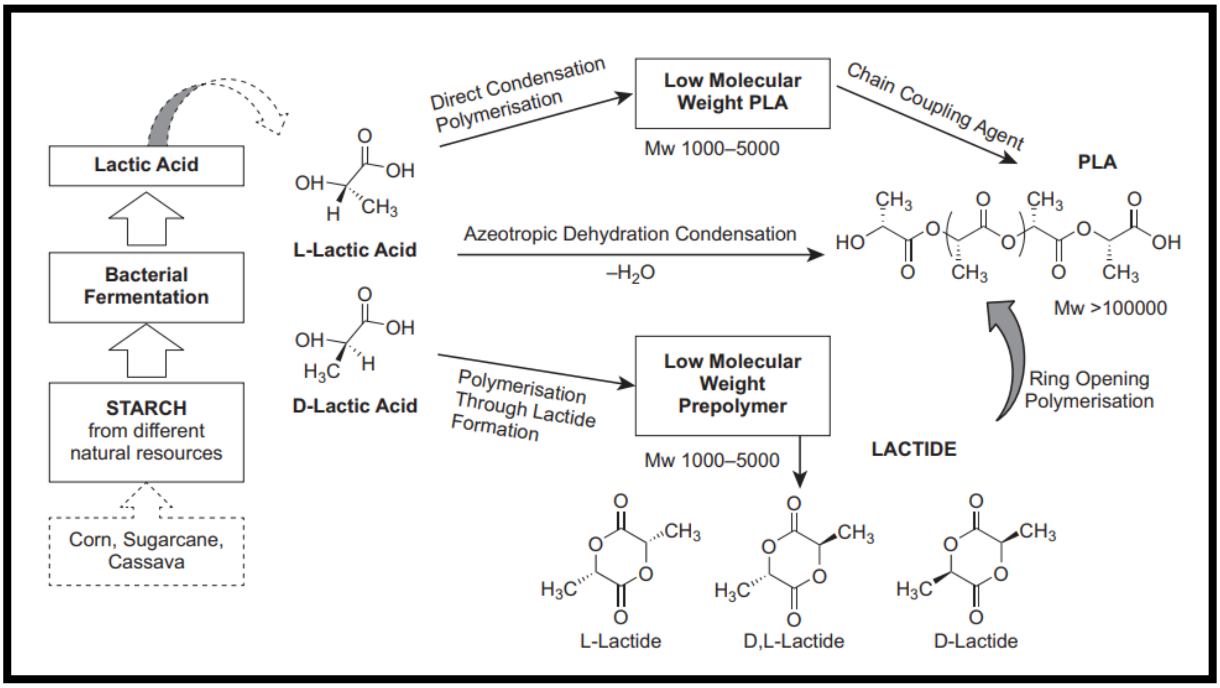


Figure 25 Synthetic routes to PLA[33]

3.2 PROPERTIES OF PLA

The properties of PLA depend on the component isomer, processing temperature, annealing time, and molar mass. PLLA is semicrystalline with a crystallinity of around 37%, a crystalline melting temperature (Tm) between 170 and 180 C, and a glass transition temperature (Tg) between 60 and 67 C. PLLA can be normally dissolved in halogenated hydrocarbons such as chloroform, methylene chloride, 1,1,2-trichloroethane, and dichloroacetic acid, and is partially soluble in ethyl benzene, toluene, acetone, and tetrahydrofuran. PDLLA is an amorphous polymer and has a Tg in the region of 50e60 C. Because of its crystallinity, PLLA is a more slowly degrading polymer than PDLLA. High molar mass PLLA can take from two to five and half years for total resorption in vivo (Middleton and Tipton, 2002; Bergsma et al., 1995), while PDLLA is hydrolyzed and loses its chain length within 1e2 months and completely loses its mass within 12e16 months (Maurus and Kaeding, 2004). Because of this slow degradation rate and good tensile strength and modulus, PLLA is favored for use in load-bearing applications in the body.[34]

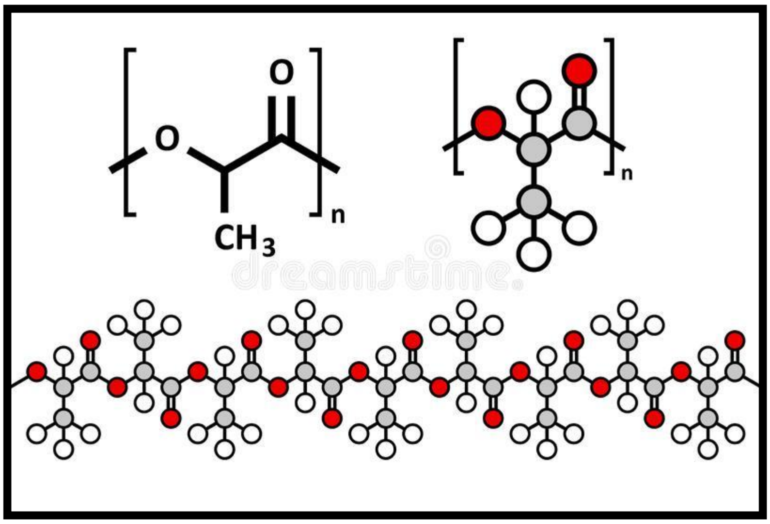


Figure 26 Crystal structure of PLA[35]

3.3 USES OF PLA

PLA, which is made from lactide, which is formed from lactic acid, a harmless chemical inherent in the human body, is commonly used as a food packaging material. As a result, when PLA is utilised as a packaging material, food contamination can be overlooked. PLA has a crystallinity similar to polyethylene terephthalate (PET), which is commonly used for beverage containers due to its high strength, good gas barrier qualities (O_2, CO_2), and low cost. PET and PLA have a gas permeability roughly 1000 times that of low-density polyethylene (LDPE), and LDPE has a gas permeability about 100 times that of silicones.

Therefore, PLA can provide an adequate barrier against water vapor and gases, enabling it to prevent food degradation and oxidation while preserving the aromas and the flavors of the food. However, the limitations of PLA for packaging are because of properties such as flexural strength and impact strength that make PLA brittle, and its narrow processing window.[36]

3.4 HOW TO IMPROVE THE PROPERTIES OF PLA ?

With the limitations of thermal properties and brittleness, PLA is frequently modified to improve its properties by copolymerization and blending with other polymers. These two strategies for improving PLA properties have been extensively investigated as useful routes to vary the structure of the copolymer over a wide range, yielding products with particular combinations of desirable properties.

Copolymerisation- PLA copolymers with other polyesters, such as poly(glycolide) (PGA), PCL, poly(beta-hydroxybutyrate) (PHB), poly(beta-hydroxyvalerate) (PHV), poly(trimethylene carbonate), have been prepared via either polycondensation of lactic acid or ROP of lactide with other monomers. Lactides in L- and DL-forms are frequently copolymerized with glycolide to produce poly(lactide-co-glycolide) (PLGA) in various compositional ranges to adjust mechanical properties, crystallinity, and hydrolytic degradation. PLA has also been extensively copolymerized with poly(ethylene glycol) (PEG), which is a biocompatible and hydrophilic polymer, to improve the hydrophilicity of PLA and its usefulness as a drug delivery system.

Blends- The main objective of blending PLA is to improve its mechanical properties especially the brittleness to decrease the price and to help improve processability, optical properties, and degradation. Many polymers, both petrochemical-based and bio-based, including nondegradable and degradable plasticizers, are blended with PLA for different applications.

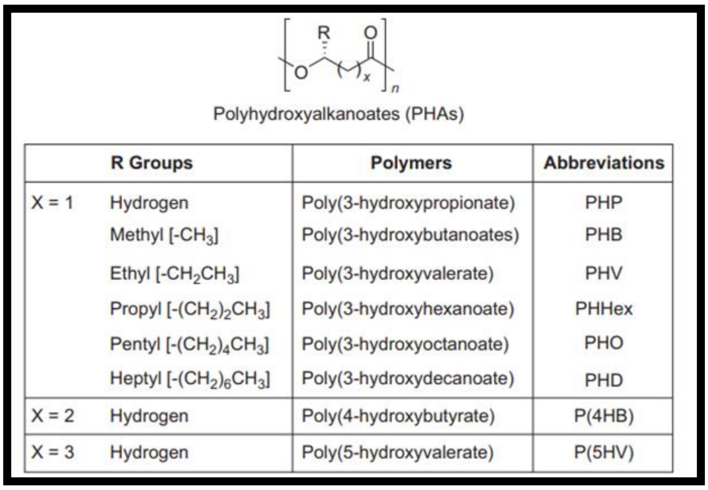
Biodegradable Blends- PLA has been blended both with plasticizers and with a number of candidate petroleum-based polymers. PCL has been extensively used to blend with PLA to increase impact strength and solve the brittleness problem, as it is a flexible polymer with low glass transition temperature and is also hydrolytically or enzymatically degradable. The PLLA-PCL-PLLA copolymer acts at the phase boundary as an interfacial agent and produces a more homogeneous distribution of particle size and a lowering of the fraction of large domains. Adding an amorphous PDLLA can affect the PLLA crystallization, as PDLLA is believed to disturb the diffusion of PLLA chains to the growth sites of PLLA crystallites, acting to reduce the brittleness of the semicrystalline PLLA. Starch is an attractive polysaccharide to blend with PLA because it offers advantages in terms of cost and biodegradability, but it is thermodynamically immiscible with PLA. Therefore, a third type of componentda compatibilizer, plasticizer, or block copolymerdis often added into PLA/starch blends to reduce the interfacial energy. This improves dispersion and consequently enhances adhesion between binary polymer phases. In order to induce better interaction between PLA and other biodegradable polymers, the blends are prepared through reactive blends, which can promote chemical reactions between the two polymers by adding a reactive third component with appropriate functional groups or a catalyst.

Plasticizer-Based Blends- Plasticizers have been used to modify properties of PLA such as glass transition temperature, toughness, and processability. However, the problem of using plasticizers in PLA blends is normally the slow migration of plasticizers into the surface of materials and phase separation during storage. Bulk properties, crystallinity, and miscibility of PLA are all influenced by the plasticizer end groups.[37]

CHAPTER 4

POLYHYDROXYALKANOATE AS A BIOPLASTIC

Polyhydroxyalkanoates or PHAs are aliphatic biodegradable polyesters that have different pendent groups at the beta-position of the repeat unit. They are a family of bacterially synthesized polymers that exist either as homo- or copolymers. The first polymer within the PHA family is poly(3- hydroxybutyrate) (PHB), sometimes abbreviated as P(3HB), which has a pendant methyl group. It is produced by bacteria and algae, with a high degree of crystallinity (Moore and Saunders, 2013). PHB has brittleness and stiffness that are unsuitable for many applications. The mechanical and physical properties of PHB are in some ways similar to PP, except that it is biodegradable. The next member of the PHA family, having a pendant ethyl group, is poly(3-hydroxyvalerate) or PHV. Having an ethyl group (HV unit) instead of the methyl group of PHB gives PHV more flexibility and less crystallinity than PHB.[38]



	R Groups	Polymers	Abbreviations
X = 1	Hydrogen	Poly(3-hydroxypropionate)	PHP
	Methyl [-CH_3]	Poly(3-hydroxybutanoates)	PHB
	Ethyl [-CH_2CH_3]	Poly(3-hydroxyvalerate)	PHV
	Propyl [-$(CH_2)_2CH_3$]	Poly(3-hydroxyhexanoate)	PHHex
	Pentyl [-$(CH_2)_4CH_3$]	Poly(3-hydroxyoctanoate)	PHO
	Heptyl [-$(CH_2)_6CH_3$]	Poly(3-hydroxydecanoate)	PHD
X = 2	Hydrogen	Poly(4-hydroxybutyrate)	P(4HB)
X = 3	Hydrogen	Poly(5-hydroxyvalerate)	P(5HV)

Figure 27 Polyhydroxyalkanoate family[38]

4.1 PRODUCTION

Production of PHAs is still on a small to medium scale compared to fossil-based polymers and also to that of some biobased polymers such as PLA and PBS. The complicated bacterial synthetic route and purification process limits the production giving a low efficiency, resulting in high production costs. PHAs are synthesized and stored by Gram-negative and Gram-positive bacteria under limitation of nutrients. This occurs through the fermentation of a wide range of substrates, especially sugars (e.g., glucose, sucrose, and xylose), fatty acids, alkanes, alkenes, and alkanoic acid. All polymers in the PHA family are completely biosynthetic and biologically polymerized, which is different from other bio-based polymers**.** Of the various members of the PHA family, only PHB, PHBV, and poly(3-hydroxyhexanoate-co-3-

hydroxyoctanoate) (P(HH-co-HO)) have been produced at relatively high concentrations with high productivity (Lee, 1996). Poly(3-hydroxybutyrate) (PHB) was first discovered in 1926 by Lemoige in the bacterium Bacillus megaterium. There are three steps in the metabolic pathway by which PHB is produced. Firstly, two molecules of acetyl-CoA are combined using 3-ketothiolase (PhaA) to form acetoacetyl-CoA. Secondly, 3-hydroxybutyryl-CoA is produced via the reduction of acetoacetyl-CoA by NADH using the enzyme acetoacetyl-CoA reductase (PhaB). Finally, PHB is polymerized from 3-hydroxybutyryl-CoA using PHB synthase (PhaC), coenzyme-A being liberated. During normal bacterial growth, 3-ketothiolase will be inhibited by free coenzyme-A released from the Krebs cycle. However, if entry of acetyl-CoA into the Krebs cycle is restricted, such as during noncarbon nutrient limitation, the excess acetyl-CoA is channeled into PHB biosynthesis.

4.2 PROPERTIES

PHAs are susceptible to degradation under both aerobic and anaerobic conditions, as well as by thermal or enzymatic hydrolysis routes. In the biological system of animal tissues, PHAs can be degraded using microbial depolymerases and by nonenzymatic and enzymatic hydrolysis. Degradation by depolymerases initially produces oligomers that further break down into monomers. However, the biodegradation rate of PHAs depends on the environmental conditions such as temperature, moisture, pH, and nutrient supply, as well as the monomer composition, additives, surface area, and crystallinity of materials. In human tissue, PHAs are immunologically inert, and having slow degradation, they are usable as devices inside the body.

HOW TO ENHANCE THE PROPERTIES OF PHA FOR BETTER PERFORMANCE FOR BIOPLASTC APPLICATIONS?

PHAs have exhibited features that are similar to the features of conventional synthetic plastics, but with a significantly lower environmental impact on the production process. With an increase in the energy crisis, the renewable and sustainable behaviors of PHAs render them the new generation of eco-friendly plastics based on non-petroleum chemicals. However, many challenges have restrained PHA applications, including complicated genetic engineering processes for producing new PHAs, inadequate mechanical strength and a lack of functionalities. The high production cost and poor processability of PHA have limited their competitive forces to substitute traditional synthetic plastics. Therefore, modification of PHAs to achieve better performance has attracted increasing attention from industry and scientific research organizations and has gained excellent achievements in materials and medical applications. Blending is one of the most useful techniques to improve the properties of polymer matrixes and lower material costs. Many polymers, compatibilizers, and other additives have been used to form blends with PHAs, especially PHB and PHBV. Examples include PLA, chitin, poly(vinyl alcohol), PCL, PBS, poly(butylene adipate-co-terephthalate), poly(vinyl acetate), poly(ethylene oxide), cellulose esters, rubber, and starch. A large number of PHA blends have involved PLA. Among all PHA blends, PHBV/PLA blends have been identified as particularly attractive to be studied in terms of morphology, rheology, and mechanical properties. The PHA blends with different types of biodegradable polymers, such as starch, cellulose derivatives, lignin, PLA and PCL, and the chemical modification PHAs to form copolymers in various block/graft architecture.

Modified PHAs have been employed to develop engineering material resins by regulating various physicochemical properties and to enhance the robustness of their use in different biomedical applications, including advanced drug delivery for cancer therapy, gene delivery and tissue engineering in emerging fields. The use of PHAs in the biomedical fields is particularly promising. For biomaterial applications, stringent requirements exist for an implantable system: first, a benign material is required; second, very low toxicity is needed; and third, the material should exhibit long-term stability in a wet, oxygen- and enzyme-rich environment. The living body possesses glutathione and other related enzymes (such as glutathione reductase and glucose-6-phosphate dehydrogenase), which protect various organs from chemical and oxidative stress. The presence of these enzymes can affect the stability of the materials that are implanted in the body. Future PHA material development should emphasize the consideration of these factors. Biodegradable and polymeric soft materials present the future of tissue engineering substrates due to their high water content, density, degradability and rheological properties, which mimic the characteristics of human tissue. Stimuli-responsive PHA-based soft materials have emerged as the material class with the most potential to succeed as an ideal implantable scaffold substitute because it possesses not only the properties of polymeric hydrogels but also added functionalities, such as the change from reversible sol to gel, due to external stimuli that facilitate easy implementation during surgery. In addition, the majority of these hydrogels have shown their efficacy as a drug delivery system.[39]

As blending is one of the most useful techniques to improve the properties of polymer matrixes and lower material costs, it is not surprising that this area has been well studied. Many polymers, compatibilizers, and other additives have been used to form blends with PHAs, especially PHB and PHBV. Examples include PLA, chitin, poly(vinyl alcohol), PCL, PBS, poly(butylene adipate-co-terephthalate), poly(vinyl acetate), poly(ethylene oxide), cellulose esters, rubber, and starch. A large number of PHA blends have involved PLA. Among all PHA blends, PHBV/PLA blends have been identified as particularly attractive to be studied in terms of morphology, rheology, and mechanical properties. For example, a 20e50% loading of PLA in PHBV was observed to increase the flexural strength and elastic modulus of the blends (but not tensile strength and elongation at break) when compared with unblended PHBV (Modi et al., 2013). In another work, the addition of PLA to the blend results in a remarkable increase in the complex viscosity of PHBV, and the barrier properties were found to be markedly dependent on blend ratio. Taken together, these results suggest significant molecular interaction between the blend components. PHB has also attracted attention, particularly for medical applications, and blends with chitin, poly(3-hydroxyoctanoate) (PHO) and poly(ethylene-co-vinyl acetate)/starch all show interesting behavior. It was reported that the crystallinity of PHB is reduced in chitin blends, probably due to the hydrogen bonding interaction between carbonyl groups of PHB and secondary amine and hydroxyl groups of chitin in the amorphous region of the blend. The behavior of poly(ethylene-co-vinyl acetate) was more straightforward and, as expected, produced blends having enhanced toughness.

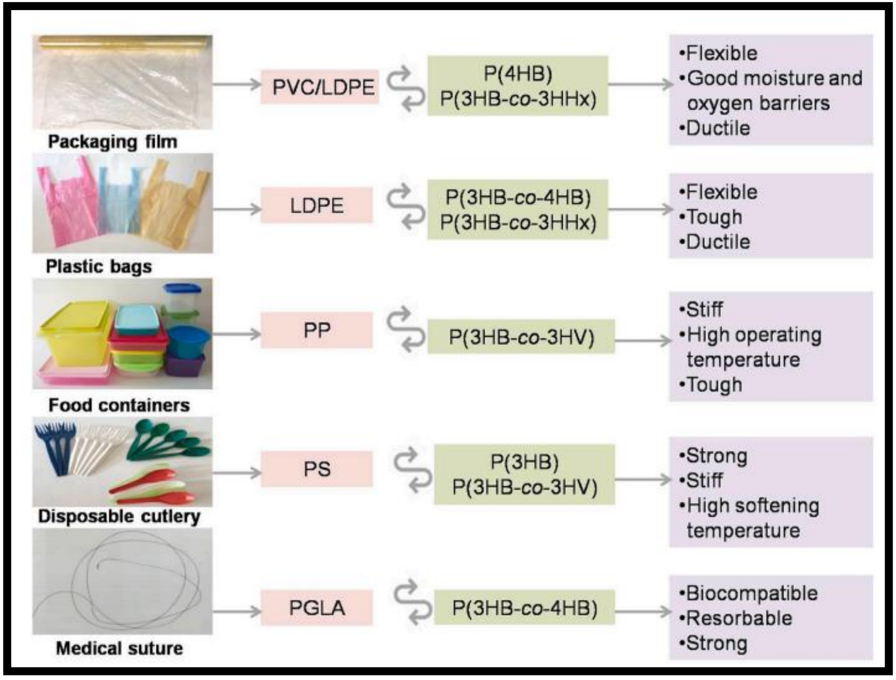


Figure 28 Prospective Substitutions by PHA[39]

Substitutions by PHA Prospective. This figure shows how day to day products that use petroleum based plastics can be manufactured with variants of PHA hence ensuring that the products are biodegradable and yet maintain the physical properties required for their application. Modified from“PHA bioplastics a ‘tunable’ solution for convenience food packaging” by Lingle, R.

CHAPTER 5

CONCLUSION

To further advance the application of bioplastic, it is very necessary to manage carefully the waste disposal. Recycling appears the best solution from that point, for disposal of the bio-based product to maximize the environmental footprint as well as reduce the renewable resources consumption. Recycling of a bioplastic leads to an overall decrease of environmental impact which may associated with the production and disposal of the bioplastic itself. It is worth noting that due to the improper management and applications of bioplastics, the information reported in this paper can be useful for the environmental reliability. PHA and PLA materials are the main resource to substitute conventional plastic use in most of the engineering applications fields. In order for PHA and PLA to replace petroleum-based plastics, they still need to go through many developments, innovations, and research in many ways. Nowadays, the PHA costs of production are too high, but further research on technology and sourcing can reduce manufacturing costs for a versatility and heterogeneity and strengthen the applications.

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