BIOPLASTICS IN THE CONSUMER MARKET

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ABSTRACT

Bioplastics in the Consumer Market

Elena Mertes Strom

The global production and mismanagement of plastic has led to plastics deposited and scatted across marine environments. Conventional plastic, which most Americans encounter every day, is produced from fossil fuels and lacks the ability to fully break down upon disposal, breaking down into microplastics that can remain in the natural environment for hundreds of years. Moving away from petroleum-based plastics could lead to a reduction in greenhouse gas emissions and decrease plastic particles in the ocean. Based on existing literature, there are three biopolymers that could serve as replacements to conventional plastics in the marketplace. These biopolymers are seen as viable replacements because of their fast biodegradation and low carbon footprint associated with production. These three biopolymers are Polylactic acid (PLA), Polybutylene succinate (PBS) and Polyhydroxyalkanoates (PHAs). This study describes the properties of each biopolymer, evaluates the existing research and studies conducted on each biopolymer, and provides analysis determining which biopolymer might be able to replace conventional plastics based on the criteria of carbon footprint, energy, and cost. When simulating the polymers for the production of a water bottle and comparing to conventional plastic PET (Polyethylene terephthalate),. PLA was the most likely biopolymer to replace PET because of a lower carbon footprint and lower energy usage during production. However, PLA is more expensive than PET and has poor biodegradation in the marine environment (15.86 years). PHB had a lower carbon footprint and lower energy usage than PET with an estimated biodegradation period of 1.19 years. However, PHB is more expensive than both PLA and PET. Because of these results, there needs to be more research focused around strengthening biopolymers' mechanical structure, lowering costs of biopolymer production, and for PLA – improving biodegradation in the marine environment.

Keywords:

Bioplastic, Biodegradation, Marine Environment, Polymers

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Chapter 1

1. INTRODUCTION

The mismanagement of plastic waste has become a global issue. In 2010 it was estimated that 4.8 to 12.7 million metric tons of plastic entered the ocean (Jambeck et al., 2015). As global production continues to increase (Plastics Europe & Conversio Market & Strategy GmbH, 2019), so does the chance of plastic being deposited into the world's oceans. Plastic packaging is the most abundant material collected from the ocean's surface (Law, 2017). Plastic packaging waste consists of trash bags, utensils, and other single-use products that are expected to be discarded within three years from when they were produced (Gewert et al., 2015). These products are most commonly produced from fossil fuels, using petroleum in the production of the plastic.

Plastics are considered to be extremely detrimental to the environment because of their extended afterlife and their inability to biodegrade (Venkatachalam & Palaniswamy, 2020). In the ocean environment, waves and sun will break down plastics into macroplastics or microplastics depending on the size of the pieces (Gewert et al., 2015). These plastics pose a threat to the ocean creatures in the marine environment, with 86% of sea turtles and 44% of sea birds being susceptible to death from ingestion of the plastics (Venkatachalam & Palaniswamy, 2020). To remedy this plastic pollution crisis, bioplastics are seen as a strong alternative.

Conventional plastics used today and bioplastics are both high molecular weight (i.e., have high impact resistance per unit mass) organic polymers. When it comes to producing a plastic bottle, high impact resistance is crucial in ensuring the product (i.e. water, soda, medicine, etc.) is secure in the bottle and the bottle is not easily broken. Unlike conventional plastics, the polymers used to make up bioplastics are all natural organic polymers, sourced from renewable materials including corn, algae, sugarcane, and starches (Venkatachalam & Palaniswamy, 2020). Converting from fossil fuel-based plastics to bioplastics will aid in reducing greenhouse gasses emitted into the atmosphere, as a result of fossil fuel extraction and post-use incineration. Bioplastics are also more likely to resolve concerns over waste proliferation since bioplastics biodegrade at a faster rate than conventional plastics (Emadian et al., 2017). Thus, the conversion from petroleum-based plastics to bioplastics could limit the plastic particles in the marine environment through faster biodegradation times and less environmental impacts from production.

However, bioplastics are not as widely distributed as conventional plastics. Fossil fuel-based plastics occupy 80% of the plastic packaging market (Brizga et al., 2020). These plastics are still the most common in the market because of their strength and affordability. Based on existing literature (Changwichan et al., 2018), there are three polymers that could serve as replacements to conventional plastics in the marketplace. These three are Polylactic acid (PLA), Polyhydroxyalkanoates (PHAs), and Polybutylene succinate (PBS). PLA is made from polylactic acid and is currently being produced commercially on a small scale by company, NatureWorks LLC (NatureWorks, 2009; Vink et al., 2003) using corn in their production. The main concern with PLA is the cost of the polymer, with another concern being its brittleness (Madhavan Nampoothiri et al., 2010). While brittleness may be good for biodegradation, it is a bottleneck for PLA in commercial applications, making it less easily processed into plastic packing (Madhavan Nampoothiri et al., 2010).

PHA is a broad category of polymers, containing PHB or polyhydroxy butyrate and PHBV(polyhydroxy butyrate-valerate). PHAs are produced through bacterial fermentation of lipids, sugars, or chemical substances like chloroform, methylene chloride or propylene chloride (Venkatachalam & Palaniswamy, 2020). PHAs are produced by using bacterial cultures from microorganism strains that ferment different starch-based medias (Venkatachalam & Palaniswamy, 2020). The choice of the media for fermentation is the biggest driver of PHAs price, which is high compared to conventional plastics (Rudnik, 2012; Venkatachalam & Palaniswamy, 2020). PHAs are also very brittle, and to improve their properties, sometimes researchers combine PHA with different monomers to make them stronger and less easily bent or stretched (Venkatachalam & Palaniswamy, 2020). Dilkes-Hoffman (2019) describes the biodegradation of biopolymer PHA in the marine environment, showing that PHA can degrade in the marine environment, but the time of degradation is different depending on the plastic product (Dilkes-Hoffman et al., 2019). For example, a plastic bottle of PHA would take 1.5 to 3.6 years to biodegrade and a plastic bag made of PHA would degrade in only 0.1 to 0.2 years (Dilkes-Hoffman et al., 2019).

PBS is a petroleum-based polymer that is biodegradable (Cinar et al., 2020). PBS is also commercially available and has excellent processability, being used in mulching films, compostable bags, nonwoven sheets and garments, catering goods, and foams (Rafiqah et al., 2021). Although PBS is most commonly produced from petroleum, it can be produced from either renewable or non-renewable sources (Shaiju et al., 2020). Some drawbacks of PBS are its low strength and resistance to impact and price compared to conventional plastics (Rafiqah et al., 2021; Shaiju et al., 2020).

Just as all of these bio-polymers have positive attributes, such as faster biodegradation and a smaller environmental footprint, they all also have varying drawbacks, relating to their price, mechanical make-up, and processability. More research is required that evaluates these polymers comprehensively, looking at all their positive attributes and drawbacks together. This research will aid in determining the bioplastic that has the closest price to PET, the lowest carbon footprint during production, the lowest embodied energy and the fastest biodegradation in the marine environment. Carbon footprint is measured as kilograms per kilograms of carbon equivalent and represents the mass of carbon dioxide equivalent arising directly from the production of a material per year divided by the mass of the material shipping per year (Sustainability et al., n.d.). Embodied energy is the sum of energy required to produce the polymer.

This data is needed as industries seek a plastic that will degrade in the marine environment, but also is able to be adopted easily into the commercial market. We are constituting easy adoption into the commercial market as materials that perform similar to or better than the conventional plastic PET in mechanical structure. In this paper, the mechanical structure properties that are used to analyze and compare the polymers are density, Young's Modulus, price, tensile strength, yield strength, and elongation at break.

Building on previous work, this research collects and analyzes data on the biopolymer's biodegradation in the marine environment, the biopolymer's embodied energy, carbon footprint, as well as the multiple mechanical properties of the biopolymers. We further analyze the properties of each bioplastic polymer, evaluating the existing research, as well as, conducting material analysis of each polymer, based on data provided in existing research. We examine these polymers in the software Granta Edupack, a material analysis software that contains a material database and can be used to analyze material inputs and production processes. This software allowed us to input the mechanical properties of each polymer and use that data to generate the carbon footprint, embodied energy and price, of one plastic bottle made from a particular polymer. We utilized the literature for the data that was input into the software. After generating these results for the varying polymers and comparing them to conventional PET, we recommend the most well-suited bioplastic for commercial production of plastic bottles. This data is important as it displays the differences between conventional plastics and bioplastics that are applicable to manufacturers and plastic producing companies, outlining how their mechanical structure can impact their price and their energy costs. The data is also useful as it shows the environmental impacts associated with the various bioplastics. Therefore, manufacturers/companies considering both price, energy use, and environmental impact, can have a comprehensive evaluation of the biopolymers available. Ultimately, we aim to address the issue of plastic pollution, by providing information to inform the choice of different packaging production materials.

Chapter 2

2. LITERATURE REVIEW

2.1. Plastic Impact Globally

The current global dependence on plastic materials is detrimental to the environment. No commonly used plastics are biodegradable (Jambeck et al., 2015). Additionally, plastics have been detected worldwide in various types of marine environments (Law, 2017). The most common form of plastic waste is plastic packaging. In 2003 the U.S. packaging waste accounted for 78.81 million tons (Kale et al., 2007). Plastic packaging waste consists of trash bags, utensils, and other single-use products that are expected to be discarded approximately three years from when they were produced (Gewert et al., 2015).

In 2020 there was a total of 367 million tons of plastic produced (Tiseo, 2021). Mismanaged plastics may be deposited into the marine environment. The quantity of plastic produced is expected to increase, with global plastic consumption in the next 20 years expected to be more than 600 metric tons of plastic consumed (Selvamurugan & Sivakumar, 2019).

2.1.1. Production Inputs

Plastics are organic polymers composed of varying elements. And polymers are chemical compounds, that when combined, can be modified to provide a wide range of applications (EASAC, 2020). The most common element making up conventional plastics is polyethene, which is typically obtained from petroleum or natural gas. The three most commonly used polymers for the production of plastic packaging products are polyethene (PE), polypropylene (PP), and polyethene tere- phthalate (PET) (Plastics Europe & Conversio Market & Strategy GmbH, 2019). These three plastics are all obtained from petroleum or natural gas and make up 80% of the plastic packaging market (Brizga et al., 2020). PE resin is used to produce reusable bags, trays and containers, agricultural film, food packaging film, as well as, toys, milk bottles, shampoo bottles, pipes, and houseware (Plastics Europe & Conversio Market & Strategy GmbH, 2019). PP resin is used to produce food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, bank notes, and more. And lastly, PET resin is commonly used to produce bottles for water, soft drinks, juices and cleaners (Plastics Europe & Conversio Market & Strategy GmbH, 2019). These plastics are the most prominent plastics used because of their strength, resilience and price.

While beneficial for resiliency and cost, the production of these conventional plastics has negative environmental implications. Plastic production can create toxic chemicals such as dioxins, which contribute to global warming through being released into the atmosphere upon production (Thiruchelvi et al., 2020; Yadav et al., 2020). Plastics also produce emissions through their disposal. The most common forms of disposal methods for plastics are landfills, recycling, or incineration. Incineration or burning of the plastic, can release carbon dioxide and methane into the atmosphere and contribute further to global climate change (Venkatachalam & Palaniswamy, 2020).

2.1.2. Improper Handling

Improper disposal of plastic waste is a significant source of environmental pollution (Selvamurugan & Sivakumar, 2019). Plastic packages are made of polymers and are first created in the form of pellets. If those small plastic pellets are mishandled or spilled during the production process, they can have a large impact on the natural environment, commonly through ingestion from species in aquatic environments (Law, 2017).

Plastic that has not been properly disposed of can pose threats to waterways and biological inhabitants, such as marine mammals and marine birds, t (Venkatachalam & Palaniswamy, 2020). Sea turtles, sea birds, whales, seals and sea lions, marine fish and crustaceans all have been shown to either ingest plastic or become entangled in plastic (Elias, 2017). The top three plastic items that were collected in the International Coastal Cleanup in 2015 were caps and lids, plastic beverage bottles and food wrappers and containers (Elias, 2017). In just one day in 2015, over one million plastic beverage bottles were collected from coastal shores (Elias, 2017).

Plastics are also a threat to the marine environment as the breakdown process or biodegradation is even slower than on land (Elias, 2017). This is largely because plastics in the ocean are not exposed to thermal oxidation which occurs on land (Elias, 2017). Additionally, plastics that are polluted tend to absorb chemical pollutants present in the ocean, such as DDT or dioxins (Elias, 2017). This further increases the plastic's toxicity and in turn increases the threat to the marine species ingesting the plastic.

2.1.3. PET

PET or polyethylene terephthalate is the most common form of plastic used currently to produce plastic bottles (Plastics Europe & Conversio Market & Strategy GmbH, 2019). PET is used commonly for bottled water and food because it is hygienic, strong, resistant to attack by microorganisms (*PET Basics*, 2021). PET is also preferred for food and beverage packing because it is lightweight, not easily breakable, and easy to transport (*PET Basics*, 2021).

However, PET's resilience and strength can lead to environmental issues when the plastic is polluted. Being that it is not breakable and cannot be attacked by microorganisms, PET products could take nearly 450 years to fully biodegrade (Davis, 2021). And the recycling rate of PET in 2018 was only 29.1 percent (EPA, 2021). There is little known about PET's ability to degrade in the marine environment. In 2016, Ioakeimidis and colleagues conducted the first study looking at PET samples degradation in the marine environment (Ioakeimidis et al., 2016). This study discusses the difficulty in determining biodegradation time of PET, as biodegradation rates depend on the local environment where the plastic is present (i.e. ocean surface, ocean floor, deep ocean). While Ioakeimidis and colleagues are still gathering data on the biodegradation of PET in the marine environment, they found that the surface roughness or texture of the PET plastic was still present after 15 years in the marine environment (Ioakeimidis et al., 2016). Muller et al. identified biodegradation rates for PET to be between16 to 48 years (Müller et al., 2001), however their research was not specific to the marine environment.

Aside from biodegradation, there is also concern surrounding PETs toxicity. Many PET bottles are produced by using antimony-based catalysts in their production in order to make the plastic clear (Westerhoff et al., 2008). Antimony has been proven toxic and is currently regulated by the U.S. Environmental Protection Agency (EPA) (Westerhoff et al., 2008). There is concern surrounding the leaching of antimony into drinking water as well as into the environment when littered (Westerhoff et al., 2008).

2.2. Bioplastic

2.2.1. Production Impact

Bioplastics are also seen as an avenue to reduce carbon dioxide emission and energy consumption through their production (Selvamurugan & Sivakumar, 2019). Bioplastic bottles are produced through the same process of conventional plastic bottles, and that is through the process of injection blow molding (Ashter, 2016). However, special attention needs to be given to biopolymers because of their moisture content. Biopolymers have a high moisture content, so before processing, moisture needs to be removed from the polymer (Ashter, 2016). Additionally, most conventional polymers are processed at high temperatures. These high temperatures can alter the mechanical properties and degradation of the material. Therefore, biopolymers should be processed at low temperatures and this often leads to modification of the processing equipment (Ashter, 2016). However, processing at low temperatures could aid in a reduction of energy.

According to paper by Selvamurugan and Sivakumar in 2019, the production of bioplastics could emit 80% less carbon dioxide and consume 65% less energy (Selvamurugan & Sivakumar, 2019). The production of bioplastics large-scale could lead to preservation of non-renewable resources and shift towards using more renewable resources, also avoiding environmental risks associated with fossil fuels (Selvamurugan & Sivakumar, 2019). However, bioplastics are produced on a much smaller scale than conventional plastics. Currently, bioplastics make-up 300,000 metric tons or 1% of the plastics market (Madhavan Nampoothiri et al., 2010). But the bioplastic market is growing 20-30 percent yearly (Madhavan Nampoothiri et al., 2010).

2.2.2. Cost

Bioplastics have disadvantages that should be acknowledged. Similar to conventional plastics, improper handling and uncontrolled disposal can be harmful to the environment (Selvamurugan & Sivakumar, 2019). Another drawback of bioplastics is the cost. Because bioplastics are relatively new they are not cost competitive with petroleum-based plastics (Venkatachalam & Palaniswamy, 2020). Additionally, the cost of bioplastics commonly depends on the cost of the biomass that is needed for production (i.e. corn, sugarcane, algae, etc.), as well as the size of production, with the size of production having a great effect on the price (Venkatachalam & Palaniswamy, 2020).

2.2.3. Toxicity

There is also concern about the toxicity of bioplastics. While bioplastics are sourced from natural materials, little is known regarding what chemicals they contain and the safety of these compounds (Zimmermann et al., 2020). Study conducted from

Zimmermann et al. concluded bioplastics are similarly toxic to conventional plastics and urge a need to focus more research towards chemical safety when designing biopolymers (Zimmermann et al., 2020). The toxicity of these bioplastics illustrate that bioplastics still pose threats to wildlife under degradation in the marine environment. However, depending on their rate of biodegradation, that impact can be minimalized.

2.2.4. Biodegradation

Unlike fossil fuel-based polymers, bioplastic polymers are more likely to biodegrade because of their composition of natural materials. Biodegradation is the ability for a material to degrade into environmentally acceptable materials such as water, carbon dioxide, and biomass (Karak, 2016). Key attributes that influence the ability of these bioplastics to biodegrade in certain environments include temperature, pH and moisture content (Emadian et al., 2017).

The process of biodegradation is outlined in three steps (Emadian et al., 2017). The first step being biodeterioration, which is the modification of the polymer properties once microorganisms have been in contact with the substance. The second step is bio fragmentation which is when those polymers break down and convert into oligomers or monomers by microorganism activity. And the third and final step is assimilation, when the microorganisms convert the polymer into carbon dioxide, water, and biomass (Emadian et al., 2017).

2.2.4.1. Biodegradation Standards

Biodegradation amongst plastics can be measured through using the American Society for Testing Materials or ASTM Standards. The standards are wide ranging, studying materials such as iron and steel, metals, paints, plastics, rubber, nuclear technology, among others. A standard is a document that acts as an evaluation criteria or way to categorize a material's characteristics. Buyers and sellers can use the standards incorporating them into contracts, scientists and engineers also use the standards in laboratories and architects refer to them in their plans. The standards are voluntary, meaning their use is not mandated (ASTM, 2021).

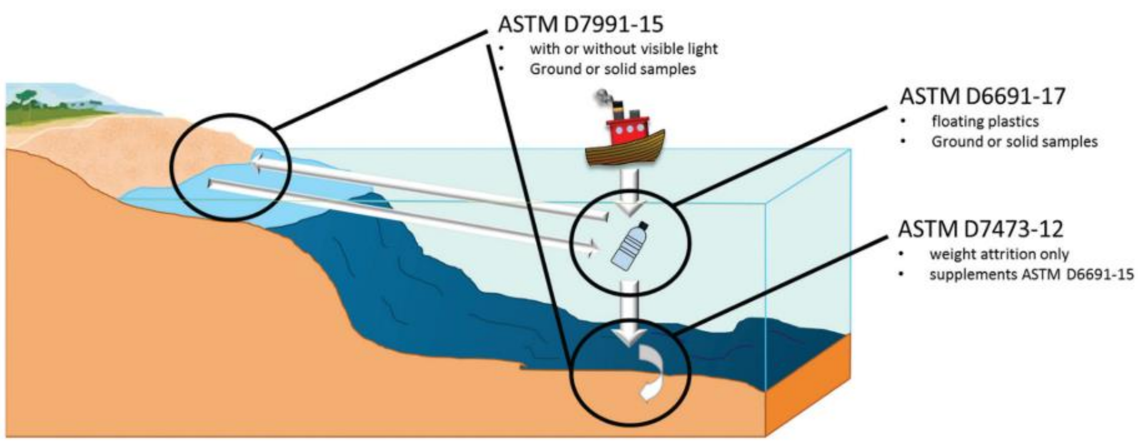


Figure 1. ASTM Standards for the marine environment. Image sourced from Meerbeboer et al., 2020.

The ASTM standards evaluate plastic biodegradation in multiple environments and include three standards to study various plastics in the marine environment. The three are 1) ASTM D6691-17, which studies floating plastics at 30 degrees Celsius; 2) ASTM D7472-12, which studies plastics buried in the sediment underwater; and 3) ASTM D7991-15, which looks at plastics in a combination of water and sediment, with possible light imitating day light and temperatures of 15 to 25 degrees Celsius (Meereboer et al., 2020). Figure 1 displays the three standards.

2.2.4.2. Bioplastic Biodegradation

Biodegradation is an import attribute of bioplastics as the process mimics that of a plant death. When a plant is growing it is taking in carbon dioxide, and when a plant dies it releases carbon dioxide. Similarly, when bioplastics are being produced, the plants/ natural materials that form the biopolymers take in carbon dioxide, and then release carbon dioxide when the bioplastics biodegrade (Venkatachalam & Palaniswamy, 2020).

In order to create a biodegradable plastic, the polymers must be derived from biological sources. Biological sources could include starch/food sources, microorganisms, soy, algae, cellulose, as well as less studied alternatives (Venkatachalam & Palaniswamy, 2020). The starch-based plastics can be made from wheat, potatoes, rice or corn sources, and are the most utilized bioplastic in the market currently, making up 80% of the bioplastic market (Venkatachalam & Palaniswamy, 2020).

The biodegradation process requires certain conditions in order for bioplastic polymers to biodegrade in various environments. Yet, despite the abundance of plastics in the world oceans, there is a significant lack of knowledge of the biodegradation of plastics in water (Emadian et al., 2017) or aquatic environments (Karamanlioglu et al., 2017). Plastic biodegradation is crucial in solving the problem of pollution in the ocean. For this reason, we go into more depth on the three common forms of bioplastics (PLA, PHA, and PBS), and their biodegradation characteristics, environmental impacts throughout their life cycle, and associated costs.

2.3. PLA

PLA or polylactic acid is a biodegradable thermoplastic (Datta et al., 1995) and a polyester polymer produced from the condensation of lactic acid (Ho et al., 1999). PLA polymers are transparent after production which is crucial when it comes to the needs of packaging materials such as water bottles (Datta et al., 1995). PLA is already present commercially, projected to produce approximately $3.1 to 4.4 million per year (Datta et al., 1995). The main sources PLA is derived from include corn, sugar, potato and sugar cane. The lactic acid that makes up PLA is produced through the fermentation of renewable sources, such as corn, sugar, or potato.

2.3.1. Biodegradation

PLA shows strong biodegradation in composts and soils, taking 11 months to fully degrade in a home composting unit (Emadian et al., 2017) consisting of nutrient rich soil from the breakdown of food and yard wastes. PLA also shows sufficient biodegradation in agriculture soils, this is presumed to be because of the high organic content of the agriculture soils, providing the PLA polymers with suitable microorganisms (Emadian et al., 2017).

Looking at the ability of PLA to biodegrade in the marine environment, PLA degradation is sensitive to temperature and moisture, with increased degradation in higher temperatures and humidity but less degradation in lower temperatures (Ho et al., 1999). A report published in 2017 by Karamanlioglu et al. discusses the lack of information on the decomposability of PLA in aquatic environments, the report states that what is known of PLA degradation in marine environments has shown very slow to no degradation (Karamanlioglu et al., 2017). Zhao et al. described PLA to have a biodegradation in a simulated marine environment of 3 to 4 percent weight loss in 180 days (X. Zhao et al., 2020). However, PLA is not recognized as having marine degradation under any of the ASTM Standards, as there is not sufficient research regarding PLA's ability to degrade in the marine environment (Meereboer et al., 2020).

2.3.2. Environmental Impacts

Chiarakorn and colleagues (2011) assessed the environmental impact of PLA compared to a petroleum-based polymer, looking at the carbon dioxide (CO2) emissions during production. The study showed PLA to have higher CO2 emissions than the petroleum-based polymer, particularly in the category of electricity use during production (Chiarakorn et al., 2011). This is likely attributed to the differences in advancement of production between the two polymers (PLA being less advanced than petroleum-based polymers). Additionally, CO2 emissions surrounding the material input of PLA were significantly lower than the petroleum-based polymer. This decrease of emissions came from using renewable material rather than fossil fuel-based material (Chiarakorn et al., 2011). The PLA discussed in this study was sourced from cassava starch, a product from the cassava plant.

Another environmental impact that is prominent in Chiarakorn's study is PLA's inability to degrade in marine environments. There is very little way to represent this measure as an environmental impact, however, it is definitely a factor to consider when evaluating the environmental sustainability of this product and its ability to decrease ocean pollution.

2.3.3. Production Costs

As for the economics of bioplastic PLA, Chiarakorn also conducted a cost benefit analysis of the bioplastic PLA. The report showed that PLA is more expensive than conventional petroleum-based polymers(Chiarakorn et al., 2011). In 2010 it was estimated that the price of PLA was $2.2 per kilogram (Madhavan Nampoothiri et al., 2010). In the Granta Edupack software, PLA is shown to be 2.99 USD/kg (*GRANTA EduPack 2020*, n.d.). This data is based off a collection of online sources involving material analysis and information.

The largest producer of PLA is NatureWorks, company owned by Cargill. NatureWorks created a biopolymer of PLA called Ingeo (NatureWorks, 2009). In 2011, Ingeo was priced at $0.90 to $1.00 per pound, which can be converted to about $2 to $2.2 per kilogram (Chow, 2011). Marketing director at NatureWorks believes their production in Nebraska releases 60 percent less greenhouse gasses and 50 percent less non-renewable energy, compared to traditional plastics (Chow, 2011).

2.4. PHAs (PHB, PHBV and Cyanobacterial PHB)

PHAs or polyhydroxyalkanoates are a group of biopolyesters that are synthesized by numerous bacteria that allow for a wide range of application (Thellen et al., 2008; Venkatachalam & Palaniswamy, 2020). PHAs also contain similar mechanical and thermal structures to fossil fuel-based plastics PP and PE (Thellen et al., 2008). PHAs are the most studied bioplastics (SN & G, 2016). The primary reason PHA is considered as a viable plastic replacement is its ability to biodegrade in multiple environments. PHA is a broad category of bioplastics PHB and PHBV, which are analyzed further below. In this report we also dive deeper into PHB, analyzing Cyanobacterial PHB.

PHB or polyhydroxy butyrate is a form of the PHA polymer. PHB is most commonly compared to PP, one of the most common forms of petroleum-based plastic, most commonly used for the production of food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, and bank notes (Plastics Europe & Conversio Market & Strategy GmbH, 2019). PHB contains similar crystallinity and melting temperature to PP (Thellen et al., 2008). The most attractive attribute of PHB is its production and degradation (SN & G, 2016). PHB is produced by bacteria, algae, and genetically modified plants

PHBV or polyhydroxy butyrate- valerate is also a form of the PHA polymer. The difference between PHBV and PHB lays in its molecular structure. It has been found that between PHB and PHBV, PHBV has higher barrier properties to water vapor and oxygen than that of PHB (Thellen et al., 2008). PHBVs higher barrier properties to water vapor and oxygen are useful when looking at plastic packaging, as a large reason why there is a need for plastic packaging is dependent on sanitation and creating a strong barrier to outside sources.

Cyanobacterial PHB is the final form of PHA polymer we will discuss. A common form of algae used in the production of biopolymers is cyanobacteria, also known as blue-green algae (Ansari & Fatma, 2016; Singh et al., 2017; Yashavanth et al., 2021). Cyanobacteria have been shown to have the potential to synthesize PHB using carbon substrates such as glucose, acetate and maltose (Singh et al., 2017). Cyanobacteria are photoautotrophic organisms and are unique because they can be grown without supplementation of organic carbon sources and oxygen (Singh et al., 2017).

2.4.1. Biodegradation

Materials made from PHAs are biodegradable in composts, landfills and aquatic systems (Jain et al., 2010). PHAs follow ASTM standards for marine biodegradation, being the only class of polymers that exhibits efficient marine biodegradation (Meereboer et al., 2020). Dilkes-Hoffman (2019) describes the biodegradation of bioplastic PHA in the marine environment, showing that PHA can degrade in the marine environment, but the time of degradation is different depending on the plastic material. Figure 2 displays how various PHA materials can degrade in the marine environment (Dilkes-Hoffman et al., 2019).

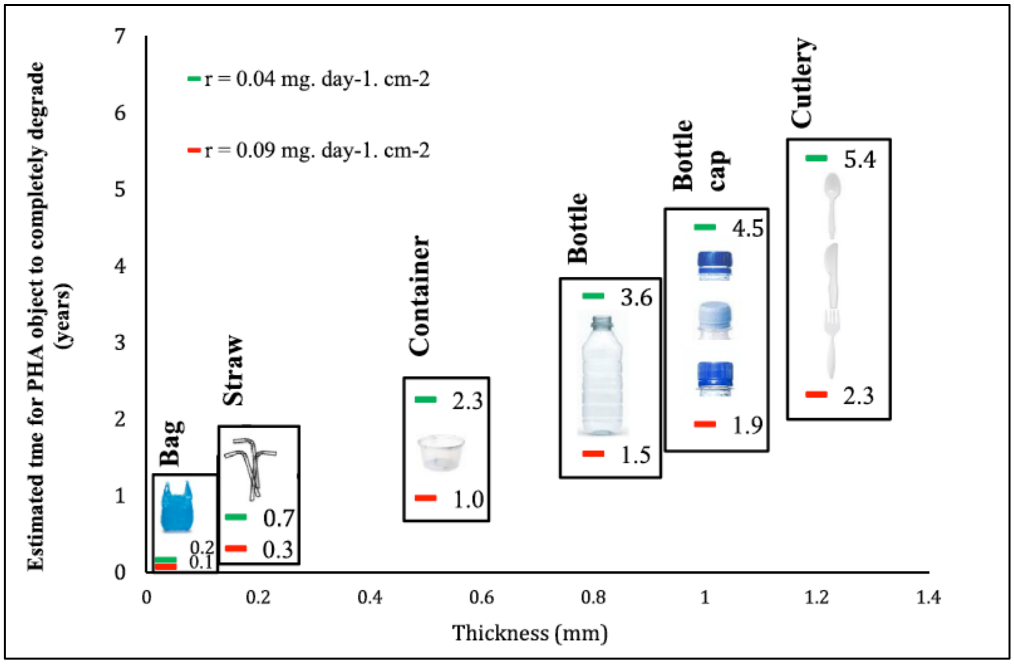


Figure 2. PHA degradation. Lifetime values estimated using the 95% confidence interval for the mean of the rate of biodegradation of PHA in the marine environment. Figure sourced from Dilkes-Hoffman et al., 2019.

However, something to consider when trying to understand the degradation of PHA is its composition. PHA contains heteroatoms in its backbone which makes it denser than water, causing it to sink in most marine environment (Dilkes-Hoffman et al., 2019). This may be a factor leading to its biodegradation capabilities, being that is comes in contact with sediment, compared to other plastics that are less dense than water and tend to float on the water's surface. However, there are concerns about the durability of PHA when it is used in food packaging (Jabeen et al., 2015).

As for the biodegradation of PHB, it is biodegradable in compost, soil and the marine environment. PHB is slightly more biodegradable than PLA (Evans, 2010), but combining PHB with other substances may increase its biodegradation rate. For example, in a soil environment, PHB combined with potato peel waste fermentation residue biodegraded more than the original PHB polymer (Emadian et al., 2017). PHB treated with microorganisms can also decompose into water and carbon dioxide (SN & G, 2016). PHB has been shown to degrade in a simulated marine environment, experiencing 38 to 45 percent weight loss in 180 days (X. Zhao et al., 2020). However, aside from biodegradability, there are concerns of PHB's strength when it comes to providing the same attributes of conventional plastics. Report published by Jain et al. in 2010 addresses the brittleness of PHB and thermal instability, stating PHB is more brittle and unstable than conventional plastics (Jain et al., 2010).

PHBV has a higher starch content which supports deterioration in marine environments (Imam et al., 1999). PHBV has been shown to be able to biodegrade in seawater, with 54 percent weight loss in 160 days (Volova et al., 2010). PHBV is also able to biodegrade in both water and sand when deposited in marine environments (Meereboer et al., 2020). Cyanobacterial PHB's biodegradation has not been evaluated for the marine environment, as it is a very new biopolymer. However, there have been studies evaluating Cyanobacterial PHB in other environments such as soil and compost, showing to experience 24.58 percent weight loss in 60 days in a soil environment (Ansari & Fatma, 2016).

2.4.2. Environmental Impacts

The main parameters affecting PHB's fermentation process are pH and temperature (SN & G, 2016). Like most other bioplastic polymers, PHB releases methane when it biodegrades. Chidambarampadmavathy et al. (2017) discusses the idea of using PHB as a bioplastic through methane recycling. This method would utilize the methane emitted from the decomposition process back into the production of the PHB bioplastics (Chidambarampadmavathy et al., 2017). However, the release of methane, if not contained into a recycling process, could show as a negative environmental impact for PHB.

2.4.3. Production Costs

The cost of PHA has also been discussed in the literature, much of the discussion involving the circular economy approach, in effort to lessen the cost of the polymer. Yadav et al. published a report in 2020 discussing the high costs of PHA bioplastic production (Yadav et al., 2020). PHA was discussed as an option in utilizing a circular economy method. This method would take surplus feedstock materials and put them back into the production process in efforts to create a closed loop (Yadav et al., 2020). Report published by Chidambarampadmavathy in 2017 also found that PHB (a form of PHA), when produced from methane requires less energy costs than PHB from sugars or PLA. It also had the highest yield of the three (Chidambarampadmavathy et al., 2017), making it the most cost effective when combined with methane.

PHAs are high in price because of the media sources used in production (Venkatachalam & Palaniswamy, 2020). The conversion from lactose into glucose is a large contributor to the price. There is a focus to find cheap media such as molasses, corn whey, wheat and rice bran, that could aid in decreasing the price of PHAs (Venkatachalam & Palaniswamy, 2020). Currently, PHAs are priced at $3-4 per kilogram (Choi & Lee, 1997; *GRANTA EduPack 2020*, n.d.). PHBV has been described as more expensive, with an estimated price of $6.86-20.26 per kilogram (X. Zhao et al., 2020).

2.5. PBS

PBS or Polybutylene succinate is a biodegradable polymer that can be sourced from petrochemical sources or natural sources (Changwichan et al., 2018; Rafiqah et al., 2021; Rudnik, 2012; Shaiju et al., 2020). PBS can be processed the same as all other polymers, through the process of injection, extrusion or blow molding (Rafiqah et al., 2021). The primary applications of PBS include film, containers, cutlery and packaging materials (Shaiju et al., 2020).

PBS is considered a promising alternative to conventional plastic because of its comparable mechanical properties (Shaiju et al., 2020) and wide range of applications. However, PBS has also been shown to have poor tensile properties, low melt viscosity and gas barrier properties, which all could restrict the application and use of PBS (Shaiju et al., 2020).

2.5.1. Biodegradation

Although PBS is produced from petroleum-based sources, its biodegradation is much higher than that of polymers such as PET and other conventional plastics (Rafiqah et al., 2021). PBS showed strong biodegradation in compost, experiencing a weight loss of about 60% after 90 days (J. H. Zhao et al., 2005). However, PBS has been found to have slow biodegradation in seawater (Shaiju et al., 2020), largely due to the inconsistent environmental conditions of the marine environment (Nakayama et al., 2019). Another study on the biodegradation of PBS showed that the deterioration of PBS in marine conditions was minimal compared to other bioplastic polymers, showing some biodegradation in fresh water and minimal in salt water (Meereboer et al., 2020; Sekiguchi et al., 2011). However, PBS is not recognized under the ASTM standards as there lacks sufficient detail in the literature for evaluation under the three standards (Meereboer et al., 2020).

2.5.2. Environmental Impacts

PBS also has a lower carbon footprint compared to conventional plastics. Conventional plastics such as PET have an average carbon footprint of about 2.73 kg/kg while PBS has a carbon footprint of about 2.04-4.06 kg/kg (Patel et al., 2018). PBS does have some environmental concerns, still primarily being produced from fossil fuel-based sources. PBS is typically fossil fuel-based because succinic acid is derived from oil, however, succinate acid can also be derived from the fermentation method. Deriving PBS through fermentation increases the price of PBS significantly leading to a lower potential for has commercial application (Rafiqah et al., 2021).

Even though it is more expensive, PBS from sugar-cane has a low environmental footprint (Changwichan et al., 2018). Changwhichan and colleagues looked at sugar-cane based PBS, produced via bacterial fermentation, and observed PBS to have a lower global warming potential than PLA and PHAs due to the amount of energy required in the production process (Changwichan et al., 2018).

2.5.3. Production Inputs and Cost

PBS is also less expensive compared to other biopolymers. A US-based joint venture, formed by NatureWorks and BioAmber (two bioplastic manufacturers) are selling PBS. sourced from a combination of succinic acid and corn, for 2-2.50 USD per pound, which can be converted to approximately 0.907-1.133 USD/kg (D. D. Guzman, 2012). This is relatively inexpensive for a bioplastic polymer as compared to PLA's price at 2.99 USD/kg.

2.6. Conclusion

Putting together all the information gathered above, we can see there is a lot of data surrounding biopolymers. However, much of the data in the literature is mainly focused on the properties of the biopolymers and not the polymers as products, such as a plastic bottle or food packaging. While it is crucial to understand the properties of the polymers used to construct packaging materials, more needs to be understood surrounding the polymer's performance in a product. We feel this information is crucial in understanding the applicability of these polymers into large-scale production. Alongside that, we need to understand the biodegradation of these polymers in the marine environment. Synthesizing data surrounding the biodegradation of the polymers with their product effectiveness will provide information for manufacturers and producers to better understand various plastic alternatives. Additionally, this information should provide insight regarding environmental impacts in bioplastic production.

Chapter 3

3. METHODOLOGY

This study aims to answer which bioplastic polymer has the best price, carbon footprint, embodied energy and biodegradation compared to conventional plastic, PET. We address this question through utilizing data from literature sources surrounding carbon footprint, energy, price, and biodegradation in the marine environment. In order to do this, we first identified papers with relevant information to our study, using key search terms outlined in table1 and table 2. We then extracted data from those papers to use in our models. We used the data retrieved from these sources to analyze the various biopolymers. We analyzed the various polymers for their biodegradation. We also used data in various literature sources to conduct analysis in Grant Edupack. The analysis in Granta Edupack evaluated the biopolymers price, carbon footprint and embodied energy during production. We also utilized Granta Edupack to model the polymers as plastic bottles and compare them during the production process.

3.1. Identification of Papers

We collected data regarding bioplastic polymers and their biodegradation, carbon footprints, and economic viability through first searching “bioplastics”. After reading documents from this broad search, we identified six papers that we then used to narrow our search to the specific bioplastics we wanted to investigate (Changwichan et al., 2018; Cinar et al., 2020; Dilkes-Hoffman et al., 2019; Rudnik, 2012; Selvamurugan & Sivakumar, 2019; Venkatachalam & Palaniswamy, 2020). These six papers all contain information on multiple polymers, allowing us to further distinguish how and where to narrow our search. We selected papers that were published in the last 10 years, included discussion on two or more biopolymers, and made comparisons between biopolymers. From these papers we selected polymers PLA, PHB, PHBV, Cyanobacterial PHB and PBS for further analysis.

The search was split into categories. Those containing information for biodegradation of the polymers (Table 1), and those containing information on the carbon footprint, cost and embodied energy (Table 2). Of this literature, the studies that contained sufficient information on the rate of biodegradation, carbon footprint, energy or cost were selected. When investigating biodegradation, we made a focus to only include studies that discussed biodegradation in the marine environment.

Table 1: Search Terms for Biodegradation Information

Polymer Type	Biodegradability	Environment
PLA	Biodegradation	Marine
PHA	Decomposition	Aquatic
PHB	Degradation	Seawater
PHBV		
PBS		
Algae-based bioplastic		
Cyanobacterial PHA		
Cyanobacterial PHB		

Table 2: Search Terms for Granta Edupack

Polymer	Data Inputs
PLA	Density
PHA	Price
PHB	Young's Modulus
PHBV	Embodied Energy
PBS	CO2 Footprint
Cyanobacterial PHB	Yield Strength
	Tensile Strength
	Elongation

3.2. Biodegradation Calculations

After reading multiple sources on these polymers and their biodegradation, the sources were compiled into a table summarizing the biodegradation of each polymer. The measure of biodegradation was expressed in percent weight loss per number of days, for all but one literature source we used (Dilkes-Hoffman et al., 2019). In order to make the results more comprehensive and units consistent, we converted all the percent weight loss to 100 percent, representing complete biodegradation. We also converted the time into years.

To complete the conversion to 100 percent biodegradation, we first had to average all the time values and weight loss percent values that were collected from literature sources. The averages can be found in Appendix A. We then used the following equation (Equation 1) to get a value for estimated 100 percent biodegradation or complete biodegradation.

Equation 1. Calculation for estimated number of years for 100% or complete biodegradation of the polymer. Calculation utilizes data from Appendix A.

$$100\%\ biodegradation\ (yrs) = \frac{\left[\left(\left(\frac{100 - avg\ \%}{avg\%}\right) X\ avg\ days\right) + avg\ days\right]}{365}$$

3.3. Modeling Data

The data modeling has been conducted in Granta Edupack (*GRANTA EduPack 2020*, n.d.). This software is a database of material processes and information. The software can be used to model different materials and production process, as well as compare those materials for varying attributes. In our study we want to use this software to look at the price, carbon footprint, and embodied energy of the varying polymers. In the software price is represented as U.S. dollars or USD, per kilogram (kg). Carbon footprint is measured as kilograms per kilograms and represents the mass of carbon dioxide equivalent arising directly from the production of a material per year divided by the mass of the material shipping per year (Sustainability et al., n.d.). And embodied energy is the sum of energy required to produce the polymer. We chose to evaluate price, carbon footprint and embodied energy because we believe those three categories are the most important when evaluating a product for its processability and sustainability. Processability referring to a products ability to be produced. Carbon footprint and embodied energy will help determine the environmental footprint of a polymer and price will provide insight on any barriers to processability.

Being a material information database, Granta Edupack already has information on several polymers. Therefore, we have used the data in the software for polymer PLA and our baseline polymer PET. We used PET as our baseline polymer as it is the most common polymer used in the production of plastic water bottles. Additionally, the software includes PHA as a material, but we wanted to be more specific and represent PHB, PHBV and Cyanobacterial PHB as separate polymers to see how they compare. Therefore, because PHB, PHBV and PBS are not found in the software, we have used the information gathered from our literature review to create these materials in the software. These polymers were input using the data terms from Appendix B. All of the data for PLA and PET was present in the software. For PHB and PHBV, values that were not seen in the literature were replaced with values from PHA seen in the software, as PHA is a broad category of both PHB and PHBV. Another limitation of the software is that it does not contain information on the biodegradation of materials. So, for this reason we have produced a separate biodegradation table based off the search terms in Table 1 that outlines various polymer's biodegradation time for 100 percent biodegradation (using Equation 1) specific to the marine environment.

3.4. Data Input and Analysis

The data categories needed for Granta Edupack analysis are price, density, price per unit volume (which is the density multiplied by the price), Young's Modulus, embodied energy, tensile strength, yield strength, elongation at break and carbon footprint. Young's Modulus represents the stiffness of a material, or how easily the material could be bent or stretched. Yield strength is the stress a material can withstand without being permanently deformed. Tensile strength is the resistance of a material to breaking under tension. And elongation at break is the ratio between the new length and initial length of a material after breaking the material. We selected these attributes as they all impact the polymer's ability to form a bottle and can alter the price dependent on the amount of material required to produce one bottle. Young's modulus and tensile strength are important in bottles as it ensures the plastic can't be easily broken or stretched. These values can impact a polymer's price as the amount of polymer required to produce a bottle may increase if the polymer has low Young's modulus or tensile strength. Meaning more polymer may need to be produced in order to reach the desired strength and stiffness of a bottle.

The values for all the data categories is seen in Appendix B and were input into Granta Edupack to represent polymers PET, PLA, PHB, PHBV, Cyanobacterial PHB and PBS. We wanted to compare the bioplastics to conventional plastic in a way that displays environmental and economic characteristics of sing-use plastics. To do this we modeled for one plastic bottle using Granta Edupack. To simulate one plastic bottle made out of our polymers, within the software, we selected the polymer form. This selection is outlined in Appendix C, with the equations that were performed within the software shown in the "performance index" box. The form we selected was a rounded product with internal pressure. Selecting a rounded product with internal pressure determines that the polymer will be manufactured into a product most similar to a plastic bottle, a product that is round and has pressure inside of it. We assigned our polymers to the product form and then selected which attributes to represent, in our case, carbon footprint, embodied energy and cost. We chose to represent these attributes as we feel they give us the information that can best compare biopolymers to the conventional PET.

The software also allows us to assign a function or limiting constraint to the polymer. In doing so we can see how effectively the polymer can produce the shape of a bottle, and how the function impacts its price, carbon footprint and embodied energy. The two limiting constraints we are looking at are strength and stiffness. Appendix C displays the modeling for stiffness and strength with their equations. Stiffness represents a polymers bendability and takes into consideration a polymer's Young's modulus. And strength represents a polymer's breakability under stress and considers a polymer's yield strength.

Chapter 4

4. RESULTS

4.1.Biodegradation Table

The rate of biodegradation for polymers PLA, PHB, PHBV and Cyanobacterial PHB were found in terms of percent weight loss and time taken to produce that weight loss. Table 3 displays findings from previous studies converted to 100 percent weight loss. The first polymer in Table 3, PET, is shown as a reference to compare with the biopolymers. The environment is also listed for each polymer. Our aim is to only look at biodegradation in the ocean, however, for some biopolymers, their marine biodegradation was simulated rather than observed. Cyanobacterial PHB, being a very new form of polymer, lacks any data in the literature on its marine or aquatic biodegradation. So, the environment shown for Cyanobacterial PHB is mixed microbial cultur. The biodegradation value for PET is not clearly defined in the marine environment, however, PET generally takes 450 years to fully degrade (Davis, 2021).

Using the calculation discussed in the methods section 3.2., the values in Table 3 show the longest period for 100 percent biodegradation for polymer PLA with an estimated time of 15.86 years. PBS shows a biodegradation period of 1.2 years in seawater. PHBV and Cyanobacterial PHB displayed shorter biodegradation in the marine environment with an estimated 0.81 years and 0.67 years respectively. PHB showed an estimated biodegradation time of 1.19 years and PHA displayed 2.50 years. One thing to note is that PHA is a broad category of both PHB and PHBV and the value shown for 100 percent biodegradation came directly from the literature (Dilkes-Hoffman et al., 2019). Additionally, the value for PHA was calculated in terms of one water bottle (Dilkes-Hoffman et al., 2019). All other values represented the degradation of the polymer, not the polymer in water bottle form.

Table 3. Biodegradation of Polymers PET, PHA, PLA, PHB, PHBV, Cyanobacterial PHB and PBS collected from other sources (noted in first column) and converted to 100% biodegradation in last column (green).

Source	**Polymer**	**Polymer Feedstock**	**Environment**	**Biodegradation (% weight loss)**	**Time**	**Time for 100% biodegradation**
(Davis, 2021)	PET	Purified terephthalic acid	--	100	450 years	450.00
(Dilkes-Hoffman et al., 2019)	PHA	Normalization of multiple sources	Marine	100	1.5-3.5 years	2.50
(Greene, 2011)	PLA	Corn	400 mL of ocean water and 100 g of ocean bottom soil	3.11	180 days	15.86
(X. Zhao et al., 2020)	PHB	Bacteria	Simulated Marine Environment	38-45	180 days	1.19
(Volova et al., 2010)	PHBV	Bacteria	Seawater	54	160 days	0.81
(Ansari & Fatma, 2016)	Cyanobacterial PHB	Cyanobacteria	Mixed Microbial Culture	24.58	60 days	0.67
(Shaiju et al., 2020)	PBS	Sugar-cane	Seawater	16%	70 days	1.20

4.2. Analysis in Granta Edupack

As noted in the methods, Granta Edupack was utilized to compare the polymers for their footprint, embodied energy and price, taking into account their properties shown in Appendix B. These values were all input into the software to aid in generating comparison figures that we see below.

4.2.1. Polymer Price and Footprint

Figures 3 and 4 are shown below. These figures do not consider attributes such as density, young's modulus, tensile strength and elongation. Their display is simply focused on the labels presented on the axes. Figure 3 shows PBS, PET and PLA to have the highest carbon footprint with 2.04 to 4.6 kg/kg, 2.73 kg/kg and 2.84 kg/kg respectively. Cyanobacterial PHB, PHBV and PHB have lower carbon footprints, with 1.69 to 1.97 kg/kg, 0.86 to 0.94 kg/kg and 0.43 kg/kg. As for price, PHBV is the highest, with the PHB and Cyanobacterial PHB the next highest in price (6.86 to 20.26 USD/kg and 3 to 4 USD/kg respectively). PBS and PET experience the lowest prices at 0.91-1.13 USD/kg and 1.20 USD/kg respectively.

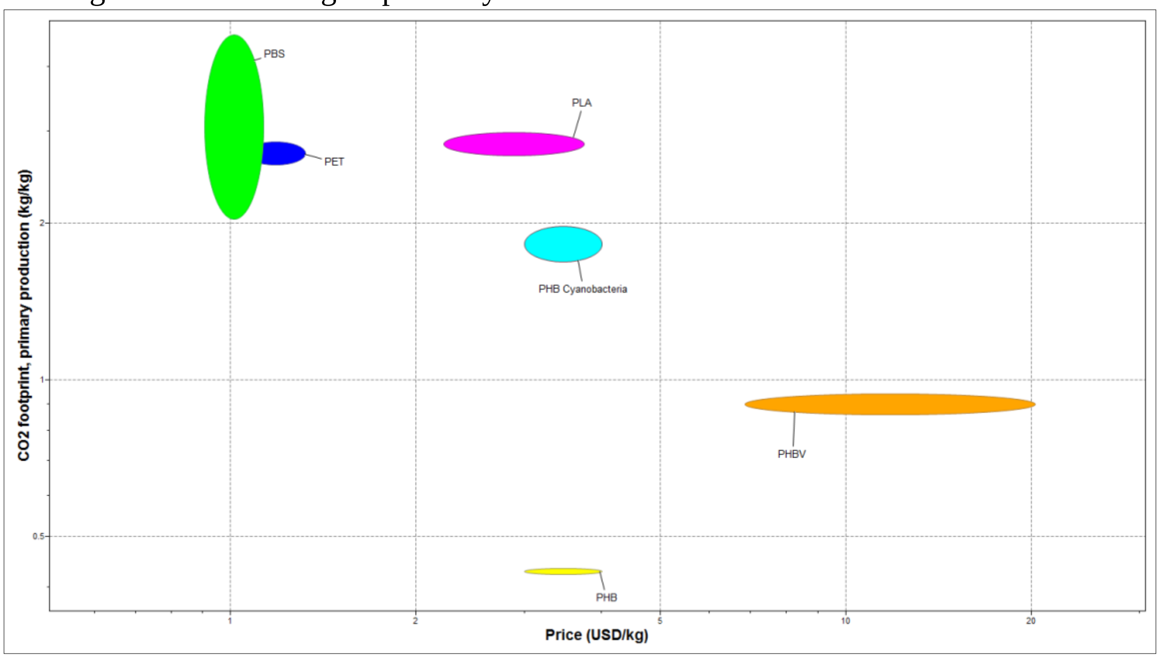


Figure 3. Price and CO2 Footprint of polymers PLA, PBS, PHB, PHBV, PHB Cyanobacteria, and PET. PLA and PLA were sourced from Granta Edupack. PHB, PBS, PHBV and PHB Cyanobacteria were all input from the data in Appendix B.

The embodied energy of the same six polymers were also evaluated (Figure 4). Embodied energy is the total energy associated with the extraction and processing of a product. As you can see in Figure 4, PHB, PHBV and Cyanobacterial PHB all have the highest embodied energy (81.4-89.8 MJ/kg). PHB, PHBV and PHB Cyanobacteria, all were missing this data in the literature, so we used the values represented in Granta Edupack under PHA to fill in these values (shown in Appendix B). PET and PBS are also relatively high and just below the PHAs, at 82.4 MJ/kg and 76 MJ/kg respectively. PLA on the other hand has a lower embodied energy, at 55.4 MJ/kg. The prices are the same as seen in figure 3.

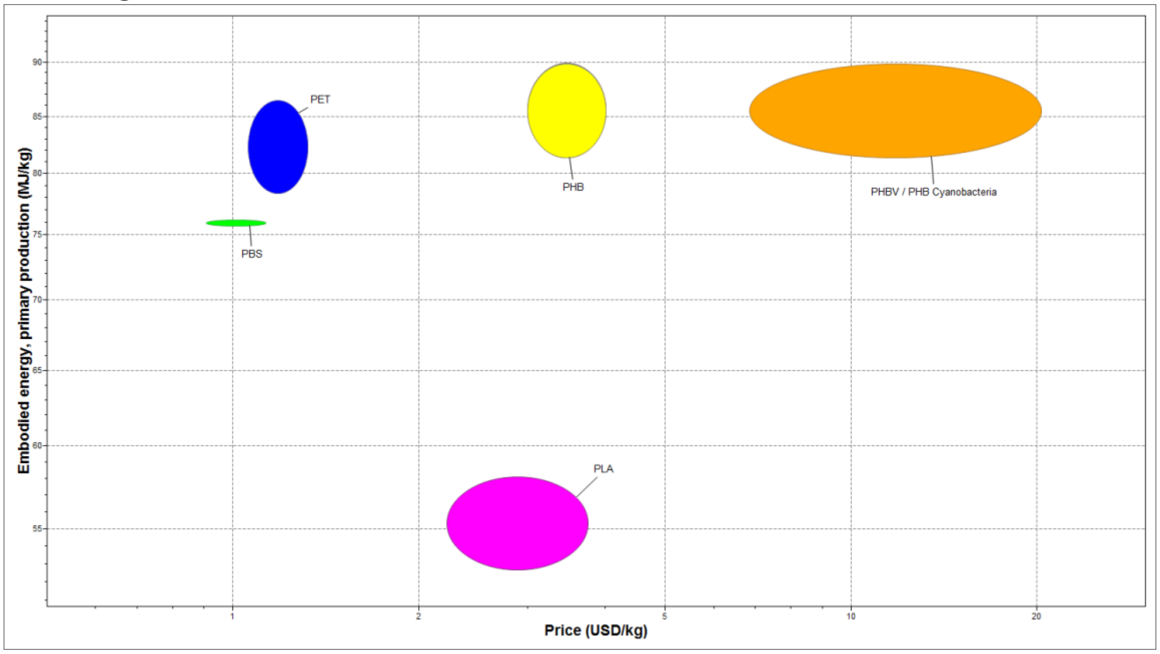


Figure 4. Price and Embodied Energy of polymers PLA, PBS, PHB, PHBV, PHB Cyanobacteria, and PET. PLA and PLA were sourced from Granta Edupack. PHB, PBS, PHBV and PHB Cyanobacteria were all input from the data in Appendix B.

4.2.2. Simulation for 1 Plastic Bottle

The following figures are modeled for production of a plastic bottle as described in the methods. Figures 5 through 8 vary from the figure 3 and figure 4, as they display the polymers being modeled for a plastic bottle, accounting for limiting factors stiffness and strength.

In figures 5 through 8, stiffness and strength are both shown as variable per unit of stiffness or variable per unit of strength. Therefore, the values on the x and y axis are ratios. For example, if a polymer is thin and flimsy, its cost per unit of stiffness will be high, as it will cost more to make the polymer as stiff as it needs to be to produce a water bottle. Same goes for “per unit of strength”; if a polymer is weak and has difficulty holding a liquid, the cost per unit of strength may increase as it may need to produce more of the polymer to hold the liquid. This same concept can be applied to carbon footprint and embodied energy. Dependent on the properties of the polymer, there may need to be an increase in the amount of polymer produced or an increase in the energy required to produce it.

4.2.2.1. Carbon Footprint

When considering carbon footprint per unit of strength and cost per unit of strength, PHB, PHBV and Cyanobacterial PHB have the highest cost when applying the limiting factor of strength (97.4-133, 99-135, and 118-158 respectively). However, PHBV and PHB have lower carbon footprints (27.7-34.5 and 13.2-15.1 respectively). PET on the other hand, shows low cost (26.7-34.2) but high footprint (64.3-75.1). PBS has the highest footprint (83.7-189) and PLA is somewhat in the middle in terms of price (53-90), but comparable to PET in term of carbon footprint (63.4-72.7 versus 64.3-75.1).

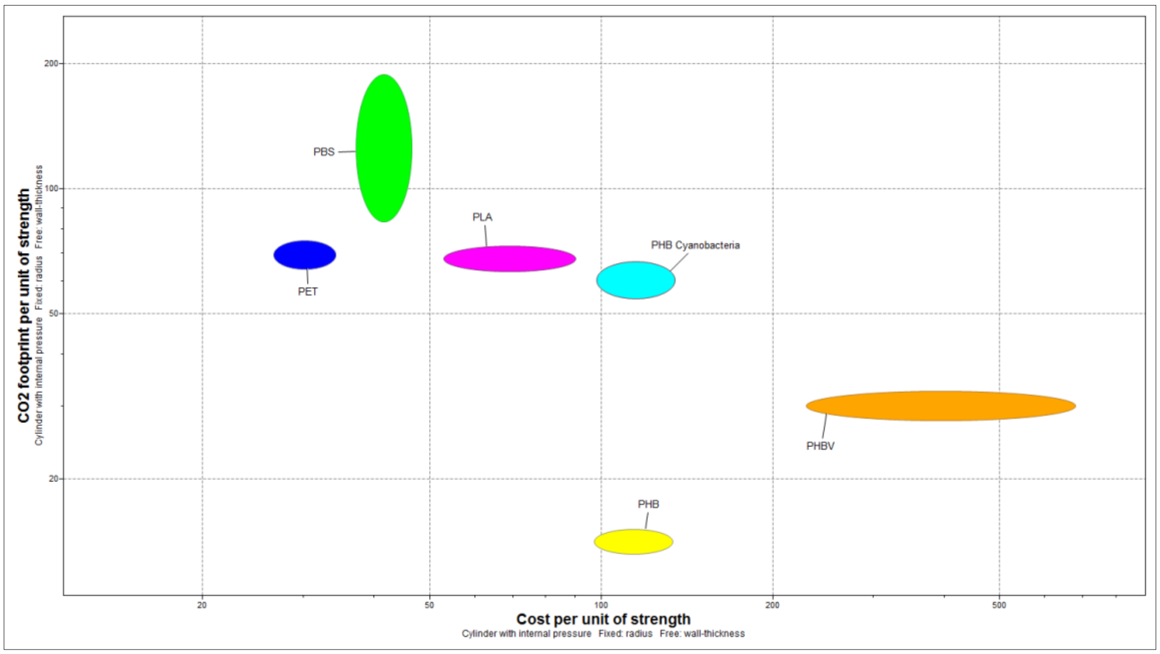


Figure 5. Carbon Footprint and price for 1 water bottle per unit of Strength.

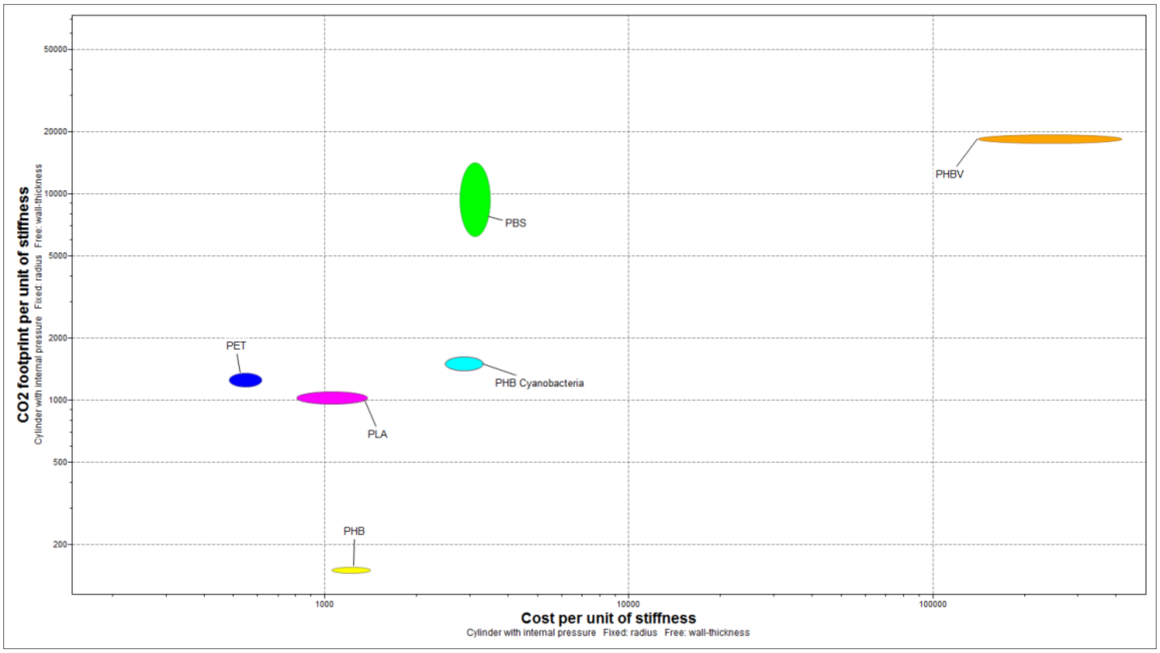


Figure 6. Carbon footprint and price of 1 water bottle per unit of stiffness.

Results from figure 6 show PHBV to be high in both cost and carbon footprint per unit stiffness (61500-82000 and 17600-19300 respectively) and PHB having the lowest carbon footprint for stiffness (151). PET remains low in price per unit stiffness (485-616). PLA shows relatively low cost and carbon footprint per unit stiffness (806-1370 and 967-1100), compared to the other biopolymers, apart from PHB (1050-1410 and 151).

4.2.2.2. Embodied Energy

Figures 7 and 8 represent 1 simulated plastic bottle and examine the bottle's expected embodied energy per unit of strength and stiffness. In figure 7, we see the price of the polymers following a similar trend to figure 4. PHB, Cyanobacterial PHB and PHVB are all fairly similar in embodied energy per unit strength (2590-3050, 2610-3080 and 2630-3100 respectively). PLA has the lowest embodied energy (1240-1420). And PBS shows high embodied energy (3120) and low price (37.2-46.8) compared to the other five biopolymers. PET displays the lowest price per unit strength. Price per unit strength in figure 7 is the same as price per unit strength in figure 5.

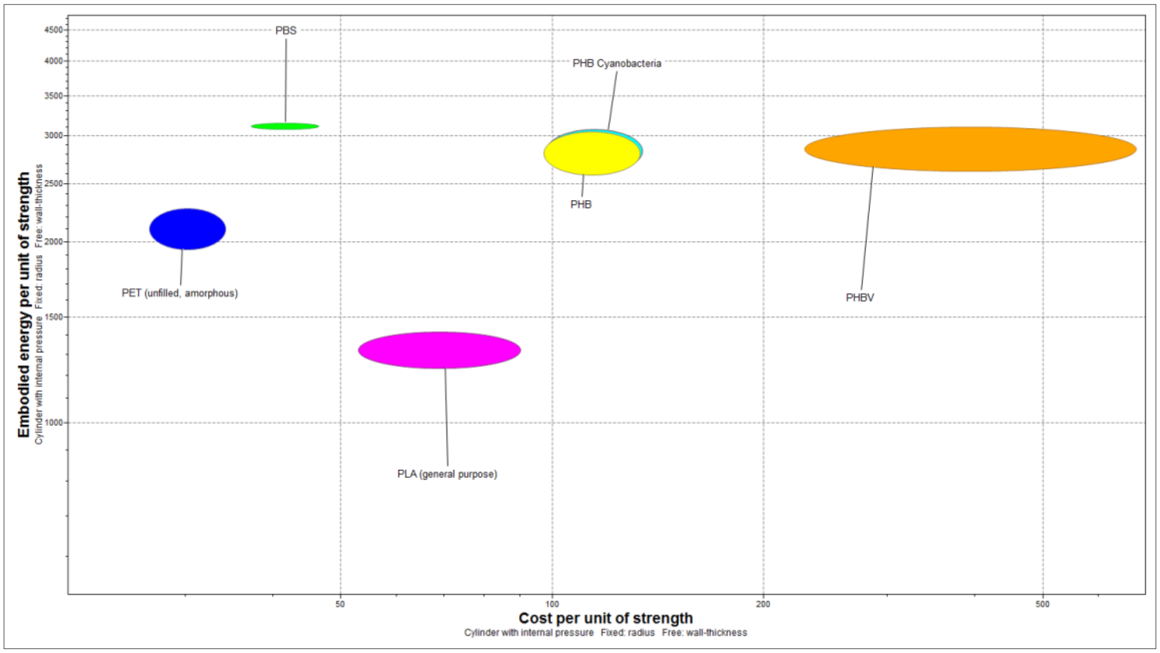


Figure 7. Embodied Energy and price for 1 water bottle per unit of Strength.

Figure 8 shows embodied energy and cost per unit of stiffness. In this figure we see PHVB with the highest embodied energy (1.67e6-1.84e6) and cost per unit of stiffness. PBS and PHB Cyanobacteria are similar in cost per unit stiffness (2790-3500 and 2980-3890 respectively), but PBS is higher in terms of embodied energy (234000 versus 67200-74400). PLA and PHB are low in terms of embodied energy per unit stiffness (18900-21500 and 28600-31600 respectively). However, none of the biopolymers are as low as PET in terms of cost per unit stiffness. PHB and PLA are also both lower in embodied energy per unit stiffness than the conventional PET (35500-40800), with PLA being the lowest (18900-21500). Cost per unit of stiffness values are the same in figure 8 as they are in figure 6.

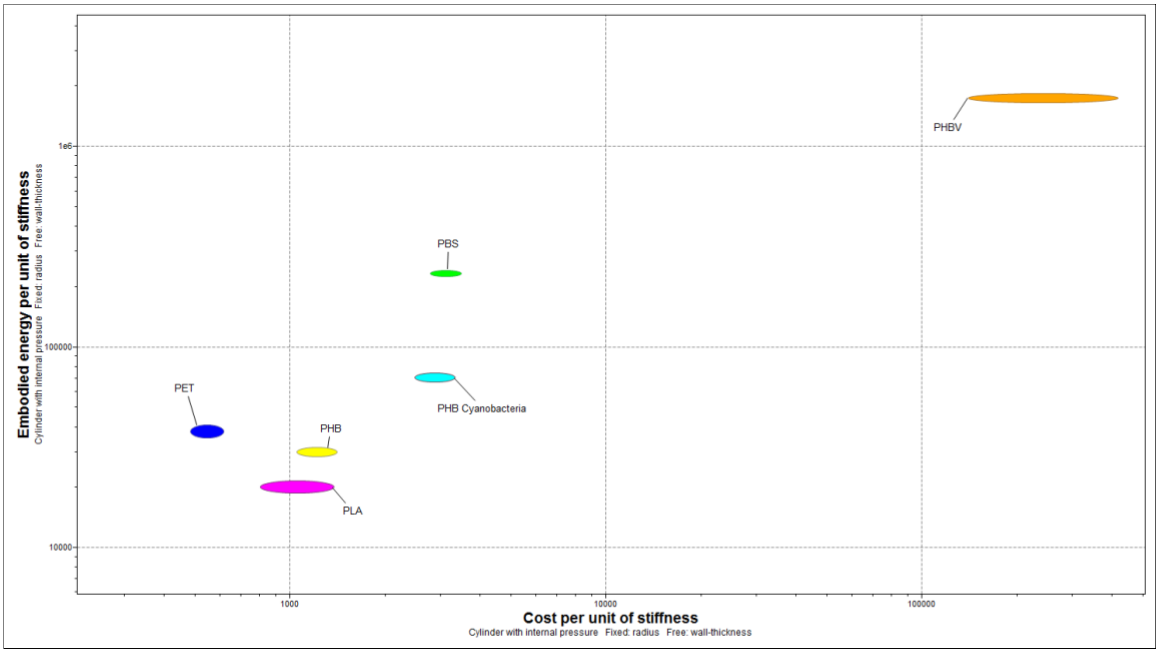


Figure 8. Embodied energy and price of 1 water bottle per unit of stiffness.

4.3. Compiled Results

After obtaining results from the literature and compiling both the biodegradation table and figures 3 through 8, we put the results together in a comprehensive table to show the polymers results comparatively for multiple variables (Table 4). This table includes PET's raw data results from figures 3 through 8, in effort to outline the biopolymers in comparison to PET. The green checks represent areas where the biopolymer may have a more favorable result. Note that for all these values we are categorizing a favorable result as one with a value lower than PET. Also, for all categories besides biodegradation, PET's results are in a ratio, as expressed in figures 3 through 8. Therefore, the smaller the ratio, the more favorable the polymer. This explains why we are representing values lower than PET with a green check.

All biopolymers exceed PET in terms of cost and thus have red negative symbols in both cost columns. Conversely, all biopolymers have faster biodegradation times compared to PET. The polymer with the greatest number of green checks is PLA, showing lower carbon footprint, embodied energy and biodegradation compared to PET. However, PLA exceeds PET in both cost categories. PHB shows the second best result, being less than PET in terms of carbon footprint and embodied energy per unit stiffness. However, PHB is greater than PET in price and embodied energy per unit strength. PHBV and PHB Cyanobacteria show close to the same result, both containing higher price, embodied energy, and carbon footprint per unit stiffness compared to PET. PBS has the most results higher than the conventional, only being lower than the conventional in terms of biodegradation time.

Table 4. Compiled Results Table in comparison to conventional polymer PET.

Polymer	Biodegradation	Cost per unit stiffness	Cost per unit strength	CO2 per unit stiffness	CO2 per unit strength	Embodied Energy per unit stiffness	Embodied Energy per unit strength
PET	**450 years**	**485 – 616**	**26.7 – 34.2**	**1170 – 1350**	**64.3 – 75.1**	**35500 – 40800**	**1950 – 2270**
PLA	✓	—	—	✓	✓	✓	✓
PHB	✓	—	—	✓	✓	✓	—
PHBV	✓	—	—	—	✓	—	—
PHB Cyanobacteria	✓	—	—	—	○	—	—
PBS	✓	—	—	—	—	—	—

Green check = favorable in comparison to the conventional (PET). Red Negative = less than favorable in comparison to the conventional (PET). Green circle = neutral in comparison to the conventional, utilized when range overlaps with the range of the conventional (PET).

Chapter 5

5. DISCUSSION

The aim of this paper was to determine which bioplastic is best suited to act as a replacement to conventional plastic (PET), in effort to decrease the impact of plastic to marine environments. We analyzed five different biopolymers evaluating their price, carbon footprint, embodied energy, and biodegradation. Looking at the various evaluation criteria; we ranked the four in terms of importance based on our review of the literature and problem. We feel biodegradation is the most important criteria in this study as it is the highest contributor to decreasing ocean pollution. Our next evaluation criteria of importance is price, as we feel price will have the strongest influence on the bioplastic being adopted into commercial markets. The criteria ranked at third most importance is carbon footprint, and fourth, energy. We ranked carbon footprint higher than energy as we feel carbon footprint is more important in terms of long-term sustainability of a product and its associated impacts.

The key result of this study is the compilation of evaluation criteria for all five biopolymers (Table 4). This table determined that when looking at all evaluation criteria, PLA had the greatest number of results lower than (favorable to) conventional PET. PLA contained lower biodegradation time, embodied energy and carbon footprint compared to conventional plastic PET. None of the biopolymers evaluated were comparable to PET in terms of price. PHB was shown to be the next best biopolymer for overall results, having a lower carbon footprint, biodegradation, and embodied energy per unit stiffness than PET.

However, even though PLA produced favorable results compared to the conventional plastic, it had the slowest biodegradation rate in the marine environment among all the biopolymers. PLA's rate of biodegradation in the marine environment was 15.86 years for full degradation; over six times longer than any other bioplastic. This is concerning as the toxicity of bioplastics are estimated to be similar to conventional plastics (Zimmermann et al., 2020). As toxicity is still present, the degradation of the biopolymer will pose the same impact as microplastics sourced from petroleum-based plastics during the 15.86 years in the marine environment. PLA was also higher than PET in terms of price. However, PLA had the closest price to PET of all the biopolymers, priced at $2.99 per kilogram compared to PET's $1.2 per kilogram.

This brings us to PHB. PHB shows strong results in terms of marine biodegradation, taking only 1.19 years to fully degrade in the marine environment, however, it was continually high in price. PHB has a price of $3-4 per kilogram, compared to PET's price of $1.2 per kilogram. This high price would make it more difficult for the large-scale adoption of PHB.

In summary we believe none of these polymers are at a stage to fully replace conventional PET. PHB shows strong results in terms of marine biodegradation but was high in price. PLA also shows favorable results comparable to PET but could not match its price and did not degrade well in the marine environment. Additionally, these plastics still contain negative environmental impacts. The production of the bioplastics consumes significant energy being more brittle and weaker in their make-up, and there are still emissions present during production. Even though these plastics do degrade faster than the conventional PET, their degradation process remains a threat to marine species. And all of the biopolymers are significantly more expensive than PET. Because of all these reasons, conventional plastics have been able to continually dominate the market. The mechanical properties of PET combined with the price, makes it difficult for other polymers to compete.

Other studies that have analyzed biopolymers, such as work conducted by Changwichan and colleagues, 2018, determined PBS to be the best option comparing PBS, PLA and PHA. However, this study was only looking at environmental impacts and did not take into account the mechanical properties of the polymers and how it pertains to commercial production. As well as, the biodegradation of the polymers in the marine environment. Our research provides an analysis of the polymer's marine biodegradation, paired with insight on the polymer's mechanical properties, in order to comprehensively analyze these polymers and consider both their commercial application and environmental footprint in the marine environment.

However, our results lack information on the impacts of biodegradation (aside from the time to degrade). Using the software, we gained insight on the impacts associated with production, but we are missing data for the impacts of biodegradation. Including emissions and environmental impacts associated with biodegradation could've allowed for us to provide a full life cycle analysis of the biopolymers. Future research could investigate environmental impacts associated with biodegradation, including emissions and toxicity. With more research on the toxicity of biopolymers along with advancements geared towards limiting the toxic elements, biopolymers could show significant benefits compared to PET.

Overall, our results suggest that in order to implement bioplastics that are cost competitive and show a reduction in environmental impacts, there would need to be more research on the polymers and their impacts across their life cycle. In the meantime, alternative strategies may need to be investigated in order to lessen the current impact of plastic. One possible strategy being to increase the emphasis towards reusable containers. Creating a system with more reliance on refillable beverage containers could decrease plastic's detrimental impacts. Additionally, education should be promoted to advance awareness of plastic pollution and plastic's significant impact on the environment.

APPENDIX A. Averages for Biodegradation Calculations

Source	Polymer	Biodegradation (% weight loss)	Time	Biodegradation (% weight loss) AVERAGE[2]	Time (days) AVERAGE
(Dilkes-Hoffman et al., 2019)	PHA	100%	1.5-3.5 years	100	912.5[1]
(Greene, 2011)	PLA	3.11	180 days	3.11	180
(X. Zhao et al., 2020)	PHB	38-45	180 days	41.5	180
(Volova et al., 2010)	PHBV	54	160 days	54	160
(Ansari & Fatma, 2016)	Cyanobacterial PHB	24.58	60 days	24.58	60
(Shaiju et al., 2020)	PBS	16%	70 days	16	70

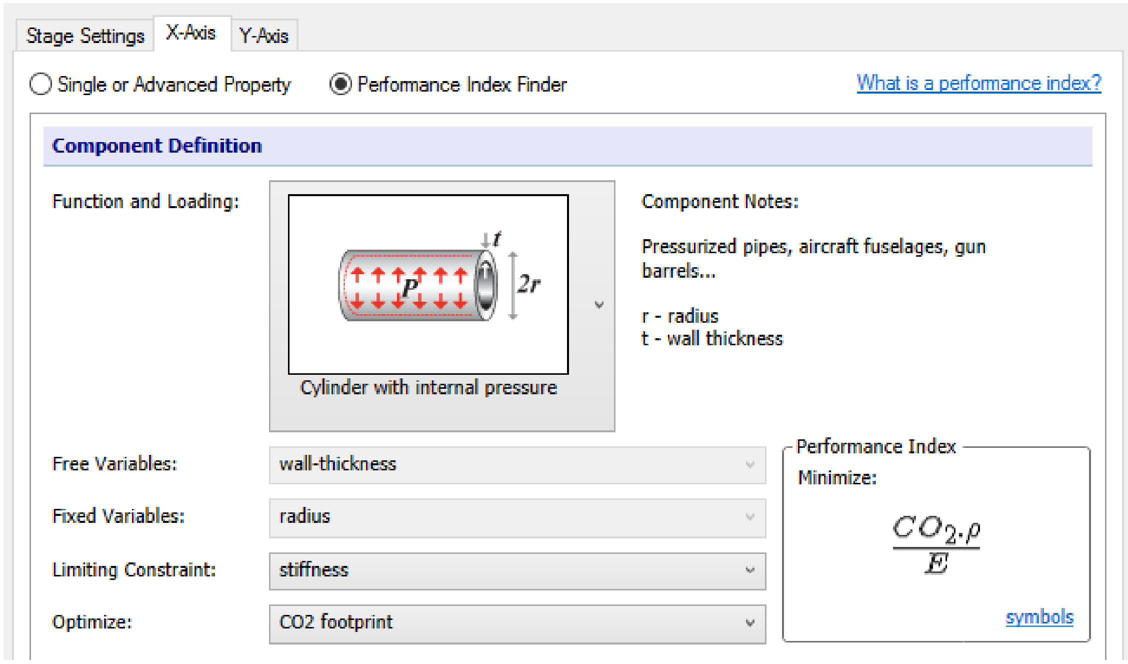
[1]Time converted to days to be used in equation 1.
[2]Ranges converted to averages to be used in equation 1.

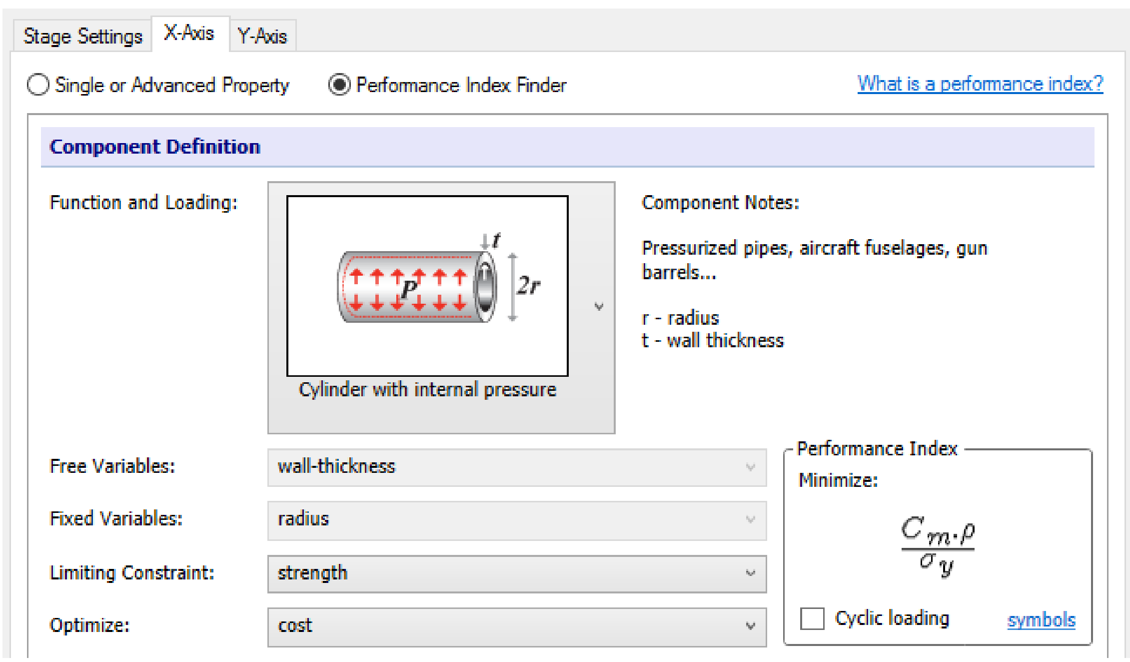
APPENDIX B. Granta Edupack Data Inventory

Polymer	Price USD/kg	Density (kg/m^3)	Price per unit volume (USD/m^3)[4]	Young Modulus (GPa)	Embodied Energy (production) MJ/kg	CO2 footprint (kg/kg)	Yield Strength (MPa)	Tensile strength (MPa)	Elongation (%)
PET[1]	1.2	1340	1608	2.9	82.4	2.73	52.5	55-60	280-320
PBS	0.907-1.133[5]	1260[6]	1134-1436	0.41[9]	76[9]	2.04/ 4.6[11]	30.7[10]	32.6[9]	10.5[9]
PLA[1]	2.99	1255	3752.45	3.45	55.4	2.84	52.5	55-72	2.5-6
PHB	3-4[7]	1230[8]	3690-4920	3.5[17]	81.4-89.8[2]	0.43[3]	35-40[2]	35-40[2]	1.89 +/- 0.13[8]
PHBV	6.86-20.26[12]	1250[13]	8575-25325	0.06098[14]	81.4-89.8[2]	0.86-0.94[2]	35-40[2]	20-40[12]	1.5-5.5[12]
PHB Cyanobacteria	3-4[2]	1230-1250[2]	4430-5870[2]	1.5[15]	81.4-89.8[2]	1.69-1.97[16]	35-40[2]	31.1[15]	8.6[15]

[1] Values present in Granta Edupack and not retrieved from a literature source.
[2] Values were not present in literature and therefore filled with measures from PHA (present in Granta Edupack).
[3] Value calculated from Kim & Dale, 2008
[4] Values calculated using equation – Price X Density
[5] D. De Guzman, 2016
[6] *BioPBS*, 2021
[7] Choi & Lee, 1997
[8] Bucci et al., 2007
[9] Shaiju et al., 2020
[10] Patel et al., 2018
[11] Wang et al., 2009
[12] X. Zhao et al., 2020
[13] Rivera-Briso & Serrano-Aroca, 2018
[14] Berthet et al., 2015
[15] Ansari & Fatma, 2016
[16] Medeiros et al., 2015
[17] Khanna & Srivastava, 2005

APPENDIX C. Granta Edupack Modeling Equations





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