STUDY ON MECHANICAL, BIODEGRADABILITY AND COMPOSTABILITY OF AGRICULTURE WASTE LOADED BIODEGRADABLE POLYMER

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STUDY ON MECHANICAL, BIODEGRADABILITY AND COMPOSTABILITY OF AGRICULTURE WASTE LOADED BIODEGRADABLE POLYMER

by

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Thesis submitted in fulfilment of the requirements for the degree of Bachelor of Engineering with Honours (Materials Engineering)

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DECLARATION FORM

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Study on mechanical, biodegradability and compostability of agriculture waste loaded biodegradable polymer”. I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

M_w	Molecular Weight
T_g	Glass Transition temperature
T_m	Melting temperature
ΔH_{m100}	Enthalpy of melting of 100% crystalline
X_c	Degree of crystallinity

LIST OF ABBREVIATIONS

ASTM	The American Society for Testing and Materials
ATRH	Alkali-treated rice husk
BDO	1, 4-butanediol
CA	Contact angle
DCP	Dicumyl peroxide
EN	European standards
DSC	Differential scanning calorimetry
FDA	United States Food and Drug Administration
FTIR	Fourier transform infrared spectroscopy
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear-low density polyethylene
MAH	Maleic anhydride
MDI	Methylene diphenyl diisocyanate
MESTECC	Ministry of Energy, Science, Technology, Environment and Climate
MTS	Modified tapioca starch
PBAT	Poly(butylene adipate-co-terephthalate)
PBATg-MA	Poly(butylene adipate-co-terephthalate) grafted maleic anhydride
PBS	Poly(butylene succinate)
PBSA	Poly(butylene succinate-co-adipate)
PCL	Polycaprolactone
PHA	Polyhydrocyalkanoates
PHB	polyhydroxy butyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Polylactic acid

PP	Polypropylene
PS	Polystyrene
PE	Polyethylene
PVC	Polyvinyl chloride
PSA	Particle size analyzer
RH	Rice husk
SEM	Scanning electron microscope
TS	Tapioca Starch
UPR	Unsaturated polyester resin
USM	Universiti Sains Malaysia

KAJIAN MENGENAI MEKANIKAL, KEBOLEHBIODEGRADAN DAN KEBOLEHKOMPOSAN SISA PERTANIAN BERMUAT POLIMER TERBIODEGRADASI

ABSTRAK

Polimer terbiodegradasi adalah penyelesaian terbaik untuk mengurangkan isu pencemaran putih. Poli(butilen adipat-ko-tereftalat) (PBAT) mempamerkan kebolehbiodegradan dan sifat mekanikal yang baik, tetapi kosnya yang tinggi mengehadkan penggunaannya yang luas. Penggabungan pengisi semula jadi ke dalam PBAT boleh mengurangkan kos dengan ketara, tetapi sifat mekanikal komposit PBAT/pengisi yang diperolehi berkurangan secara mendadak. Di sini, sifat mekanikal komposit PBAT yang serasi dengan menggunakan kanji diubah suai (MS), sekam padi terawat alkali (ATRH) dan pengisi hibrid; MS dan ATRH melalui kaedah pencairan mudah telah dikaji. Selain itu, pelbagai teknik pencirian termasuk FTIR, SEM, DSC, penyerapan air, sudut sentuhan air, ujian tegangan dan ujian kadar penghantaran oksigen akan dilakukan pada komposit. Kemudian, biodegradasi akan dinilai dengan mengukur berat yang hilang semasa ujian pengebumian tanah. Kebolehkomposan komposit PBAT akan dijalankan dengan mengukur ketinggian benih bawang dan kadar percambahan benih dalam pasu untuk tempoh 25 hari. Dalam penyelidikan ini, keputusan menunjukkan bahawa sifat mekanikal PBAT/kanji diubah suai menerima sifat mekanikal yang luar biasa (TS:8.027MPa; YM:67.938MPa; EAB: 202.585%) diikuti dengan pemuatan pengisi hibrid (60PBAT/30MTS/30S/10ATRH) dengan (TS:7.384MPa; YM:83.211MPa; EAB: 28.59%) dan akhirnya sekam padi terawat PBAT/alkali dengan (TS:9.975MPa; YM:179.693MPa; EAB: 15.235%). Penambahan kandungan sekam padi dalam pemuatan hibrid mengurangkan pemanjangan semasa putus tetapi mempercepatkan peratusan biodegradasi. Hal ini disebabkan penambahan sekam padi menyebabkan pengisi tergumpal dalam matriks PBAT serta memberikan sifat rapuh kepada komposit. Kebolehbiodegradan PBAT/kanji diubah suai dan filem PBAT/MTS/ATRH selepas 12 minggu menunjukkan penurunan berat sebanyak 91.23% dan 91.94 %, menunjukkan ia adalah bahan terbiodegradasi. Dalam ujian kebolehkomposan, kedua-dua sampel mencapai kadar percambahan yang sama dan pertumbuhan normal benih bawang berbanding dengan PBAT (sampel kawalan) pada penghujung 25 hari, menunjukkan kesan tidak ketoksikan terhadap komposit. Komposit berasaskan PBAT dengan prestasi cemerlang dan kos rendah dengan pemprosesan kaedah campuran lebur yang mudah akan menunjukkan menjanjikan untuk aplikasi pembungkusan yang berpotensi

STUDY ON MECHANICAL, BIODEGRADABILITY AND COMPOSTABILITY OF AGRICULTURE WASTE LOADED BIODEGRADABLE POLYMER

ABSTRACT

Biodegradable polymer is the best solution to reduce white pollution issues. Poly(butylene adipate-co-terephthalate) (PBAT) exhibit good biodegradability and mechanical properties, but its high cost limits its wide applications. The incorporation of natural fillers into PBAT can significantly lower the cost, but the mechanical properties of the obtained PBAT/filler composites are dramatically reduced. Herein, the mechanical properties of compatibilized PBAT composites with using modified starch (MS), alkaline treated rice husk (ATRH) and hybrid filler; MS and ATRH by simple melt-blending method was investigated. Besides, various characterization techniques including FTIR, SEM, DSC, water absorption, water contact angle, tensile testing and oxygen transmission rate test will be performed on the composite. Then, the biodegradability will be evaluated by measuring weight lost during soil burial test. The composability of the PBAT composite will be carried on measuring the height of onions seeds and seed germination rate in the pot for the duration of 25 days. In this research, the results showed that the mechanical properties of PBAT/modified starch received remarkable mechanical properties (TS:8.027MPa; YM:67.938MPa; EAB: 202.585%) followed by hybrid filler loading (60PBAT/30MTS/30S/10ATRH) with (TS:7.384MPa; YM:83.211MPa; EAB: 28.59%) and finally the PBAT/alkaline treated rice husk with (TS:9.975MPa; YM:179.693MPa; EAB: 15.235%). The increment of rice husk content in hybrid loading lower the elongation at break but accelerate the biodegradability percentage. This is due to the addition of rice husk cause filler agglomerate in the PBAT matrix as well as impart the brittle nature to the composite. The biodegradability of the PBAT/modified starch and PBAT/MTS/ATRH film after 12 weeks showed 91.23% and 91.94 % weight loss, indicating it is biodegradable material. In the compostability test, both samples achieved the same germination rate and normal growth of the onion seeds compared with PBAT (control sample) at the end of 25 days, demonstrating non-toxicity effect towards the composite. The PBAT-based composites with excellent performance and low cost by simple melt-blending method processing will show promising for potential packaging applications.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Plastic is the essential material that boost an incredible growth of our modern economy in this industrialised area. Most industrial plastics are manufactured from petrochemicals and synthetic or semi-synthetic organic elements. The raw material of plastic includes cellulose, coal, natural gas, salt, and crude oil (Hossain et al., 2020). The most frequently used plastics are polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC), followed by poly(ethylene terephthalate) (PET), polyurethane (PUR), and polystyrene (PS) (Muhonja *et al.*, 2018; Urbanek *et al.*, 2018; Danso *et al.*, 2019) which shown in Figure 1.2. These six types of plastic account for more than 90% of all plastics ever manufactured (Sánchez *et al.*, 2020). The growing supply of these plastic-containing products are due to the advantages of durability, cost-effectiveness, versatility, elasticity, resilience, and longevity (MacArthur *et al.*, 2017; Brahney *et al.*, 2020). Thus, they are used in a variety of sectors which include building and construction, transportation, packaging, electronics, automotive manufacturing, and agriculture (Plastics Europe, 2018; Plastics Europe, 2019)

Plastic - the Facts by Plastic Europe & EPRO (2020) estimates that worldwide plastics output will nearly exceed 367 million tonnes in 2020 (Figure 1.1) and expected to grow 36.24% by 2025, growing to 500 million tonnes (Bai *et al.*, 2019; Gibb *et al.*, 2019)

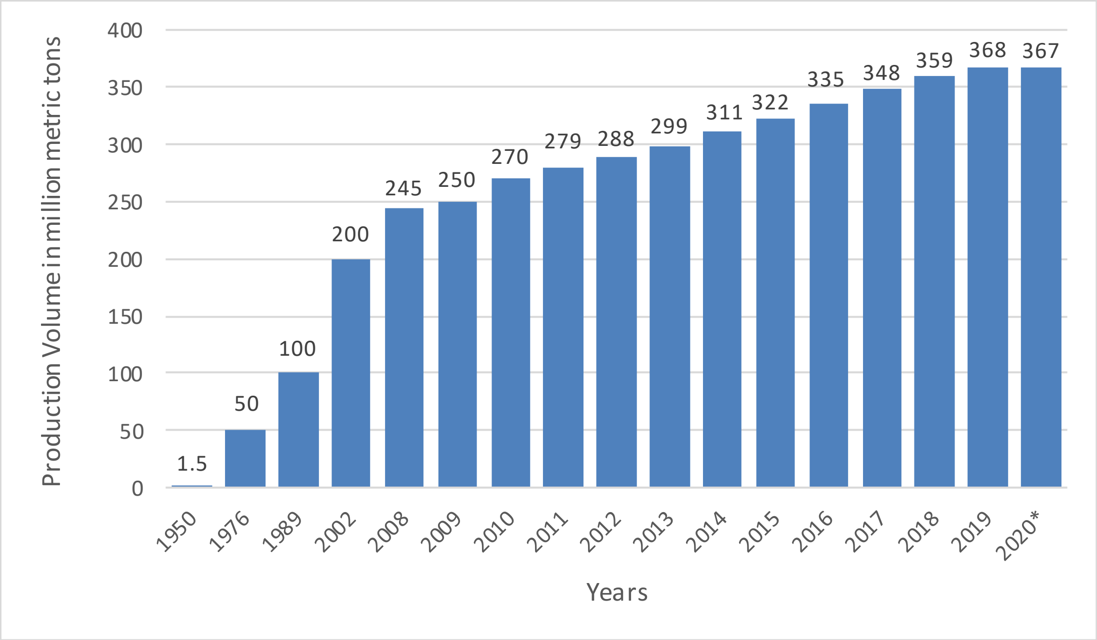


Figure 1.1: Global Plastic Production (Ian, 2022)

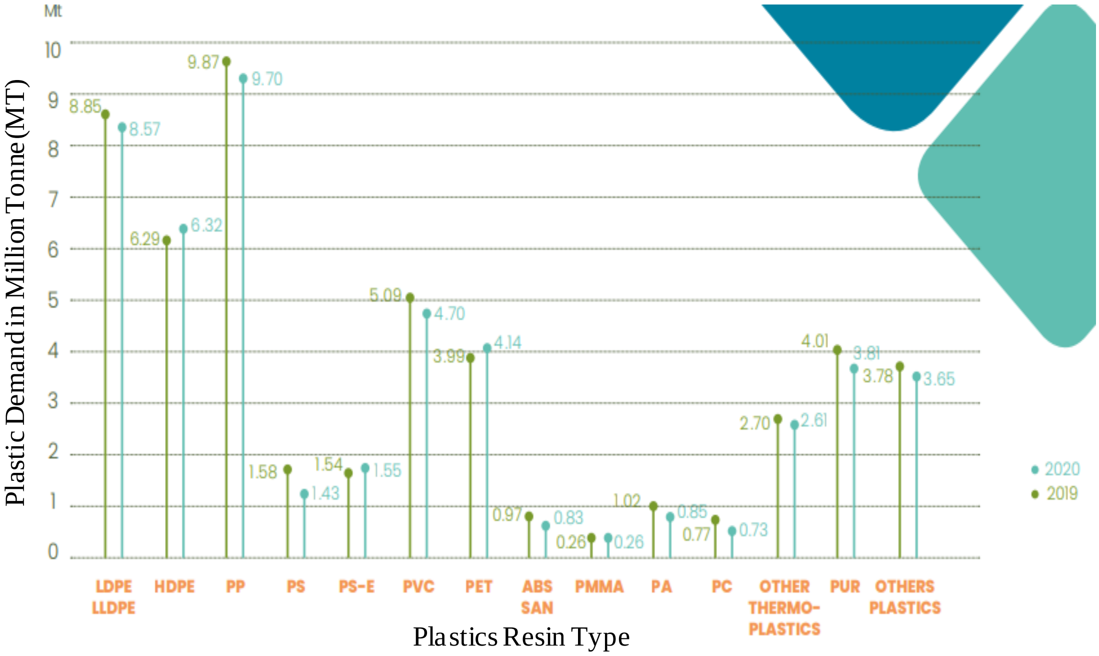


Figure 1.2: Plastics demand by resin type in 2020 (PlasticEurope & EPRO, 2020)

However, poor biodegradability, excessive usage and widespread mismanagement of plastics have led to the fact that plastics are now ubiquitous, causing massive pollution to air, soil and water bodies. Plastics are life-threatening and are known as one of the most widespread and persistent anthropogenic changes in Earth's biosphere (Geyer *et al.*, 2017).

According to a 2019 report published by the World-Wide Fund for Nature (WWF), Malaysia has the second-highest for yearly per capita plastic use in Asia, with the consumption of 16.78kg per person. In 2020, Malaysia's plastic consumption reached 543.5 kilo tons (Taylor, 2020). Same with majority of developing countries in Southeast Asia, Malaysia do not have a proper waste management system for dealing the plastic waste produced (Kaza *et al.*,2018). Notably, by 2018, Malaysia generated over 940,000 tonnes of the mismanaged plastic waste annually (MESTECC *et al.*, 2018; Jambeck *et al.*, 2015). Referring to the global input of marine plastic waste in 2019, Malaysia ranks third in the world, accounting for about 7.46% of the world's marine plastic waste, as shown in Figure 1.3. The mishandling of plastic waste endangers both the terrestrial and marine ecosystems, as well as human health.

This plastic wastes consist flame retardants, bisphenol A (BPA), phthalates and heavy metals such as lead and cadmium which will leach from landfills and have a negative impact on organisms and the environment. The plastic waste blocks waterways, causing standing water to become a breeding niche, resulting spreading of mosquitoes, pests, and vector-borne diseases, as well as disrupt natural cycles (terrestrial biogeochemical cycles) (Sanchez *et al.*, 2014; Raamsdonk *et al.*, 2020). Beside terrestrial ecosystem, plastics also cause significant harm to aquatic ecosystems. Plastic pollution deprives corals, sponges, and other bottom-dwelling species of light, food, and oxygen, causing oxygen deficiency in the sediment and thus result decrease in the number of organisms in the sediment (Green *et al.*, 2015; Balestri *et al.*, 2017). This bring negatively impact ecosystems and provide a foothold for pathogens, which can adversely affect marine life. Additionally, microscopic plastic particles are easily ingested by living things, causing internal injury and the accumulation of fat deposits, leading to a decline in the fitness of marine organisms that can ultimately lead to death and inevitably affecting the food chain. According to Jambeck *et al.* (2015), by 2050, approximately 600 species marine animals may have endangered due to plastic ingestion and entanglement.

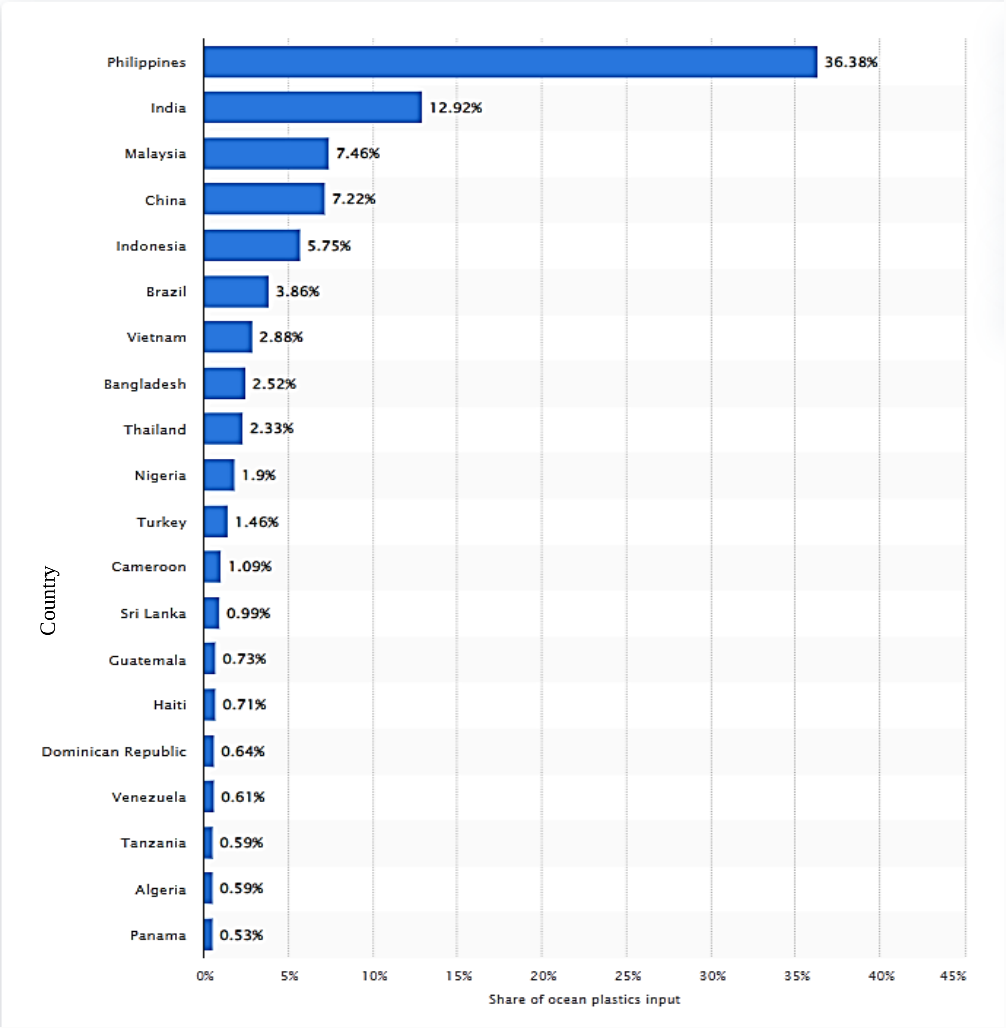
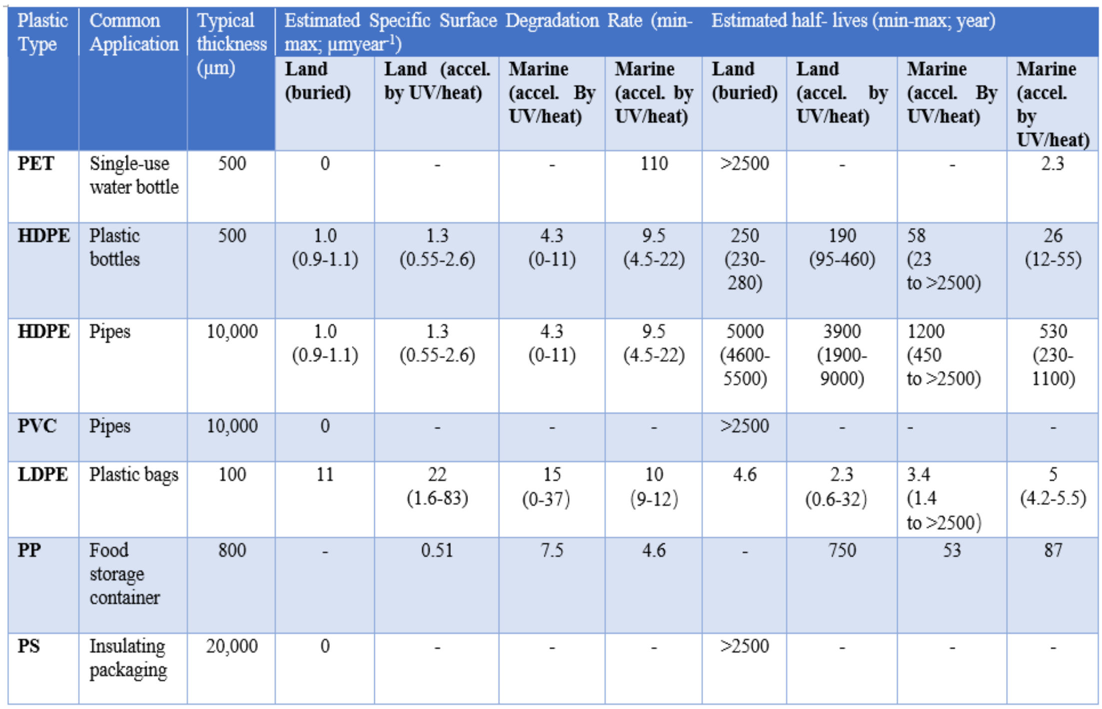


Figure 1.3: Ocean plastic waste inputs worldwide 2019, by country (Ian, 2021)

Due to its non-biodegradable nature, plastics continue to be discarded globally and generate large amounts of waste (Mwanza *et al.*, 2017). A key issue with handling plastics in the solid waste management cycle is that when plastics degrade in landfills, they cannot be permanently eliminated from the environment (Geyer *et al.*, 2017). This is because most plastic are resistant to biodegradation. Plastics require hundred to thousand years to break down into microplastic which is tiny particle of plastic (Giacovelli *et al.*, 2018; Blettler *et al.*, 2018; Wang *et al.*, 2016; Chen *et al.*, 2021) as shown in Table 1.1. Consequently, plastic will accumulate in landfill rather than decompose in landfills or the natural environment which result in huge impact to environment (Matjašič *et al.*, 2021).

Table 1.1: Estimated Half-Lives of Common Plastic Items (Chamas, 2020)



Plastic Type	Common Application	Typical thickness (μm)	Estimated Specific Surface Degradation Rate (min-max; μmyear^{-1})				Estimated half- lives (min-max; year)			
			Land (buried)	**Land (accel. by UV/heat)**	**Marine (accel. By UV/heat)**	**Marine (accel. by UV/heat)**	**Land (buried)**	**Land (accel. by UV/heat)**	**Marine (accel. By UV/heat)**	**Marine (accel. by UV/heat)**
PET	Single-use water bottle	500	0	-	-	110	>2500	-	-	2.3
HDPE	Plastic bottles	500	1.0 (0.9-1.1)	1.3 (0.55-2.6)	4.3 (0-11)	9.5 (4.5-22)	250 (230-280)	190 (95-460)	58 (23 to >2500)	26 (12-55)
HDPE	Pipes	10,000	1.0 (0.9-1.1)	1.3 (0.55-2.6)	4.3 (0-11)	9.5 (4.5-22)	5000 (4600-5500)	3900 (1900-9000)	1200 (450 to >2500)	530 (230-1100)
PVC	Pipes	10,000	0	-	-	-	>2500	-	-	-
LDPE	Plastic bags	100	11	22 (1.6-83)	15 (0-37)	10 (9-12)	4.6	2.3 (0.6-32)	3.4 (1.4 to >2500)	5 (4.2-5.5)
PP	Food storage container	800	-	0.51	7.5	4.6	-	750	53	87
PS	Insulating packaging	20,000	0	-	-	-	>2500	-	-	-

Currently, a variety of strategies are used to deal with plastic waste, including landfilling, recycling, composting and incineration (Kale *et al.*, 2007; da Luz *et al.*, 2013). However, recycling, incineration and landfilling are are inefficient and expensive (Kale *et al.*, 2007; Amobonye *et al.*, 2021). Incineration and pyrolytic conversion of waste plastic releases hazardous atmospheric pollutants such as polyaromatic hydrocarbons, CO_2 and persistent organic pollutants such as dioxins, which contribute to global warming and air pollution, whereas recycling is not effective as it requires advanced collection system to process. Composting is not only a cost-competitive method, but also an alternative that returns carbon to the environment in the form of carbon dioxide, soil or fertilizer (Hahladakis *et al.*, 2020; Kijchavengkul and Auras *et al.*, 2008). Given this scenario, the best option which is efficient and environmentally friendly for plastic waste disposal is to use biodegradable plastic to substitute polyolefin plastics.

The example of biodegradable polymers is starch, cellulose, polyhydroxylkanoates (PHA), Poly 3-hydroxybutyrate (PHB), Polyhydroxy (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polycaprolactone (PCL), polylactic acid (PLA), polybutylene succinate (PBS) and polybutylene adipate-coterephthalate (PBAT). Among biodegradable polymers, PBAT has demonstrated to be a promising combination of strength and flexibility due to the aromatic-aliphatic components (Jian *et al.*, 2020). The mechanical properties of PBAT are more flexible than most biodegradable polyesters, such as polylactic acid (PLA) and polybutylene succinate (PBS), and are comparable to low density polyethylene (LDPE) (Nagarajan *et al.*, 2013). However, the widespread use of PBAT is still low, owing to its expensive price than traditional non-biodegradable commodity plastics. Its price is three times greater than low-density polyethylene (LDPE), which limits its wide-scale applications for practical use (Danmmark *et al.*, 2020).

The addition of natural fibres or cellulose derivatives is an effective technique to improve polymer characteristics at the same time lowering their final cost (Mariano *et al.*, 2014, Sauza *et al.*, 2010 ; Botta *et al.*, 2017; Fiore *et al.*, 2014; Oksman *et al.*, 2016). Starch is a commonly used natural filler since it is inexpensive and one of the most abundant renewable resources. It is a completely biodegradable polysaccharide produced by a variety of plants (Datta *et al.*, 2015). However, starch is difficult to process as a thermoplastic because of the intermolecular forces and hydrogen bonding (Khan *et al.*, 2017). Therefore, plasticizers such as urea, glycerol, sorbitol, glycerol and water are needed to make deformable thermoplastic materials which known as thermoplastic starch (TPS). A plasticizer's primary role is to increase the flexibility, processability and ductility of composites (Wei *et al.*, 2019).

Recently, due to rising population, carbon overloading, and environmental distress, agricultural waste is a critical issue that we are facing globally. Rice husk is one of the most commonly available agricultural wastes (Hossain et al. 2018). For every 100 kg of rice processed, around 20 kg of rice husk waste will be generated (Ghosal *et al.*, 2015; Moulik *et al.*, 2015). In 2019, over 756 million metric tonnes of rice were produced worldwide, with Asia accounting for 90% of total output (Suhot *et al.*, 2021). In Malaysia, approximately 700,000 hectares of paddy fields are planted on vast farmland, generating more than 800,000 tonnes of rice husk (RH) and straw waste each year (Manickam *et al.*, 2015). The common method of disposing of rice husk waste is open burning, which releases carbon dioxide, resulting harmful to the environment and even damages the land. As a result, numerous studies attempt to use rice husk as reinforcement in composite applications, which not only improves the composite's reinforcing property as well as reduced the pollution generated by it (Zhang *et al.*, 2020b). The advantages of availability, low cost, sustainability, low density, toughness, weather resistance, high specific strength, and capacity to expedite biodegradability makes the rice husk can be used as a reinforcement to biodegradable polymer composites. Aside from these basic benefits, commercial applications of these underutilised renewable resources will result in economic growth in rural areas (Feng *et al.*, 2011). Hence, in this work, the possibility and effectiveness of hybridizing rice husk with tapioca starch for fabricating the hybrid filler-filled PBAT based eco-friendly plastic film was studied by determine their mechanical properties, biodegradation and compostability.

1.2 Problem Statement

1.2.1 Poor filler-matrix interfacial bonding

Hydrophobic nature of PBAT matrix with hydrophilic nature of filler (tapioca starch and rice husk), has inhibited the effective adhesion between the matrix of biodegradable polymer and filler, causing non-uniform spreading of the fibers inside the matrix which result to poor mechanical properties of the biodegradable polymer composite (Rahman *et al.*, 2019; Nurazzi *et al.*, 2021). Therefore, surface modifications are conducted on filler to improve their adhesion with the matrices. Alkaline treatment is the most common treatment in fiber. Sodium hydroxide (NaOH) that used in alkali treatment act to remove certain amount of lignin, wax and silica and depolymerization of cellulose, resulting in increasing the surface roughness and hence more exposure of short length crystallites. Short length crystallites enhance the number of reaction sites thus filler is more compatible with polymer matrix (Camargo *et al.*, 2020; Vijay *et al.*,2019; Boonsuk *et al.*, 2020; Plengnok *et al.*, 2020). Previous study

Bisht *et al.* (2018) found that the alkali treatment of rice husk has increased 36% in tensile strength for the polymer composite as NaOH treatment resulted in reaction of Na and OH ions to react with pectin, lignin, cellulose and other substances present on its surface and leach out, making it rougher thus improve the mechanical properties.

Previous research by Zahiruddin *et al.* (2019) demonstrated that starch modified with sorbitol had the highest tensile strength among the starch fillers because the molecular size of sorbitol was larger than glycerol, owing to the rigidity, strength, and thermal stability of the film. However, increasing the PBAT/TPS ratio from 80/20 to 60/40 resulted in decreased tensile strength and elongation at break from 8.3MPa to 6.8 MPa and 819% to 551%, respectively (Garalde *et al.* 2019). Fourati *et al.* (2018) found that adding of maleic anhydride (MAH) as compatibilizer agent even at 2wt% significantly enhanced the elongation at break. Thus, in this study, starch was modified with sorbitol while rice husk was alkali-treated with NaOH to form modified starch and alkali-treated rice husk. Maleic anhydride was incorporated as compatibilizer to improve the interfacial bonding between PBAT and filler (starch and rice husk).

1.2.2 Poor Biodegradability

Although PBAT is a biodegradable polymer, its biodegradability has been inhibited by its long-chain polymer structure, high molecular weight, and hydrophobicity (Urbanek *et al.*, 2018). There are few studies on biodegradation of PBAT under real soil condition showed poor biodegradability. Oliveira *et al.* (2019) found that mass loss percentage of pure PBAT that burial in soil was 5.7% only after 75 days of degradation. Similar result observed by Wang & Wei *et al.* (2015) who found mass loss of pure PBAT was around 2.3wt% in the three-month test and Moraes *et al*, (2020), reported that the pure PBAT films presented a mass loss only 33% after 168 days of degradation. The same material will take much longer to fully biodegrade under different natural environment due to the biodegradation rate of samples buried in soil was mainly influenced by the soil microorganisms and moisture, where the microbial activity depends on temperature and moisture content in the soil (Diao *et al.*, 2022).

The addition of starch or rice husk found that can accelerate the biodegradation compared to pure PBAT. Previous studies Danmmak *et al.* (2020) found that the rate of degradation in PBAT/TPS in the presence of MA is faster compared to pure PBAT. In addition, Datta and Halder *et al.* (2019) incorporated rice husk into corn starch/Low density polyethylene (LDPE) composites and proved that the rice husk content improved the degradation rate of the samples. These are due to the hydrophilic properties of starch and rice husk, which allow them to absorb water quickly. With the addition of rice husk to the polymer matrices, the water absorption capacity increased due to the presence of cellulose in the fibre structure, which tends to absorb moisture from the surrounding environment (Laftah *et al.*, 2021). The higher water absorption may have accelerated hydrolysis activity, which catalysed the degradation and breaking of polymer linkages, especially glycosidic bonds, resulting in high biodegradability (Krishnaiah *et al.*, 2018). In addition, water absorbed by the films facilitate the microorganisms to grow and break down the biopolymers. However, high water absorption of rice husk makes the PBAT composite weaker, more permeable result in poor mechanical properties, which could be counterbalanced by the addition of starch (Singh *et al.*, 2019). Thus, in this work, hybrid starch and rice husk filler were incorporated into PBAT matrix to facilitate the biodegradation as well as achieve the balance in water absorption capacity and mechanical properties.

1.2.3 High Cost of Biodegradable Polymer

With increasing environmental concerns, bio-based and biodegradable polymers are rising in importance due to the generation and disposal of plastic waste. Biodegradable polymers are the alternative solution to these problems. Because of its ease of processing and particularly high ductility, PBAT is expected to overtake competitors such as polybutylene succinate (PBS) and polycaprolactone (PCL) as the preeminent flexible bioplastic in the coming years. However, commercialization of PBAT has been limited in various application because the price is expensive compared to conventional plastic (Dammak *et al.*, 2020; Ferreira *et al.*, 2019). The price of PBAT in 2020 is RM12550.29–RM13871.37 per ton, which is about 2.5 times more than traditional plastic (PE) (Eleneza *et al.*, 2020). These limitations can potentially be overcome by using PBAT composites.

The effective solution to reduce the price problem in PBAT is replacing a specific portion of natural filler into PBAT as the natural filler are inexpensive and available abundantly (Koh *et al.*, 2018). Starch, one of the most promising natural polymers, provides an attractive low-cost basis for novel biodegradable polymers due to the low material cost and ability to be processed using conventional plastics processing equipment (Jiang *et al.*, 2020). Previous study Bai *et al.* (2020) compared the costs of PBAT and PBAT/TPS used in the making of films, found that the cost of PBAT/TPS was 25% cheaper compared to the pure PBAT film, with the estimation price of PBAT/TPS blend that include surface modification is RM9.76-RM10.65/kg. Therefore, PBAT/TPS blend is more affordable compared with pure PBAT alone. Furthermore, rice husk, a waste agricultural product that is generally abundant and inexpensive, is normally employed as a filler in polymer composite for a low-cost alternative. Thus, in this work, blending of starch and rice husk with PBAT are investigated to achieve low-cost biodegradable polymer composite.

1.3 Research Objective

The research objectives of this project are as followed:

i. To investigate the effect of surface modification of filler (tapioca starch & rice husk) on mechanical properties of PBAT composite.
ii. To investigate the effect of the hybrid filler loading (tapioca starch & rice husk) into PBAT matrix to obtain the best mechanical properties of the composite.
iii. To evaluate the biodegradability and compostability of the PBAT composite that possess the good mechanical properties.

1.4 Scope of Study

In this research, the hybrid filler (tapioca starch & rice husk) filled biodegradable polymer (PBAT) were used to produce agriculture waste loaded biodegradable polymer film. In the first stage of the experiment, the effect of surface modification of both fillers was carried out. Two polymer composites were prepared for each filler, whereas one is with the modification and another one is without the modification. A plasticizer (sorbitol) was used for surface modification of tapioca starch, and the optimal tapioca starch:sorbitol ratio was fixed at 100:30. Besides, the chemical treatment with 4wt% (NaOH) was used for surface modification of rice husk. Fourier transformed infrared spectroscopy (FTIR), scanning electron microscope (SEM), x-ray diffraction (XRD), differential scanning calorimetry (DSC) and tensile testing were used to evaluate the films. Maleic anhydride (MAH) as compatibilizer and dicumyl peroxide (DCP) as radical initiator were utilized to improve the interfacial adhesion between filler and matrix.

In a subsequent experiment, the best-optimized sample for each surface modification of filler (modified starch/ alkali-treated rice husk) were combined and reinforced into PBAT. Then, hybrid filler loading of modified tapioca starch/alkali treated rice husk in PBAT was investigated. The filler loading of tapioca starch/ alkali treated rice husk was fixed with total at 40wt% and distributed into 30/10 wt%, 20/20 wt% and 10/30 wt% respectively. The scanning electron microscope, tensile properties, differential scanning calorimetry, water absorption, water contact angle and oxygen transmission rate analysis were conducted on the film.

Next. the biodegradability of the samples was studied where the sample is buried under the soil with the duration of 12 weeks and the mass loss percentage for each sample were measured every 2 weeks. In the last stage, the best optimized sample for the previous part was chosen to undergo composability test. During the composability test, the height of the onions seed was measured and the seed germination rate were calculated. The results were then compared to the pure PBAT (control sample) to study the toxicity induced by the samples.

1.5 Thesis Outline

This thesis consists of 5 chapters. Chapter 1 elaborates the issues of plastic pollution, impact of plastic waste issues as well as the possibility of using agriculture waste (rice husk) to fabricate an eco-friendly and affordable biodegradable polymer. The problem that encountered to fabricate filler (tapioca starch/ rice husk) loaded into biodegradable polymer was addressed in the part of problem statement. Besides, the objective of the research to address limitation, scope of study and thesis outline also will be elaborated in chapter 1. In chapter 2, the literature review presents the significant information of previous research papers which related to biodegradable polymer (PBAT) and filler (tapioca starch / rice husk). Type of plasticizer and chemical treatment that used for the surface modification of the filler and type of compatibilizer that used to improve interfacial adhesion between matrix and filler were also elaborated in this chapter. Chapter 3 detailed the raw material, experimental procedure, experimental design and the characterization method to fabricate the PBAT composite film. Chapter 4 presented the experimental result that obtained from this research. Chapter 5 concludes the findings of the research provides few recommendations of the future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section is divided into three parts. The first part describes the details of biodegradable polymer, definition of biodegradability and compostability. The second part elaborates the agriculture waste issues. The third parts reviews the important factors to control the properties of biodegradable polymer that include effect of filler, effect of plasticizer in tapioca starch, effect of chemical treatment in rice husk and effect of compatibilizer.

2.2 Biodegradable Polymer Production

Biodegradable polymer is the best solutions to reduce the issues of plastic waste management which replace the synthesis plastic, especially in the packaging application (Monica *et al.*, 2015). Global bioplastic production capacity reached 2.42 million tonnes in 2021 where biodegradable polymer commands 64.2% while biobased and non-biodegradable polymer commands 35.8%. Among the total capacity of biodegradable plastics, the four most productive materials were PBAT, PLA, starch blends and PBS, which accounted for 19.2 %, 18.9%, 16.4% and 3.5% respectively as shown in Figure 2.1. From the perspective of the regional capacity development of bioplastics in 2021, Asia reached 49.9% as the top production of bioplastic region, followed by Europe (24.1%), North America (16.5%), South America 9.1% and Australia/Oceania (0.4%) as shown in Figure 2.2 (European Bioplastic, 2021). In 2021, packaging will continue to be the largest market segment for bioplastics, accounting for 1.15 million tonnes of the total bioplastics market that shown in Figure 2.3 (European Bioplastic, 2021). Rapid development of PBAT (polybutylene adipate terephthalate) and PBS (polybutylene succinate) polymers, as well as the steady growth of polylactic acids (PLAs), are believed to contribute to the increase in the production of biodegradable plastics to nearly 5.3 million tonnes by 2026.

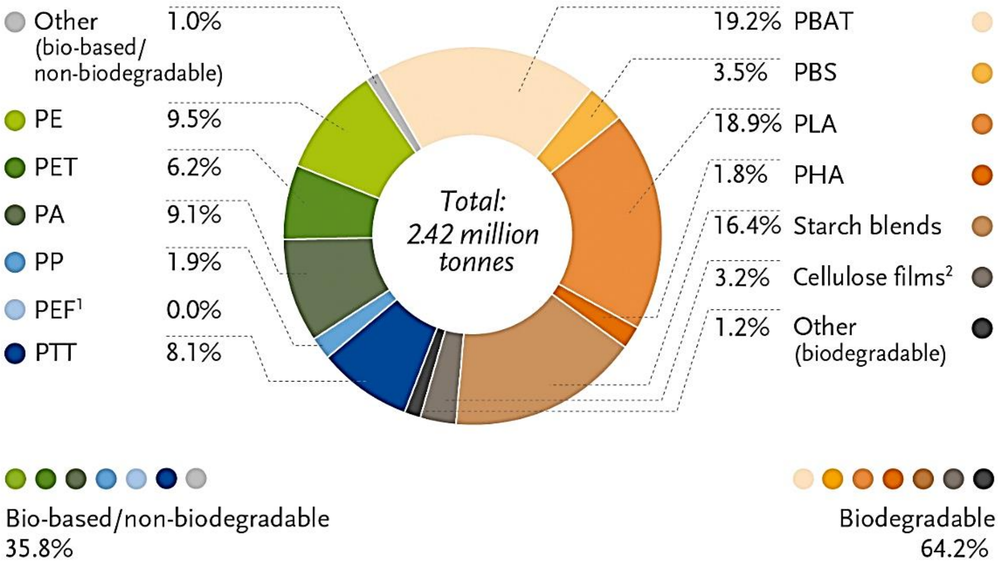


Figure 2.1: Global production capacities of bioplastic 2021 (European Bioplastic, 2021)

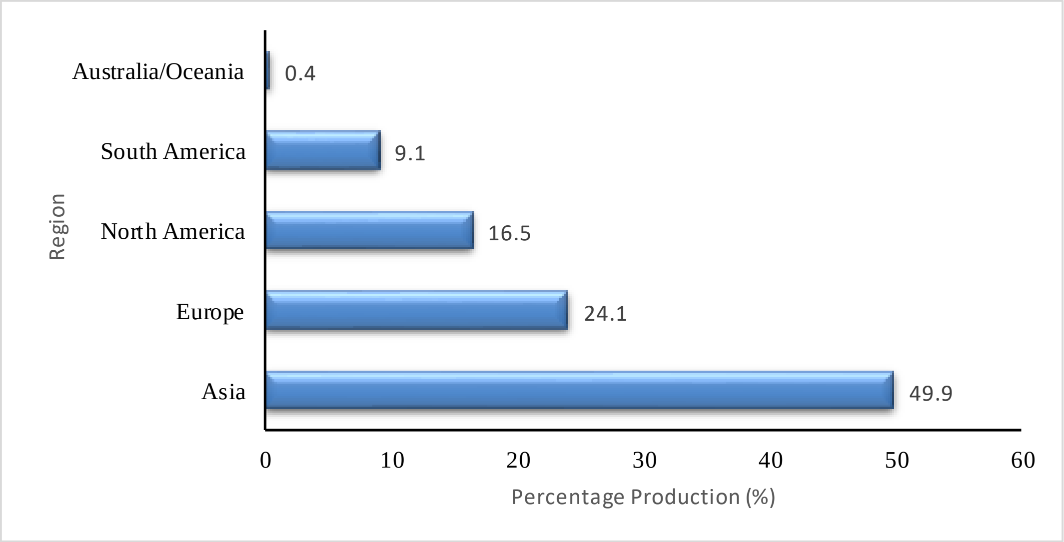


Figure 2.2: Global Production Capacities of Bioplastics in 2021 (by region) (European Bioplastic, 2021)

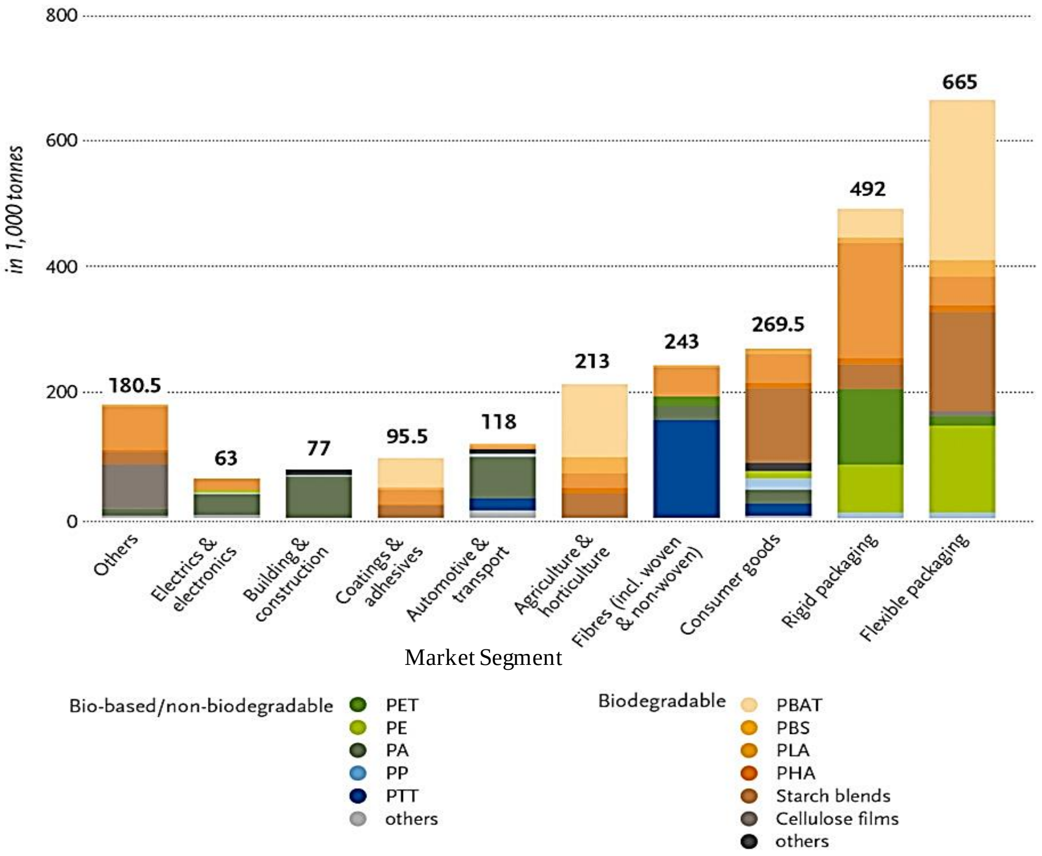


Figure 2.3: Global production capacities of bioplastic 2021 for market segments (European Bioplastic, 2021)

In the following section, the details of biodegradable polymers, biodegradation, composability and agriculture waste will be reviewed in detail.

2.3 Classification of Bioplastic

Bioplastics are bio-related polymers deemed suitable for replacing conventional plastics derived from fossil fuels. It consists of two distinct concepts: biobased and biodegradable which shown in Figure 2.4. Despite the fact that bio-based and biodegradable plastics are sometimes used interchangeably, they are distinct. Bio-based plastics are polymers whose carbon is derived in whole or in part from renewable resources such as proteins and lipids (Koch *et al.*, 2018; Song *et al.*, 2009). Even though some plastics made from fossil fuels may be capable to biodegradation, however biobased polymers are not necessarily biodegradable (European, 2020). Biodegradable plastics are polymers that, in the presence of favourable environmental condition, can decompose into carbon dioxide, water, methane, inorganic chemicals, or biomass through the enzymatic action of microorganisms (Urbanek *et al.*, 2017; Soroudi *et al.*, 2013; Adhikari *et al.*, 2016; Ashok *et al.*, 2019).

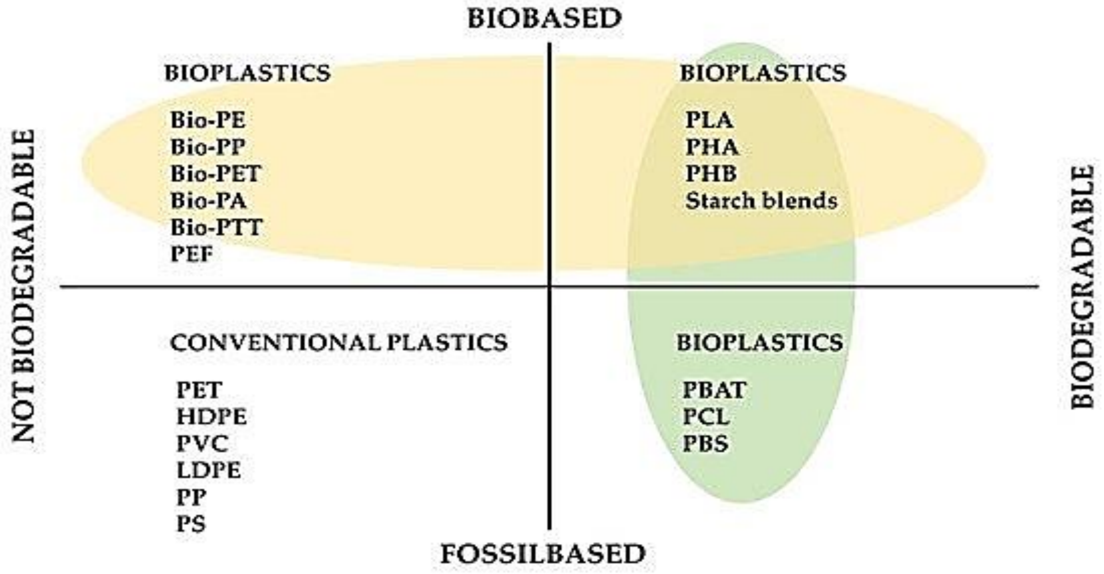


Figure 2.4: Types of plastics and bioplastics (European Bioplastic, 2019)

2.4 Biodegradable Polymer Classification

The chemical and physical properties of polymer which deteriorate and degrade when subjected to microorganisms, aerobic, and anaerobic processes are known as biodegradable polymer (Chen *et al.*, 2012). Biodegradable polymer-based is classified based on their source and biodegradability which shown in Figure 2.5. The details of each biodegradable polymer will be discussed in the subsequent section.

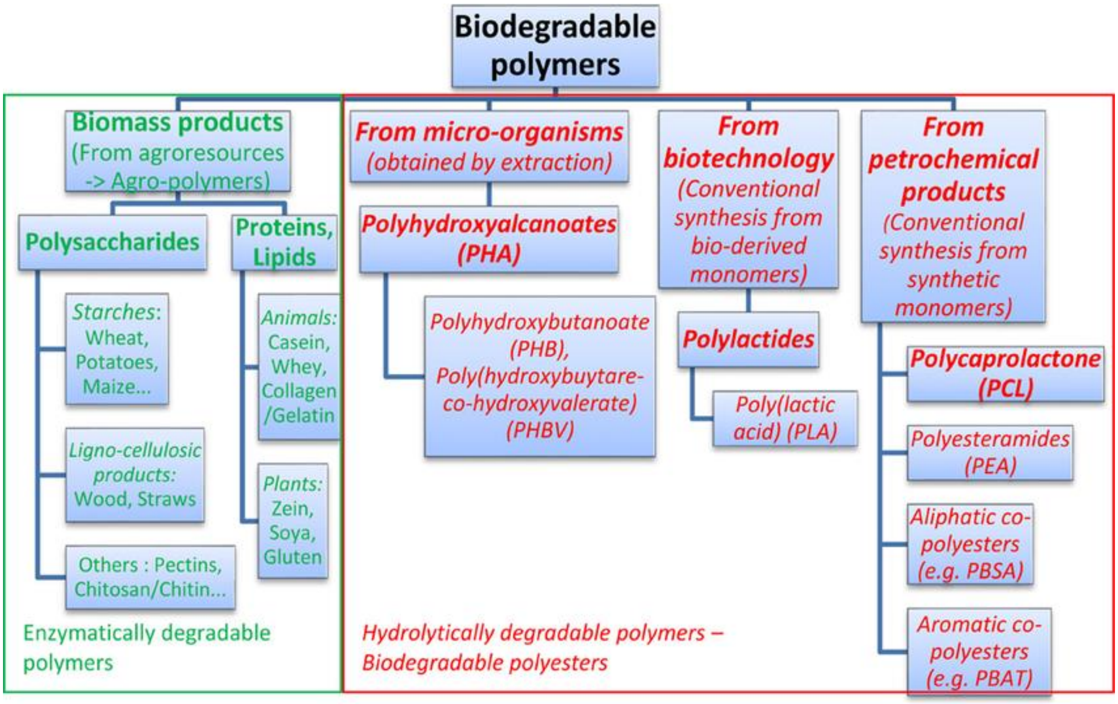


Figure 2.5: Classification of the most known biodegradable polymer (Kfoury, 2013)

2.5 Biodegradation Process

Biodegradation is the process in which microbial secretases catalyse an enzymatic hydrolysis process. Biodegradation processes cause polymer corrosion by breaking the polymer's hydrolytic or enzyme-sensitive bonds (Chamy, 2013). It consists of three phases: fragmentation, hydrolysis, and assimilation as shown in Figure 2.6 (Zhang *et al*., 2018; Laycock *et al*., 2017). Firstly, under the influence of weathering, ultraviolet radiation, mechanical force, microorganisms, etc., the polymer is broken down into small fragments or microplastics. The ester bond of the polymer then undergoes hydrolysis, resulting in a decrease in molar mass and the formation of soluble oligomers, dimers, and monomers. These degradation products are then absorbed by intracellular enzymes, which use them as carbon sources and energy to increase cell biomass and generate simple end products such as CO_2, methane, and water. This method is known as bio-assimilation and mineralization (Wang and Huang, 2021).

When assessing biodegradability, one must take into account whether the terms refer to the material being completely mineralized by microbial metabolism or to the chemical structure being altered by microorganisms.

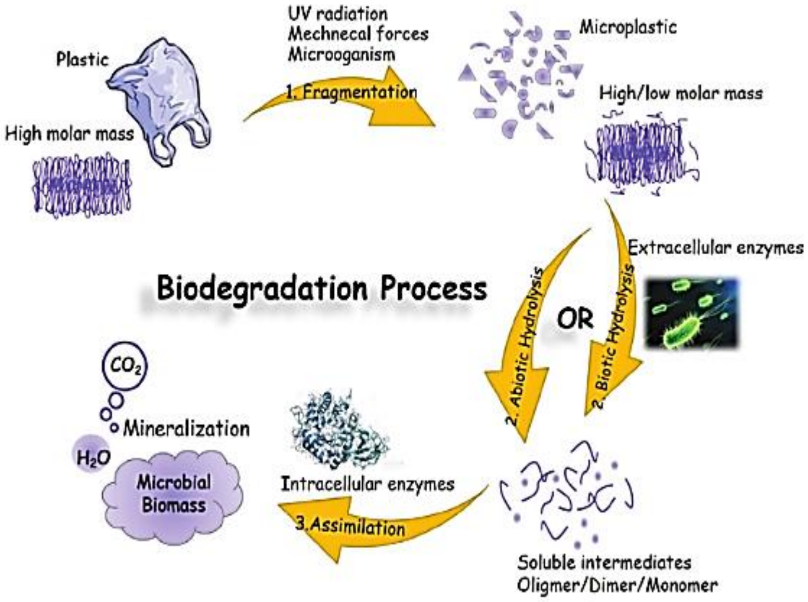


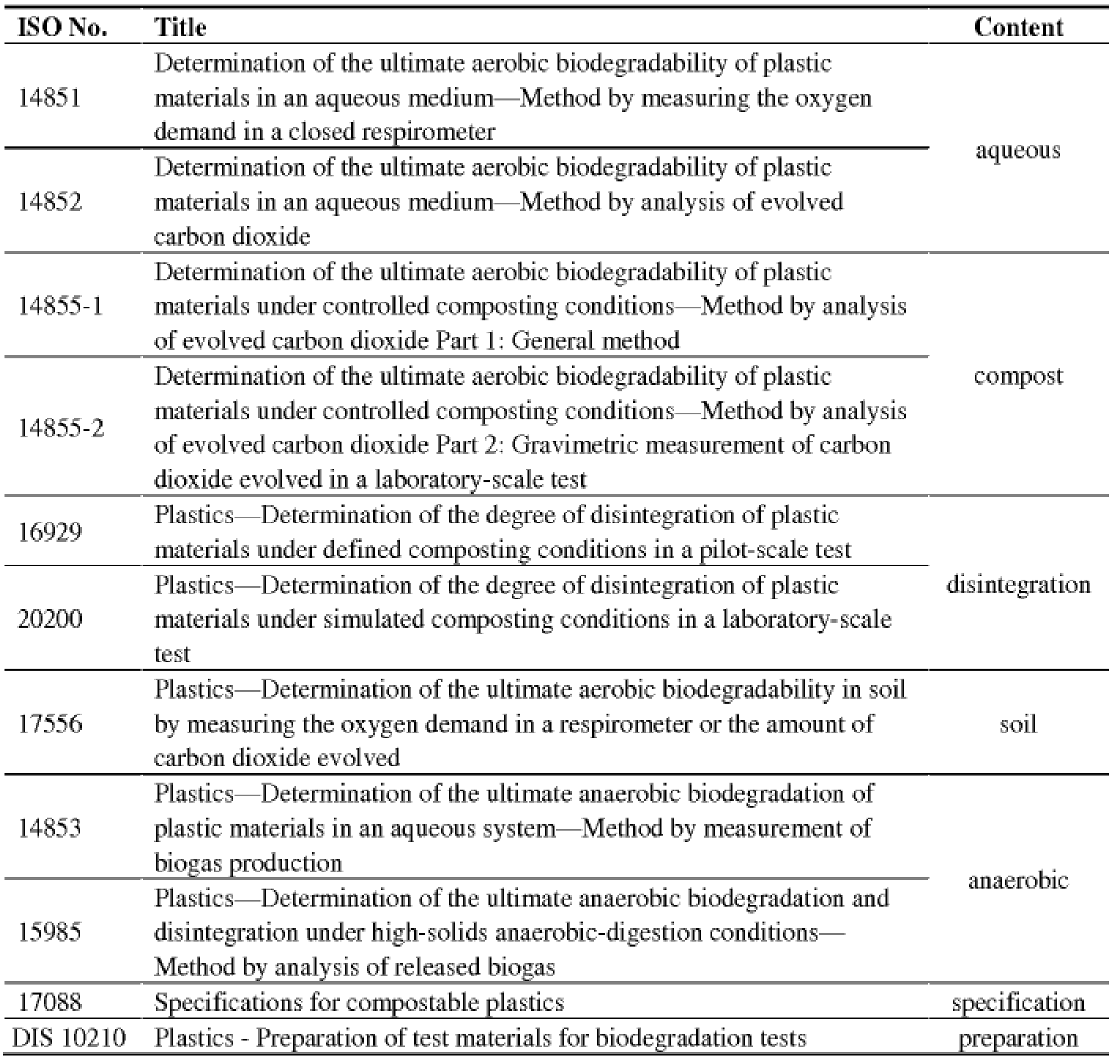
Figure 2.6: Schematic representation of the different steps involved in biodegradation (Wang and Huang, 2021)

2.5.1 Definition of Biodegradability

Biodegradability is the ability of an organism to biodegrade organic materials by living organism into water, carbon dioxide, methane, fundamental element and biomass (Goswami *et al.*, 2016). Biodegradation can occur in numerous environments, including landfills or soil burial, anaerobic digestion, composting, and marine or aquatic environments. Table 2.1 displays the ISO standards list regarding the biodegradation of plastics as discussed by TC61/SC5/WG22 (Funabashi *et al.*, 2009). For majority products, soil burial and composting will be the primary measures to the biodegradation.

According to ISO 14855:1999, the acceptable biodegradability criterion is at least 90 percent total biodegradability, or 90 percent of the maximal disintegration of a reference substance in less than six months (Wilde *et al.*, 2013). The biodegradation test is conducted at 58°C±2°C and 50% of relative humidity. A modified approach was used with the sample being buried beneath the natural soil at atmospheric conditions, taking into account if the landfill temperature and humidity do not reach 58°C±2°C and 50% of humidity (Bardi *et al.*, 2014). Once this process is completed, the samples is ready to be tested to see whether any ecotoxic residue of it by using compostability test. This helps to ensure that the sample doesn't have a harmful effect to environment.

Table 2.1: ISO standards list about the biodegradation of plastics (Funabashi,2009)



ISO No.	Title	Content
14851	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by measuring the oxygen demand in a closed respirometer	aqueous
14852	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by analysis of evolved carbon dioxide	
14855-1	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide Part 1: General method	compost
14855-2	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test	
16929	Plastics—Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test	disintegration
20200	Plastics—Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test	
17556	Plastics—Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved	soil
14853	Plastics—Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system—Method by measurement of biogas production	anaerobic
15985	Plastics—Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions—Method by analysis of released biogas	
17088	Specifications for compostable plastics	specification
DIS 10210	Plastics - Preparation of test materials for biodegradation tests	preparation

2.6 Compostability

Compostability is a property of a packaging that allows it to biodegrade in a composting process, according to CEN (European Committee of Standardisation). To claim compostability, it must be proven that a packaging may biodegrade and disintegrate in a composting system (as evidenced by conventional test procedures) and that the biodegradation is completed during end-use of compost. The compost must meet all of the required quality standards ASTM D6400. The influence of the compost samples on plant growth is evaluated in order to demonstrate that the test material does not release toxic to plants and the environment during degradation (Innocenti *et al.*, 2003).

The sample were put in the pots and then covered with layered of soil. After that, the seeds were counted and then planted on each sample to get the average height (Aseem *et al.*, 2020). The percentage of germination is determined by using percent germination of the control as 100%. If 75% or more than 75% of the seed have germinated and grow with normally height, it indicated that the compost is suitable for any application. Germination and growth of plants were stimulated compared to the reference samples (Adamcová *et al.*, 2015). Poor plant growth revealed incomplete composting.

2.7 Type of Biodegradable Polymer

Aliphatic polyesters and aromatic polyesters are the two main types of polyester polymer. PHA, PHB, PLA, PCL, PBS, and PBAT are commercially available biodegradable polyesters. Table 2.2 summarises the properties, advantages and drawbacks of various biodegradable polymers.

Table 2.2: Properties and disadvantages of the various biodegradable polymer

Biodegradable polymer	**Properties**	**Advantages**	**Disadvantages**	**Reference**
PLA	TS: 21–60 MPa YM: 0.35–3.5 GPA E: 2.5–6 %	• An eco friendly product • Biocompatibility • Better thermal processibility • Requires 25–55% less energy to produce • excellent bioresorption capabilities	• Poor toughness: Brittle , <10% elongation at break • Slow degradation rate • Relatively hydrophobic • Lack of reactive side-chain groups • Higher permeability to carbon dioxide, oxygen and water vapour	(Casalini *et al.*, 2019; Farah *et al.*, 2016; DeStefano *et al.*, 2020)
PHA	TS: 15–40 MPa YM: 1-2 GPa E: 1-15 %	• Biodegradability and biocompatibility • Easy processing • good resistance to UV rays • Insolubility in water	• The cost of PHA production is much high as compared to other bio-based plastics.	(Sharma *et al.*, 2021)
PHB	TS: 35–50 MPa YM:1670–2600 MPa E: 2–4 %	• Excellent gas barrier • Availability • Physical properties comparable to petroleum-based thermoplastics	• low strain at break • High costs of production • thermal instability • High fragility • Poor processability and formability	(McAdam *et al.*, 2020; Arrieta *et al.*, 2017 , Yeo *et al.*, 2018)
PHBV	YM: 2.38GPa E: 1.4 %	• Excellent oxygen barrier properties • Chemical inactivity • Greater flexibility compared to PHB	• Rigid and rather brittle • low impact resistance • poor thermal stability as compared with the petroleum-based polymer	(Rivera-Briso *et al.*, 2018 , Yeo *et al.*, 2018)

PCL	TS: 23-33MPa YM: 430-500MPa E: 450-1100%	• Easy availability • Cost efficacy • Non toxic • Tissue compatible	• Exhibits a longer degradation time (2–3 years)	(Dwivedi *et al*., 2019)
PBS	TS: 24-30MPa E: 170-380%	• Good thermal stability • Able to degrade at high rates over short periods of time • High heat resistance	• high production cost • low melt viscosity • gas barrier properties • Brittleness • Insufficient impact strength	(Rafiqah *et al*., 2021; Muthuraj *et al*., 2015, Huang *et al*., 2018, Rudnik *et al*., 2019)
PBAT	TS: 32-36MPa E: near 700% YM:20-35MPa	• Good biodegradability • Higher hydrophobicity and is easy to process • High elongation at break • Flexible	• High production cost • Low modulus and stiffness	(Jian *et al*., 2020; Silva *et al*., 2017, Ferreira et al., 2019)
PBAT / PBS	N/A	• Tensile strength of PBS/PBAT blends can be higher than each of the blended partner. • Good compatibility achieved between the PBAT and PBS phase in the blends	N/A	(Matos Costa *et al*., 2020; Yap *et al*., 2020)
PBAT / PCL	N/A	• Good thermal stability • Improve the toughness of polymer blends	N/A	(Sousa *et al*., 2019)