BIODEGRADATION OF POLYLACTIC ACID/STARCH BLENDS

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A project report submitted in partial fulfilment of the
requirements for the award of the degree of
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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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Specially dedicated to
my beloved mother, father, sister, and all my friends and lecturers that have assisted me in this study

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BIODEGRADATION OF POLYLACTIC ACID/ STARCH BLENDS

ABSTRACT

Compression moulded polylactic acid (PLA) 100 % and PLA/ Starch blends of PLA/Starch 80/20 and 50/50 respectively were buried in soil for 9 weeks to study the effects of starch and the addition of effective microbes into the soil on rates of biodegradation. Biodegradation of these samples were determined by appearance, tensile stress and young modulus (elasticity). In terms of appearance, no significant changes were observed in the samples buried under the soil without the addition of effective microbes. However, changes were observed in samples buried under the soil with the addition of effective microbes. PLA 100 % appeared to be decolourized at the 9th week. PLA/Starch 80/20 appeared to be distorted, displaying some brownish colour on its surface at the 3rd week. As for PLA/Starch 50/50, crevices were observed to appear on the surface at the 9th week. In general, PLA are slow to degrade in soil as it illustrated a steep decline in its tensile stress and elasticity at initial and then remain a fairly constant rate of declination throughout the burial period. Tensile stress and elasticity of the samples obtained for both soil conditions are decreasing in the order of PLA 100 % > PLA/Starch 80/20 > PLA/Starch 50/50. However, samples buried in soil mixed with microbes give a lower tensile stress and elasticity. This result shows that samples buried under the soil mixed with microbes and PLA samples blended with starch affects the tensile stress and elasticity. Addition of microbes into the soil enhances the biodegradation process of PLA. As for starch, it would decrease the effective cross-section area of the PLA continuous phase, resulting in decreases of tensile stress and elasticity. Therefore, based on this study, it is evident that soil burials are not recommended for the disposal of PLA or PLA/ Starch blends as they are slow to degrade in soil. Proper disposal alternatives such as composting or recycling or both should be considered.

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L	length
D	diameter
v/v	volume over volume
w/w	weight over weight
ρ	density, g/cm^3
MFI	melt index, g/10 min

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CHAPTER 1

INTRODUCTION

1.1 Conventional Plastic Problems

Plastic materials have played an important role in many applications in our life for many years. Every year the world production of plastic is estimated to be more than 100 million tonnes (Sriroth, Chollakup, Piyachomkwan, & Oates, 2000). The main reason for such an enormous amount of needs is due to their dominance over other materials in its exceptional properties. These properties include resistance to chemical reactions, high mechanical performances, good barrier properties and also good heat seal ability (Jamshidian, Tehrany, Imran, Jacquot & Desorby, 2010). Unfortunately, most conventional plastic products are manufactured from polyethylene, polypropylene, polystyrene, poly(vinyl chloride) and poly(ethylene terephthalate), where they are all non-biodegradable or their recycling process is either difficult or not economical (Tokiwa, Calabia, Ugwa, & Aiba, 2009).

This has been a very serious problem as the increasing amount of these conventional plastics have made acquiring sufficient areas for landfill sites to be more difficult and its accumulation in the environment will soon become a threat to the planet. Other then the non-biodegradability factor of these plastics, another serious environmental issue would be its manufacturing materials. Most of these conventional plastics are manufactured from fossil fuels which are non-renewable fuels. With the exceptional amount of plastics produced every year, high consumption of these non-renewable resources are required and this would one day lead to the depletion of these precious resources.

1.2 Biopolymers as a Solution

To solve these increasingly serious environmental issues, the society has raised its demands and directed many researches into biodegradable polymers which are called biopolymers. The word biodegradable or biodegradation is defined as the degradation of a polymer in natural environment that includes changes in chemical structure, loss of mechanical and structural properties, and finally, changing into other compound like water, carbon dioxide, minerals and intermediate products like biomass and humic materials (Jamshidian *et al.*, 2010).

Biopolymers are polymers that can be produced from natural and renewable resources and also from crude oil. There are a total of four categories of biopolymers that are widely recognized. The first category of biopolymer is polymers extracted directly from natural raw materials, such as polysaccharides like starch and cellulose. Some other examples are proteins like gelatine, casein, and silk and also marine prokaryotes. The second category of biopolymer is polymers produced by chemical synthesis from bio-derived monomers such as polylactic acid (PLA). The third category would be polymers produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), hydroxyl-valerate (PHV), bacterial cellulose, xanthan, and pullan. As for the last and fourth category of biopolymer, these polymers are produced from crude oil like aliphatic and aromatic polyesters, polyvinyl alcohol (PVA), and modified polyolefins (Jamshidian *et al.*, 2010).

1.3 The Usage of Starch

Starch may offer a substitute for petroleum-based plastics. It is a renewable, degradable, carbohydrate biopolymer derived from various sources. However, starch by itself has severe limitations because of its sensitivity to water. Articles made from starch will swell and deform upon exposure to moisture. Starch often has been blended with petroleum polymers to improve its properties, to increase its biodegradability, and to reduce the usage of petroleum polymer. For example, starch was blended with polyethylene (PE), low-density polyethylene (LDPE), poly(ethylene-co-acrylic acid) (EAA, polystyrene (PS), poly(ethylene-vinyl alcohol) (EVA), etc. However, the fraction of petroleum polymers in the blends still remains non degradable. Blending starch with biodegradable synthetic polymers became an interesting and promising target (Ke & Sun, 2000).

1.4 Biodegradability of Polymers

Between October 1990 and June 1992, confusion as to the proper definition of "biodegradable" led to lawsuits regarding misleading and deceitful environmental advertising. Thus, it became evident to the ASTM and ISO that common test methods and protocols for degradable plastics were essential. The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those which undergo a significant change in chemical structure under specific environmental conditions. These significant changes result in a loss of physical and mechanical properties, as measured by standard methods. Biodegradable plastics degrade from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Plastics may also be term as photodegradable, oxidatively degradable, hydrolytically degradable, or those which may be composted.

In order to be classified as biodegradable, materials must meet specific criteria set out by the ASTM and ISO. In general, the likelihood of microbial attack on a material is dependent on the structure of the polymer. When polymer materials were exam from a scientific standpoint, there are certain ingredients that must be present in order for biodegradation to occur. Most importantly, the active microorganisms such as fungi, bacteria, actinomycetes, etc. must be present in the disposal site. The microorganism type determines the appropriate degradation temperature, which usually falls between 20 to 60 °C. The disposal site must be in the presence of oxygen, moisture, and mineral nutrients, while the site pH must be neutral or slightly acidic at the range of 5 to 8.

Biodegradation of materials occurs in various steps. Firstly, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, which leads to a progressive enzymatic dissimilation of the macromolecule from the chain ends. However, oxidative cleavage of the macromolecules may occur instead, which leads to the metabolization of the fragments. Either way, the chain fragments will finally become short enough to be converted by microorganisms.

Innovative polymer research and development leads to large scale production by plastic converters (Lorcks, 1998). Biodegradable polymers are mostly manufactured from renewable resources, usually in the form of starch or cellulose. The biopolymers are formed into the specific end products and used by a consumer. Ideally, the biopolymer will be disposed in a bio waste collection, and later composted. This process will ultimately leave behind carbon dioxide and water, which are environmentally friendly by-products (Kolybaba, Tabil, Panigrahi, Crerar, Powell, & Wang, 2003).

1.5 Study of the Degradation Rate

The study of biopolymer’s degradation rate is very important. This is because different kind of biopolymers provides different rate of degradability in different kind of environments. These situations can be due to temperature, types and presence of microorganism, intensity of sunlight and also various combinations or mixtures with other compounds such as organic compounds and also other elements. The result of this study will provide essential information on which type of biopolymers that are suitable in certain application and in certain environment. This is because some applications require its biopolymers to sustain for a longer life compare to other applications.

Though it seems that the production of biopolymer would be the key solution for all environmental problems caused by accumulation of plastics including changes to the carbon dioxide cycle, problems in composting and increasing toxic emmisions to come to an end, but many research and studies are still required before biopolymer could be widely applied in our daily life. Currently, the price for a conventional plastic is still too cheap, at least compared with the alternatives.

1.6 Problem Statements

Polylactic Acid (PLA) has the highest potential for widespread use and it is the most commonly applied biopolymer in our daily life. However, PLA does not come with the best biodegradability properties amongst biopolymers. Degradation of PLA has been studied for several years, but understanding on this subject is still insufficient. This is clearly supported by the lack of information on the mechanisms involved and the microorganisms associated with the degradation. Many report states that PLA degradation occurred strictly through hydrolysis with no enzymatic involvement (Tokiwa & Calabia, 2006).

Several reports showed that the crystalline part of the PLA was more resistant to degradation than the amorphous part, and that the rate of degradation decreases with an increase in crystallinity (Tokiwa & Calabia, 2006). Stability of PLA also plays a very important role in its degradable rate. This is because stability of PLA in water and the scarcity of PLA-degrading microorganisms in soil environments may cause the degradation of PLA in natural environments to be very slow (Pranamuda, Tokiwa, & Tanaka, 1997).

Starch have many limitations mainly due to its solubility and poor water-resistance, thus, making starch products very sensitive to the relative humidity at which they are stored and used (Siew, Han, & Hanna, 2008). In order to overcome these challenges, several researchers have successfully blended starch with other synthetic polymers. Starch and PLA can be blended at varying concentrations to achieve the desired mechanical properties in a material for a variety of applications. However, the effect of the synthetic polymer matrix on the degradation of the starch remains unknown (Russo, O’Sullivan, Rounsefell, Halley, Truss, & Clarke, 2008).

Starch is a hydrophilic material and does not interact well with hydrophobic polyesters such as PLA, thus, resulting in unfavourable qualities of the blends.

1.7 General Objectives

The objective of this research is to investigate the degradable rate of PLA and PLA and starch blends.

1.7.1 Specific Objective

1. To determine the degradable rate of various types of biopolymers under the burial of soil with the presence of additional microbes.
2. To determine the degradable rate of various types of biopolymers under the burial of soil without the addition of microorganism.

1.8 Scope of Research

The scope of this research covers the following biopolymer materials, which are neat PLA, blend of PLA and tapioca starch. These materials were experimented under the following conditions which is under the burial of soil with and without the addition of effective microbes. Results were recorded beginning from the third week on a 3 weeks basis until the 9th week. The result of these experiments which is the degradable rate that were determined by visual inspection (phototaking) and by measuring its tensile strength. The degradablity of the particular polymer were deemed as high as the mechanical strength of the particular biopolymer becomes weaker.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiversity and Occurrence of Polymer-Degrading Microorganisms

Biodiversity and occurrence of polymer-degrading microorganisms vary depending on the environment, such as soil, sea, compost, activated sludge, etc. Thus, it is necessary to investigate the distribution and population of polymer-degrading microorganisms in various ecosystems. The major mechanisms involve in the microbial degradation of plastics is basically the adherence of the microorganisms on the surface of the plastics which is then followed by the colonization of the exposed surface. For enzymatic degradation of plastics by hydrolysis, it involves a two step process. In the first step, the enzyme would bind to the polymer substrate. As for the second step, it would catalyze a hydrolytic cleavage. Polymers are then degraded into low molecular weight oligomers, dimers and monomers and finally mineralized to CO_2 and H_2O (Tokiwa, Calabia, Ugwa, & Aiba, 2009).

The clear zone method with agar plates is a widely used technique for screening polymer degraders and for assessment of the degradation potential of different microorganisms towards a polymer (Tokiwa *et al.*, 2009). Agar plates that contain emulsified polymers are inoculated with microorganisms. Presence of the polymer degrading microorganisms can be verified by observing the formation of clear halo zones around the colonies. Such formation happens when the polymer-degrading microorganisms excrete extracellular enzymes which diffuse through the agar and degrade the polymer into water soluble materials. By using this technique, so far only a few PLA degrading microorganisms have been isolated and identified (Pranamuda *et al.*, 1997).

2.2 Factors Affecting the Biodegradability of Plastics

The properties of plastics are associated with their biodegradability. Both the chemical and physical properties of plastics influence the mechanism of biodegradation (Tokiwa *et al.*, 2009). For a biodegradation process of a polymer to occur, the surface conditions, first order structures and high order structures play very important roles. The surface conditions are the surface area, hydrophilic, and hydrophobic properties. First order structures are chemical structure, molecular weight, and molecular weight distribution. As for high order structures, it is the glass transition temperature, melting temperature, modulus of elasticity, crystallinity, and crystal structure (Tokiwa & Calabia, 2006).

In most situations, polyesters with side chains are less assimilated than those without side chains. Molecular weight plays an important role in biodegradability because it determines many physical properties of the polymer. By increasing the molecular weight of the polymer, it will decrease its degradability. The degree of crystallinity is also a crucial factor affecting biodegradability. This is because enzymes mainly attack the amorphous domains of a polymer. Molecules in the amorphous region are loosely packed, and thus make it more susceptible to degradation. The crystalline part of the polymers is more resistant than the amorphous region ((Tokiwa *et al.*, 2009).

2.3 The Emergence of Polylactic Acid

Today, the most common biodegradable synthetic polymers that are available includes aliphatic polyesters, such as poly(glycolic acids) (PGA), poly(lactic acids)

(PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV).

Under the trade name of Dexon since 1970 (Frazza & Schmitt, 1971), PGA was first developed as a fully synthetic absorbable suture that has been commercially available, but the suture tended to lose mechanical strength rapidly due to the hydrophilic nature of PGA (Reed & Gilding, 1981). PCL is a semicystalline polymer with a melting temperature of 59–64 °C and a glass transition of –60 °C. By comparing PCL with PGA or PLA, PCL has a significantly slower degradation rate and is suitable for relevant long-term application (Pitt, 1990). Unfortunately, its low melting temperature greatly limits the application. In the 1980s, PHB was identified as a promising biomaterial, and PHB and PHBV were commercially available under the trade name of Biopol in the late 1980s (Miller & Williams, 1987). Unfortunately, interest faded when it became clear that the cost of material was too high, and its properties could not match those of propylene.

Among these biopolymers, PLA is the most widely used synthetic degradable polymers in human medicine (Huang, 1989) and has been studied extensively for tissue engineering and drug delivery systems since the 1980s. PLA has good mechanical properties that are comparable to those of polystyrene (Martin & Averous, 2001) and good biodegradability. Other than that, the semicrystalinity of PLA is preferred in cases where high mechanical strength and toughness are required. All these properties have made PLA a better choice for disposable and biodegradable plastic substitutes. However, in some instances, PLA is still more expensive than conventional plastics, and the degradation rate is still slow compared with the waste accumulation rate (Ramsay, Langlade, Carreau, & Ramsay, 1993).

2.4 Background of Polylactic Acid

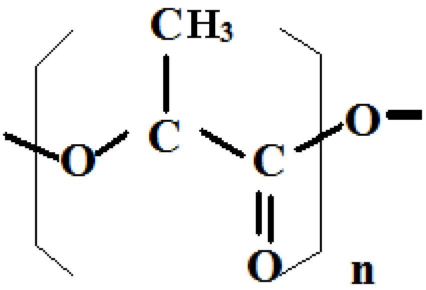


Figure 2.1: Molecular Structure of PLA

Figure 2.1 shows the molecular structure of PLA. PLA is manufactured from lactic acid dated way back in 1932 which was then pioneered by Carothers. It is a biodegradable and biocompatible thermoplastic which can be produced by fermentation from renewable resources or being synthesized either by condensation polymerization of lactic acid or by ring opening polymerization of lactide in the presence of a catalyst. This polymer exists in the form of three stereoisomers which are poly(L-lactide) (L-PLA), poly(D-lactide) (D-PLA) and poly(DL-lactide) (DL-PLA).

The degradation of PLA in soil takes a long time to start and degradation is slow. Ecological studies on the abundance of PLA-degrading microorganisms in different environments have been done and it is confirmed that PLA-degraders are not widely distributed, and thus, PLA is less susceptible to microbial attack compared to other microbial and synthetic aliphatic polymers. The first microbial degradation of PLA using *Amycolatopsis sp.* was reported by Pranamuda *et al.* (1997). Since then, several research studies dealing with microbial and enzymatic degradation of PLA have been published.

Many strains of genus *Amycolatopsis* and *Saccharotrix* were reported that are capable to degrade both PLA and silk fibroin. L-alanine and glycine are the main amino acid constituents of silk fibroin and they are found to have similarity between the stereochemical position of the chiral carbon of L-lactic acid unit of PLA and L-alanine unit in the silk fibroin. Silk fibroin is identified as one of the natural analogues of poly(L-lactide), thus, this may probably cause the PLA degrading microorganisms to identify the L-lactate unit as an analogue of L-alanine unit in silk fibroin. A number of proteinous materials such as silk fibroin, elastin, gelatin and some peptides and amino acids were found to stimulate the production of enzymes from PLA-degrading microorganisms.

Enzymatic degradation of PLA using proteinase K, bromelain and pronase have been studied. Among these enzymes, proteinase K from Tritirachium album was found to be most effective for PLA degradation. Unfortunately, proteinase K and other serine proteases are only capable of degrading L-PLA and DL-PLA but not D-PLA. Furthermore, proteinase K preferentially hydrolyzes the amorphous part of L-PLA where the rate of degradation decreases with an increase in the crystalline part. Degradation of PLA oligomers accelerated by several esterase-type enzymes was reported by Fukuzaki *et al.* (1989). The purified PLA depolymerase from Amycolatopsis sp. was also capable of degrading casein and silk fibroin. Other than that, several serine proteases such as trypsin, elastase, subtilisin were able to hydrolyze L-PLA (Tokiwa *et al.*, 2009).

2.4.1 Production of PLA

Lactic acid (2-hydroxy propionic acid), the single monomer of PLA, is produced via fermentation or chemical synthesis. Its two optically active configurations, the L(+) and D(−) stereoisomers are produced by bacterial (homofermentative and heterofermentative) fermentation of carbohydrates. Industrial lactic acid production utilizes the lactic fermentation process rather than synthesis because the synthetic routes have many major limitations, including limited capacity due to the dependency on a by-product of another process, inability to only make the desirable L-lactic acid stereoisomer, and high manufacturing costs (Datta & Henry, 2006).

The homofermentative method is preferably used for industrial production because its pathways lead to greater yields of lactic acid and to lower levels of by-products. The general process consists of using species of the *Lactobacillus* genus such as *Lactobacillus delbrueckii, L. amylophilus, L. bulgaricus, and L. leichmanii*, a pH range of 5.4 to 6.4, a temperature range of 38 to 42 ℃, and a low oxygen concentration. Generally, pure L-lactic acid is used for PLA production (Mehta, Kumar, Bhunia, & Upadhyay, 2005).

PLA has a variable molecular weight and only its high molecular weight polymer is used in the packaging industry. Three ways are possible for the polymerization of lactic acid; (a) direct condensation polymerization; (b) direct polycondensation in an azeotropic solution; and (c) polymerization through lactide formation. Other than these methods, PLA can also be produced by ring-opening polymerisation using stannous octoate as an initiator as shown in Figure 2.2. The first method is based on esterification of monomers by the aid of some solvents and exudated water is removed using progressive vacuum and high temperatures. Obtaining high molecular weight polyesters with good mechanical properties via this method is not easy, although precondensates may be of interest for the preparation of biodegradable glues or lacquers, since the –OH and -COOH end groups allow cross-linking with suitable inorganic or organic multivalent additives (Hartmann, 1998).

Producing high molecular weight PLA polymers by direct polycondensation in an azeotropic solution and also application of some catalysts is more practicable. The azeotropic solution helps to decrease the distillation pressures and facilitates PLA separation from the solvent by application of molecular sieves. The variety and content of catalysts, solvent volume percentages, and the reaction time on the preparation of PLA have been studied. The results identified by using improved experimental equipment, the proper complex catalyst, and solvent volume ratio, in order to obtain a molecular weight of PLA of 6.6 × 104 (Li, Tang, Wang, Pan, & Wang, 2006).

Polymerization through lactide formation is being industrially accomplished for high molecular weight PLA production. Lactide is a cyclic dimer formed by removing water under mild conditions and without solvent. L-lactide, meso (L,D) lactide, and D-lactide are products of L-lactic acid and D-lactic acid. The terms polylactide and poly (L-lactide) have been used in many references instead of PLA.

Lactide purification is accomplished by vacuum-distillation of high temperatures. After the vacuum-distillation of L-lactide, high molecular weight PLA with a controlled optical and crystal purity is formed by ring-opening polymerization. Ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic, and coordination mechanisms, depending on the initiator utilized. The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate (bis 2-ethyl hexanoate, SnOct2), which causes a low degree of racemisation at high temperature. It has a low toxicity and is accepted by FDA (Puaux, Banu, Nagy, & Bozga, 2007).

A kinetics study for ring-opening polymerization of L-lactide with stannous octoate has been done and a correlated mathematical modelling developed for that (Mehta, Kumar, & Upadhyay, 2007).

The choice of initiator system, co-initiator as chain control agent, catalyst concentration, monomer-to-initiator ratio, and polymerization temperature and time significantly affect the polymer properties. Properties such as molecular weight, degree of crystallinity, and residual monomer content, in turn affect the physico-mechanical properties of polylactide and its copolymers (Vink, Rajbago, Glassner, Springs, O’Connor, Kolstad, & Gruber, 2004).

New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process, include usage of crop residue such as stems, straw, husks, and leaves from corn or, potentially, other crops, and use of unfermentable residues as a heat source, as well as substituting some part of electricity energy by wind power energy. These approaches decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment (Vink, Rabago, Glassner, & Gruber, 2003).

One of the most positive points of PLA production in comparison with the other hydrocarbon-based polymers is the decrease of CO_2 emission as shown in Figure 2.3. Carbon dioxide is believed to be the most important contributor to global climate change and its warming. Because, carbon dioxide is absorbed from air when corn is grown, use of PLA has the potential to emit fewer greenhouse gases compared to competitive hydrocarbon-based polymers. “Net” or “residual” emissions are calculated as total emissions from the cradle to the factory gate minus carbon dioxide uptake that occurs during corn production. This amount is negative for present PLA production. It means the total CO_2 consumption from the cradle to factory is more than its emission to the environment (Bogaert & Coszach, 2000).

Vink *et al.*, (2003) concluded if all produced PLA articles enter into composting process which emits CO_2 in atmosphere. Nevertheless, their net CO_2 emission is less than for other polymers. Vink, Glassner, Kolstad, Wooley, and O’Connor (2007) showed the net greenhouse gas emissions of NatureWorks® PLA polymers decreased from 2 kg CO_2 eq./kg polymer in 2003 to 0.3 kg in 2006. The authors also estimated the -0.7 kg of CO_2 for next PLA generation using wind energy in the near future. By this opportunity, PLA can even become a greenhouse gas sink by the implementation of a new process technology combined with the use of green power to drive the production processes (Jamshidian *et al.*, 2010).

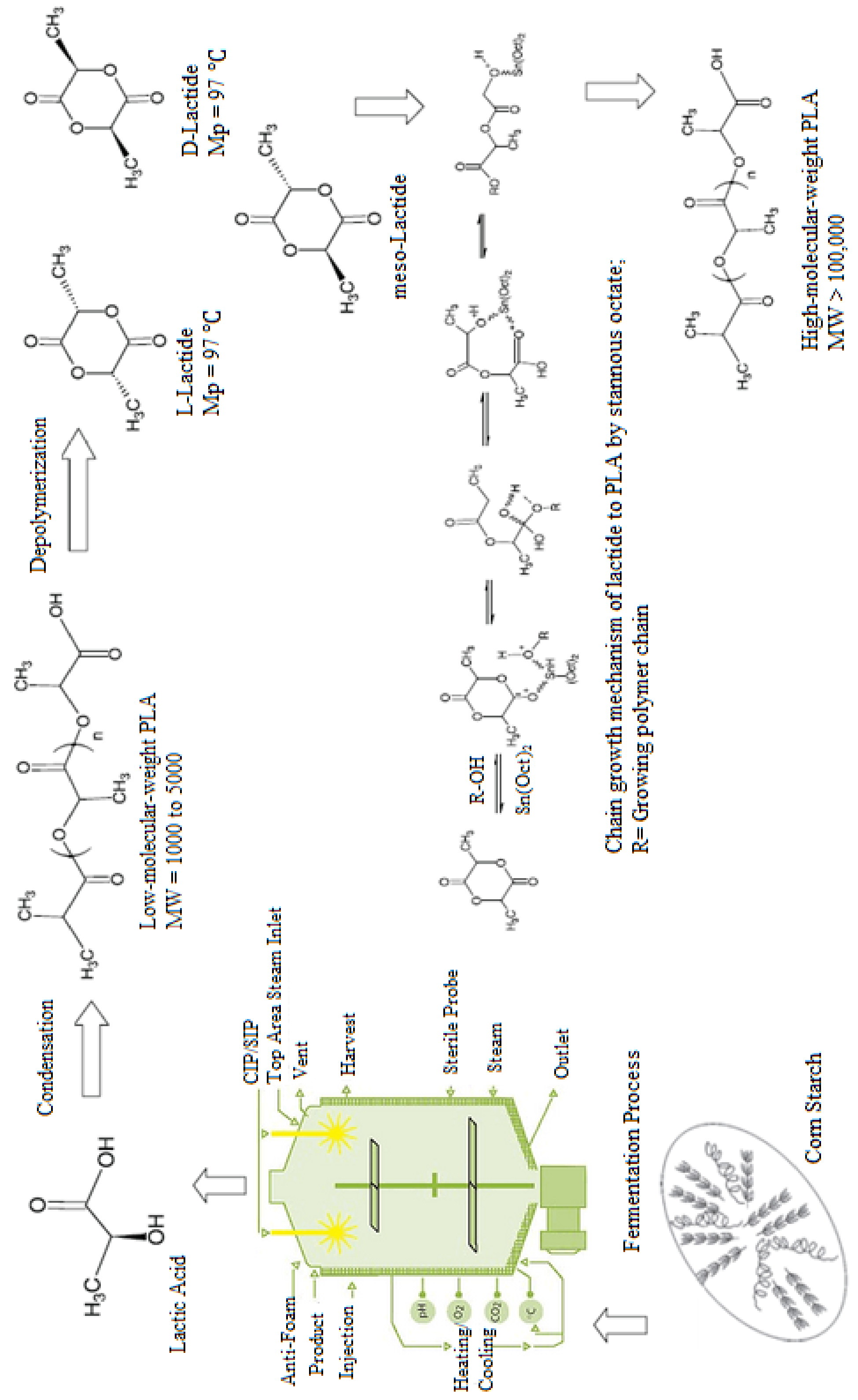


Figure 2.2: Shows PLA production steps by ring-opening polymerization using stannous octoate as an initiator.

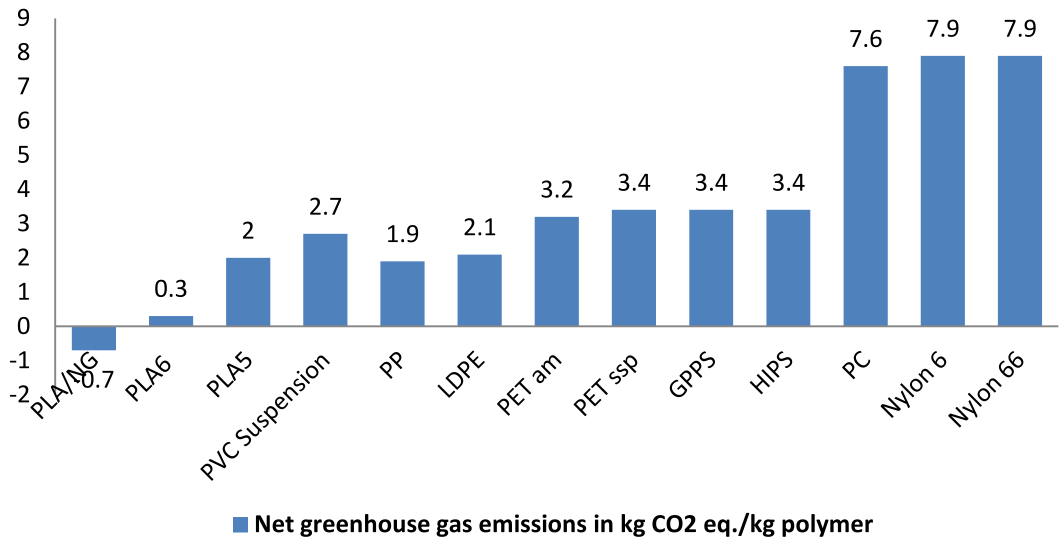


Figure 2.3: Net greenhouse gas emission of commercial PLAs and other polymers. PLA/NG = NatureWorks® PLA next generation, PLA5 = NatureWorks® PLA in 2005, PLA6 = NatureWorks® in 2006, HIPS = high impact poly(styrene), PC = poly(carbonate), GPPS = general purpose poly(styrene), PET am = PET amorph, PET ssp = PET solid sate polycondensed.

2.4.2 PLA Processing Technologies for Food Applications

The methods of manufacture for biopolymers are all established polymer-manufacturing techniques, but the control and application of these methods must be varied to cope with certain factors associated with exploiting the advantages of biopolymers. The manufacturing routes all show certain fundamental similarities, with the major differences depending on whether a thermoset or thermoplastic biopolymer is to be processed.

The conditions in biopolymer processes such as injection moulding are least damaging to polymer melts, and most problematic in continuous processes like extrusion, particularly in processes where the extrudate is stretched, such as film blowing. The limiting factors for processing conditions for biopolymers are the same as for petrochemical-based ones: degradation at the upper limits of temperature and shear, and lack of homogeneity at the lower limits. However, these limits are somewhat more tightly drawn at the upper limits for biopolymers. The results of exceeding these upper limits are degradation of the polymer, resulting in moulding defects such as weld lines, discoloration, or a strong odour in the final product (Johnson, Mwaikambo, & Tucker, 2003).

2.4.3 Extrusion of PLA

The first major step in the conversion of plastic resin into films, sheets, containers and so on, is to change the pellets from solid to melt or molten phase in an extruder.

Extrusion is a common way for processing thermoplastics and it is used for extrusion coating, cast film extrusion, blown film extrusion, and other polymer processes.

Screw extruders are typically used in the polymer industry. They consist of an electrically heated metal barrel, a hopper for feeding the resin, a motor for rotating a screw, and a die where the polymer melt exists. So, the combination of thermal energy generated by a heater and frictional heat due to friction between the plastic and the screw and barrel provide sufficient heat to melt the pellets.

The ratio of flight length of the screw to its outer diameter, which is the L/D ratio, determines the shear and residence time of the melt. Screws with a large L/D ratio provide greater shear heating, better mixing, and longer melt residence time in the extruder. Another important screw parameter is the compression ratio, which is the ratio of the flight depth in the feed section to the flight depth in the metering section. The greater the compression ratio a screw possesses, the greater the shear heating it provides (Giles, Wagner, & Mount, 2005).

2.4.4 Thermal Stability of PLA

PLA is thermally unstable and exhibits rapid loss of molecular weight as the result of thermal treatment at processing temperatures. The ester linkages of PLA tend to degrade during thermal processing or under hydrolytic conditions. PLA undergoes thermal degradation at temperatures (200 ℃) lower than the melting point (130 - 230 ℃) of the polymer, but the degradation rate rapidly increases above the melting point. It has been postulated that thermal degradation mainly occurs by random main-chain scissions. Several reactions such as hydrolysis, depolymerization, oxidative degradation, and interand intramolecular trans-esterification reactions to mononmer and oligomeric esters, are suggested to be involved in the degradation process during thermal treatments (Jamshidian *et al.*, 2010).

2.4.5 PLA Properties

PLA has unique properties like good appearance, high mechanical strength, and low toxicity; and good barrier properties have broadened its applications. Numerous researchers have studied the different properties of neat PLA and in combination with other polymers as blend or copolymer; and here some of them will be introduced.

Auras, Harte, Selke, and Hernandez (2003) studied mechanical, physical, and barrier properties of 2 PLA films by the names of 4030-D, which was made with nominally 98 % L-lactide, and 4040-D, which was made with nominally 94 % L-lactide resins. Finally, the data from these 2 PLA film samples were compared to those of polystyrene (PS) and polyethylene terephthalate (PET). PLA films showed good tensile strength with higher values than PS but lower than PET. Both 4030-D and 4040-D had lower Tm (melting point) and Tg (glass transition temperature) than PET and PS, which makes PLA better for heat-sealing and thermal processing. In terms of barrier properties of PLA, the permeability coefficients of CO_2 and O_2 were lower than those of PS and comparable to those of PET.

For tensile modulus and flexural modulus, PLA has the highest value in comparison to PS, PP, and HDPE. For notched izod impact, PLA has the lowest one between PS, PP, and HDPE. The elongation at break is low and nearly 4 % that is just higher than that of PS (Dorgan, Lehermeier, & Mang, 2000).

Low glass transition temperature of PLA limits its usages in thermally processed packages. Because of its deformation and its low melting temperature, it is better to use it for heat-sealing and thermoforming applications.

The other important property of polymers is their rate of crystallinity. Crystallinity is the indication of amount of crystalline region in the polymer with respect to amorphous content. Crystallinity influences many polymer properties including hardness, modulus, tensile strength, stiffness, crease point, and melting point. So, while selecting a polymer for a required application its crystallinity plays the foremost role.

PLA crystals can grow in 3 structural positions called α, β, and γ forms. They are characterized by different helix conformations and cell symmetries, which develop upon different thermal and/or mechanical treatments. The α form grows upon melt or cold crystallization, the β form develops upon mechanical stretching of the more stable α form, and the γ form, which only recently has been reported to develop on hexamethylbenzene substrate (Di Lorenzo, 2005).

Di Lorenzo (2005) measured crystallization rates of PLA over a wide temperature range, using both isothermal and nonisothermal methods. He determined that the crystallization rate of PLA at temperatures between 100 and 118 ℃ is very high. He concluded that the high crystallization rate of PLA below 120 ℃ has to be ascribed to the high rate of radial growth of the spherulites.

By modification of the chain architecture through the introduction of branching, different melt flow properties will be obtained. Thermal and rheological properties of 2 commercial types of PLA, linear and branched, were investigated by Dorgan *et al.*, (2000). The crystallization kinetic of the branched polymer was faster than that of the linear analogue. Longer relaxation times in the terminal region of the branched material introduced it as a higher zero shear rate viscosity. They concluded that by utilizing the structure modifications through polymer branching, the ability of using PLA in many processing operations will be extended (Jamshidian *et al.*, 2010).

2.4.6 Microbial degradation of PLA

In spite of the great need for PLA as a biodegradable plastic, till today studies on PLA degradation have focused only on enzymatic or hydrolytic degradation, and no study of microbial degradation has been reported. The study of microbial degradation is crucial because microorganisms are involved in the biodegradation of plastic polymers in the environment. Thus, the microbial degradability of PLA must be confirmed before it is widely distributed. (Pranamuda *et al.*, 1997)

The biodegradability of PLA relies heavily on the environment to which it is exposed. When it is in either the human or animal bodies, it is believed that PLA is initially degraded by hydrolysis and the soluble oligomers formed are then metabolized by cells. Upon disposal in the environment, it is hydrolyzed into low molecular weight oligomers and then mineralized into CO_2 and H_2O by the microorganisms present in the environment (Lunt, 1998). As mention previously, degradation of PLA in soil is slow and that it takes a long time for degradation to start. Ohkita and Lee (2006) reported that no degradation was observed on PLA sheets after 6 weeks in soil.

Urayama, Kanamori, and Kimura (2002) reported that the molecular weight of PLA films with different optical purity of the lactate units (100 % L and 70 % L) decreased by 20 and 75 %, respectively, after 20 months in soil. On the other hand, PLA can be degraded in a composting environment where it is hydrolyzed into smaller molecules which are oligomers, dimers, and monomers after 45–60 days at 50–60 °C. These smaller molecules are then degraded into CO_2 and H_2O by microorganisms in the compost (Tokiwa & Calabia, 2006).

2.4.7 Enzymatic Degradation of PLA

Polyhydroxybutyrate (PHB) depolymerases and lipases are the most extensively studied enzymes. Little information on L-PLA degrading enzymes has been reported so far. Williams (1981) first reported the degradation of L-PLA by proteinase K from Tritirachiam album. Since then, this enzyme has been used in studying the degradation mechanisms of L-PLA, copolymers of PLA, and PLA. Oda, Yonetsu, Urakami, and Tomomura (2000) examined the enzymatic degradation of L-PLA at 50 °C using 56 commercially available proteases. They found out that acid and neutral proteases had a little or no effect on L-PLA degrading activity but some alkaline proteases derived from Bacillus spp. showed appreciable L-PLA degrading activity.

In 2006, Tokiwa and Calabia have purified a commercially available α-chymotrypsin and compared its PLA-degrading activity with other serine proteases such as trypsin, elastase, subtilisin, and proteinase K. All tested serine proteases were able to hydrolyze L-PLA. Contrary to Oda *et al.*’s (2000) report that subtilisin could not degrade L-PLA, it is found out that the L-PLA degrading activity of subtilisin was similar to the purified α-chymotrypsin (Lim, Raku, & Tokiwa, 2005). The difference in the results was probably due to the assay method used. It should be noted that in measuring the degrading activity of L-PLA, control experiment which is reaction mixture without enzyme or with inactivated enzyme is necessary to confirm if the degradation is due to the enzyme or due to chemical hydrolysis (Tokiwa & Calabia, 2006).

2.4.8 PLA under Water Treatment Conditions

PLA under water treatment conditions was first reported by Rudeekit, Numnoi, Tajan, Chaiwutthinan, and Leejarkpai (2009). It is observed that PLA sheets slowly degraded after 1 month and small white spots on the surface of the PLA sheet could be visually observed. There were also some areas where the sheet unchanged. After 15 months, small white spots were found more distributed across the surface of the

PLA sheet. PLA sheet degrades slowly probably because of the slow rate of hydrolysis at 25-32 °C which was waste water treatment conditions. It was suggested that PLA does not biodegrade readily at temperatures less than 60 °C due to its ‘glass transition’ temperature being close to 60 °C (Rudeekit *et al.*, 2009).

2.5 Blends of PLA Family

PLA have been a much focused attention among most of the biodegradable polyester because of its biodegradability and compostable. It also have very low or no toxicity and high mechanical performance, comparable to those of commercial polymers. However, the thermal stability of PLAs is simply not high enough to be used as an alternative in many commercial polymers applications. Ikada, Jamshidi, Tsuji, and Hyon (1987) studied various PLA blends to improve their thermal properties. X-ray diffractometry and differential scanning calorimetry (DSC) shows that all the initially amorphous PLA films remained amorphous, even after autocatalytic hydrolysis for 16 and 24 months.

The ability to control the hydrolytic degradability of PLAs is very important, and several studies have been done to elucidate the effects various components in the systems. Poly(aspartic acid-*co*-lactic) (PAL) was used by Shinoda, Asou, Kashima, Kato, Tseng, and Yagi (2003) to accelerate the degradation of PLA. PAL is an amphiphilic copolymer obtained from aspartic acid and lactide. It is found to be miscible with PLA and produced homogenous blend films without impairing the inherent mechanical properties of PLA.

The blend films are capable of maintaining sufficient transparency, which is one of the most valuable advantages of pure PLA. PAL and poly(sodium aspartate-*co*-lactide) (PALNa) may be useful as antistatic agents for PLA films, as many results shows that there is an increased in hydrophilicity of the surface. With just a small amount of PAL being added into PLA in water, soil and compost can enhance its degradation rate. Blended PAL will resist hydrolysis unless it contacts water, which ensures that the blend products could have a long shelf life and be useful for a wide variety of applications. Other than that, PAL is also found to be able to improve the thermal stability of PLA containing an appreciable amount of residual catalyst (Yu, Dean, & Lin, 2006).

2.6 Blends of Hydrophobic and Hydrophilic Polymers

Most natural polymers are hydrophilic materials. This is because they contain either hydroxyl or polar groups. As for synthetic biodegradable polymers, specifically the aliphatic polyesters are hydrophobic or sensitive to moisture. The blending of these two kinds of polymers are gaining lots of interest as this could lead to the development of new range of biodegradable polymeric materials (Yu *et al.*, 2006).

2.6.1 Starch as a Hydrophilic Polymer: Structure and Properties

Starch is a hydrophilic material and are mainly made up of two homopolymers of D-glucose which are amylase, a branched amylopectin, having the same backbone structure as amylose but with many α-1, 6'-linked branch points, and a mostly linear α-D(1, 4')-glucan. There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked.

Starch chains potentially exhibit reactivity specific for alcohols due to the presence of hydroxyl groups. This allows them to be oxidized and reduced, and may participate in the formation of hydrogen bonds, ethers and esters. Starch has different proportions of amylose and amylopectin ranging from about 10–20 % amylase and 80–90 % amylopectin depending on the source. Amylose is soluble in water and forms a helical structure. Starch occurs naturally as discrete granules because short branched amylopectin chains are able to form helical structures which crystallize. Starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding formed by the hydroxyl groups on the granule surface.

The internal interaction and morphology of starch will be readily changed by water molecules due to its hydrophilicity, and thereby its glass transition temperature (*Tg*), the dimension and mechanical properties depend on the water content (Lu, Xiao, & Xu, 2009). Glass transition temperature of native starch can be as low as 60 to 80 °C when the weight fraction of water is in the range 0.12 to 0.14. This allows starch to be successfully injection moulded to obtain thermoplastic starch polymers in the presence of water. Other than that, the hydrophilicity of starch can be used to improve the degradation rate of some degradable hydrophobic polymers.

Starch is fully biodegradable in the environments. It can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water. It is worth noting that carbon dioxide will recycle into starch again by plants and sunshine. However, starch itself is poor in processability, and also in the dimensional stability and mechanical properties for its end products. Therefore, native starch is not used directly (Lu, Xiao, & Xu, 2009).

2.6.2 Blending of PLA and Starch

Blends of synthetic polymers and starch offers many benefit and one of the important benefit is the cost performance benefits because starch is renewable, cheap and available year-round. Blending of polymers with starch under controlled conditions could lead to co-polymerization that in turn results in high molecular polymers with thermoplastic properties. To blend or mix these polymers requires special machinery, such as an extruder but these polymers can be handled as easily as conventional plastic resin (Sriroth *et al.*, 2000).

Before blending of PLA and starch was reported, several blends of PLA with various non-biodegradable polymers have been investigated. Biodegradable blends of PLA with other aliphatic polyesters such as poly(ε-caprolactone), poly(butylene succinate) and poly(hydroxy butyrate) were reported. The problem with this blends are some of these blends were found to be immiscible, resulting in fairly poor mechanical properties (Martin & Averous, 2001).

PLA and starch are good candidates for polymer blends because both are biodegradable and derivable from renewable resources. Starch can improve the biodegradability and plays an important role in lowering the cost while PLA controls the mechanical properties of the blend. Starch granules become swollen and gelatinized when water is added or when they are heated, and water is often used as a plasticizer to obtain desirable product properties (Yu *et al.*, 2006).

Blends of PLA and starch are characterized in the presence of various water contents by Ke and Sun. Initial moisture content of the starch has no significant effect on its mechanical properties, but has a significant effect on the water absorption of the blends. The thermal and crystallization properties of PLA in the blend were not affected by moisture content. Blends prepared by injection moulding had lower crystallinities than those prepared by compression moulding. However, blends prepared by compression moulding had lower tensile strengths and elongations and higher water absorption values than those made by injection moulding. The crystallinities of the blends increased greatly with annealing treatment at the PLA second crystallization temperature which is 155 ℃ . The decomposition of PLA indicated that PLA degraded slightly in the presence of water under the processing temperatures used (Yu *et al.*, 2006).

Talc is a nucleating agent was blended with PLA at 1 % by volume (v/v) as a comparison. Starch effectively increased the crystallization rate of PLA, even at 1 % content, but the effect was less than that of talc. When the starch content was increased from 1 to 40 %, it can be seen that the crystallization rate of PLA increased slightly. An additional crystallization of PLA can be observed, and it affected the melting point and degree of crystallinity of PLA (Yu *et al.*, 2006).

PLA and starch might seem like a promising future for biodegradable polymer blends. However, starch is a hydrophilic material, which does not interact well with hydrophobic polyesters and this gives a thermodynamically immiscible product and hence, poor and irreproducible performance.

To solve this issue, several approaches have been proposed and developed to overcome the problem of incompatibility of starch and synthetic polymer blends.

Very good interfacial adhesions of PLA and starch blends were achieved by grafting PLA using maleic anhydride (MA). Jang, Shin, Lee, and Narayan (2007) investigated the interfacial adhesion between PLA and starch using MA and maleated thermoplastic starch (MATPS). Scanning electron microscopy (SEM) showed that MA is a good compatibilizer and PLA and starch blends had increased crystallinity. On the other hand, MATPS is not effective for PLA and starch blends. PLA and starch blends which were compatibilized with MA showed higher biodegradability than ordinary PLA and starch blends at the same PLA ratio (Tokiwa *et al.*, 2009). Unfortunately, adding of MA could have an adverse effect due to chain scission (Leadprathom, Suttiruengwong, Threepopnatkul, & Seadan, 2010).

Wang, Sun, and Seib (2001) used methylenediphenyl diisocyanate (MDI) to improve the interface and studied a blend of 55/45 (w/w) mixture of PLA and dried wheat starch in an intensive mixer with or without a low level of MDI. Blends with MDI can enhance mechanical properties and this could be explained by the in situ formation of a block copolymer acting as a compatibilizer (Yu *et al.*, 2006).

CHAPTER 3

METHODOLOGY

3.1 Materials Involved

The PLA used is an injection grade ($\rho = 1.31$ g/cm^3 and MFI = 10~11 g/10 min) from ESUN BrightChina Industrial Co. Ltd, Shenzhen, China. The tapioca starch used in this research is from Thye Huat Chan Sdn Bhd. The soil used to bury the biopolymers is black soil which was purchased from Tesco stores. The microbes used to degrade the biopolymers are natural food grade microbes which is WA-BeneficialMicrobes purchased from Worldwide Alliance Sdn. Bhd. These specific culture microbe solutions are mainly used for general purpose.

3.2 Equipments

The equipments used to blend and mix the required materials are the Brabender Plastograph EC (as shown in Figure 3.1) and then it is compression moulded using a GOTECH press as shown in Figure 3.2. The tensile strengths of the biopolymer blends were obtained from the Instron 5848 MicroTester as shown in Figure 3.3. To visually inspect the appearance of the degraded biopolymers, a conventional digital camera was used.

Figure 3.1: The Brabender Plastograph EC

Figure 3.2: GOTECH Compression Moulding

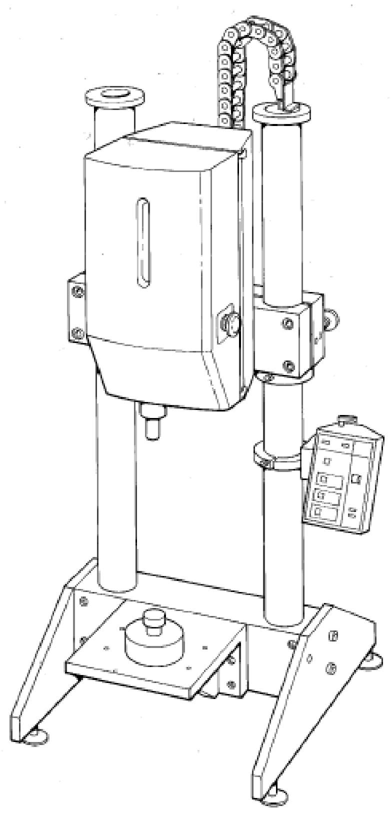


Figure 3.3: Instron 5848 MicroTester

3.3 Formulation Table

The following formulations as shown in Table 3.1 were tested in a 3 weeks basis starting from the 3rd week after the materials were compounded and the experiment were proceeded until the 9th week. This formulation was also tested under two conditions which are with the presence of additional microbes and without additional microbes in the soil.

Table 3.1: Formulation of PLA and PLA and Starch Blends

Material	Weight Distribution (%)		
	PLA 100 %	PLA 80 %	PLA 50 %
PLA	100	80	50
Tapioca Starch	0	20	50

3.4 Sample Preparation

3.4.1 Preparation of PLA 100 %

The PLA purchased comes in a granulated pellet form and it has some yellow pigmentation on it. The preparation of PLA 100 % is rather simple as no mixing is required. Thus, dismissing the need of using the Brabender mixer, the PLA pellets was compressed immediately in the compression moulding process.

Before the sample is prepared, the compression moulding machine was heated up to a temperature of 220 ℃. After the desired temperature is reached, an excess amount of PLA is placed on the heated mould. The PLA placed on the heated mould were heated for 20 minutes until all pellets were melted. The mould was then closed with a top force, and a pressure of 2000 kPa was applied by jacking the lower mould up to force the PLA into contact with all mould areas. The heat and pressure were maintained until the moulding material has cured. Finally, the heated mould was removed from the compression moulding machine and left in a bucket full of water for cooling.

After the heated mould has cooled down, the moulded PLA was removed from the mould. The PLA samples obtained were in a plate form of 19 cm × 19 cm × 0.2 cm.

3.4.2 Preparation of PLA/Starch 80/20

The preparation of PLA/Starch 80/20 requires mixing; thus, necessitate the usage of Brabender mixer. Brabender Plastograph EC is a measuring mixer. It is capable of not only mixing but also measuring the processibility of plastic and testing of plastifiable substances. Apart from these measuring tasks, the mixer is also suited for producing sample material or for reactive processing.

Before mixing, an adequate amount of samples to be prepared were determined. Similar with the PLA 100 % formulation, this PLA/Starch 80/20 sample were also prepared in the form of a 19 cm × 19 cm × 0.2 cm plate. The total volume of the plate was 19 cm × 19 cm × 0.2 cm = 72.2 cm^3. The density of PLA is 1.31 g/cm^3 and the density of starch is 1.5 g/cm^3. Since the composition of this blend contains 80 % of PLA and 20 % of starch this gives a total density of 1.348 g/cm^3 and a total weight of 97.3256 g. However, the Brabender mixer could not mix sample homogeneously at sample weighing more than 50 g; thus, the sample would need to be broken down into 42 g per sample. At 42 g per sample, the total amount of PLA at 80 % is 33.6 g and the amount of starch would be 8.4 g. Therefore, to form one single plate of sample, it would require three 42 g samples to be mixed and then moulded by compression moulding (requires excess amount of sample).

To operate the Brabender mixer, the following Set Point parameters was set.

Table 3.2: Set Point Parameters for Brabender Mixer

Sample Mass	42 g
Speed	50 rpm
Measuring Range	100 N/m

Mixer Temperature	185 ℃
Testing Time	7.00 minutes

The mixer was heated until the mixer temperature was reached. After the mixer temperature was reached, only PLA were poured into the chute followed by inserting the ram. The mixer was then allowed to mix for approximately 2 minutes. This was done to ensure that the PLA pellets become partially soft and fused partially. At the 2 minutes mark, the ram was removed and the remaining starch was then poured into the chute followed by inserting the ram and allowed the mixer to mix until it reaches 7 minutes of set point time.

After this mixing process was done, it was compressed in the compression moulding process. The compression moulding process was similar to the compression moulding process of PLA 100 % but with a lower temperature which was at 200 ℃. However, PLA and starch blends are very brittle and fragile and it is not easily removable from the mould. Thus, two pieces of OHP transparencies were used to cover the sample and then placed it on the mould while it was compressed.

3.4.3 Preparation of PLA/Starch 50/50

Preparation methods for this sample were similar with PLA/Starch 80/20 sample but with different amount of PLA and Starch. Here, the amount of PLA and starch required would be 21 g each and summing it up would give a total amount of 42 g per sample.

3.5 Testing Procedures

The mechanical testing conduct in this research was based on the America Society for Testing and Materials (ASTM) standards testing methods. The samples were first prepared according to the ASTM and then buried into two different soil conditions with one soil containing microbes and the other without microbes. 1 Litre of microbes was added on every 3 kg of soil. Both soils are exposed under environmental condition for 9 weeks with each testing done on a 3 weeks interval.

3.5.1 Tensile Strength

The ASTM standard used in this testing method is the ASTM D638-10 Standard Test Method for Tensile Properties of Plastics. The tensile stress and Young Modulus were measured on the tester.

Based on the ASTM standard, samples were prepared in a dumbbell shape. The type of dumbbell shape prepared is Type IV. To prepare the dumbbell shape, a dumbbell cutter was used. Pressure was applied from the top of the cutter and bottom of the sample to give the desired dumbbell shape. However, this method can only be applied on PLA 100 % as it has a small amount of ductile property. As for PLA and starch blends, the samples were very brittle, thus it requires the usage of an electric saw. After the samples were prepared in Type IV, they were buried into the soil. The samples were prepared in 4 batches where the first batch were tested as an initial for result comparison, as for the other 3 batches, they were buried in the soil and were tested at the 3rd week, 6th week, and finally the 9th week.

To begin testing on the samples, the samples were first removed from the soil and all soils or dirt staining on the surface of the samples was removed. After that, the sample was placed on the grips at the Instron 5848 Mircostester with a crosshead speed set at 1 mm/min. The test was completed once the sample was snap at its breaking point.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Processability

The processability results were obtained from the Brabender mixer where the fusion time and fusion torque data of the PLA and PLA and starch blends were determined. These data are essential as it is greatly affected by the composition of the compound, molecular weight of the resin, and also the method of starch addition. Thus, it is very important to specify the formulation ingredients, testing conditions, type of mixing vessel and volume, batch load, and the sample preparation when providing the processability results.

Fusion can be defined as the process whereby, the PLA agglomerates, primary particles, domain and microdomains are attached together during processing. Previous studies have shown that fusion has a profound influence on mechanical, physical, and chemical properties. In order to obtain optimum mechanical properties an appropriate level of fusion is needed (Azman, Yee, Ko, & Lukman, 2002).

4.1.1 Processability of PLA 100 %

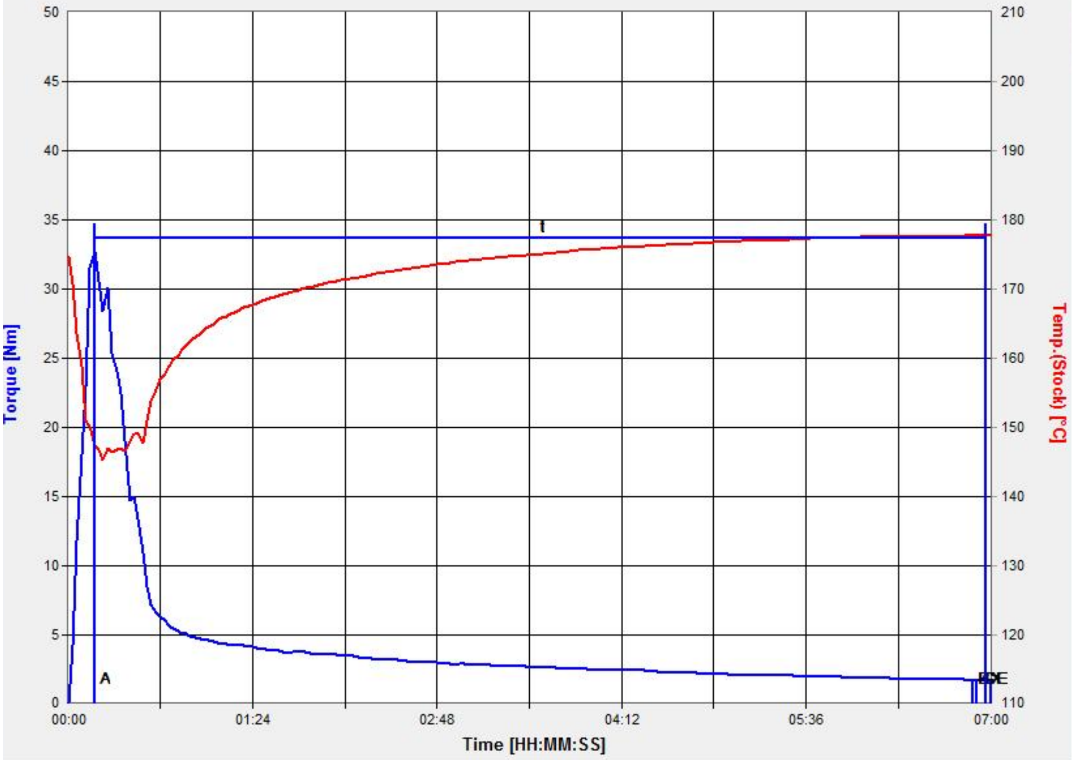


Figure 4.1: Fusion Torque and Fusion Time of PLA 100 %

From Figure 4.1, it can be observed that the temperature curve decreases at the start and increases gradually with time till a point and remain constant throughout the mixing process. Meanwhile, at the time where the temperature decreases, it can be seen that the torque increases to its peak and then decreases gradually until it reaches a constant state. The drop in temperature and the increased in torque indicating the presence of PLA pellets entering into the mixer. As the mixing process progresses, the PLA pellets begins to fused and this leads to the decrease in torque. As for the temperature it slowly roses back to its initial temperature.

4.1.2 Processability of PLA/Starch 80/20

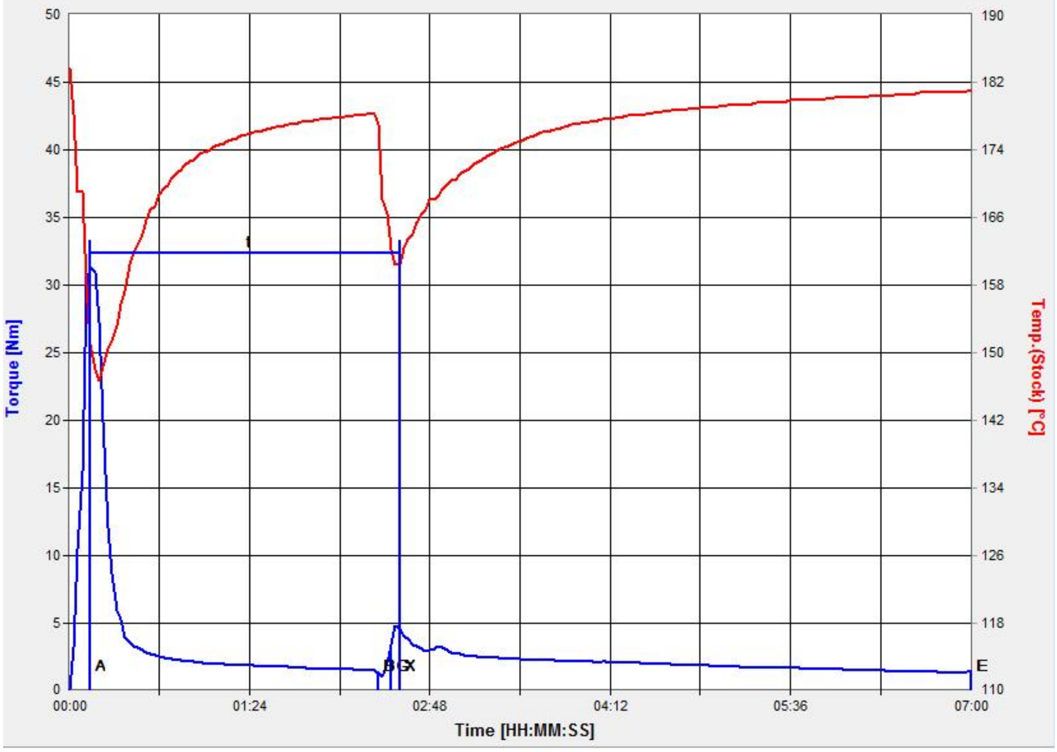


Figure 4.2: Fusion Torque and Fusion Time of PLA/Starch 80/20

Figure 4.2 shows the PLA /Starch 80/20 processability results. Initially, PLA /Starch 80/20 processability results are similar to the results obtained from the PLA 100 %. However, at approximately the 2 minute mark, there is a small increase on the torque as well as a small decrease on the temperature. This is because at this time, starch was added into the mixer. At this state, the PLA pellets are soft and sticky due to the high temperature from the Brabender mixer and the pellets are also partially fused after being mixed for 2 minutes. Thus, adding starch at this moment would allow the blends to mix homogeneously and enhance its adhesiveness. The reason starch was not added initially together with PLA are due to concerns that the outcome of the blend might not mix homogeneously. After the addition of starch, the torque’s curve increases slightly from its previous state and slowly reaching a constant state.

4.1.3 Processability of PLA/Starch 50/50

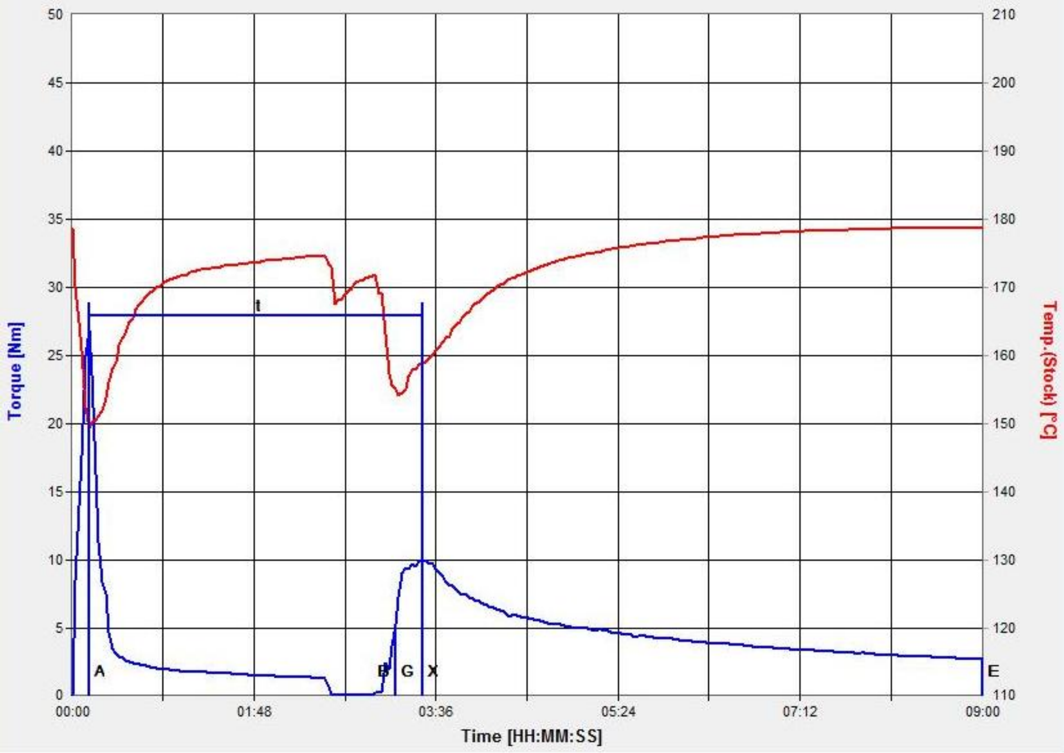


Figure 4.3: Fusion Torque and Fusion Time of PLA/Starch 50/50

The processability result for PLA/Starch 50/50 (as shown in Figure 4.3) and PLA/Starch 80/20 are similar with only slight difference. In PLA/starch 50/50 blend, the mixing time was extended to 9 minutes so that the mixing process would be more homogenize due to the higher amount of starch being added. Here, the PLA was allowed to mix for a longer period of time till approximately the 3 minute mark before starch was added. Another difference that can be observed is the sudden drop of the torque curve at approximately the 3 minute mark and then proceeded by a high increase in torque at the 3 minute 36 seconds mark. The peak of this torque curve is higher as compared with the peak of the torque obtained from the PLA/Starch 80/20. When starch was added into the chute, the sudden drop in torque is due to the large amount of starch presence into the internal mixer and it clogs the twin screws that were rotating to mix the samples. The torque increases immediately after starch was completely added in order to mix homogeneously with the PLA. As the mixing progresses, the torque slowly decreases and reaches a constant state.

4.2 Appearance and Characteristics

Figure 4.4: General Appearance of PLA pellets

Figure 4.5: Granulated PLA with yellow pigment

PLA comes in the form of pellets before it is compounded into the samples by mixing with Brabender mixer or compression moulding. Generally, the appearances of PLA pellets are colourless as shown in Figure 4.4. However, the PLA used in this project are granulated and it is pigmented with a yellowish colour as shown in Figure 4.5. But these factors did not affect the general properties of the PLA.

4.2.1 Post-Compression Moulding

When PLA pellets or PLA and starch blends (after the mixing process) were heated up and being jacked up to come in contact with all mould areas on the compression moulding machine, the excess heated PLA or PLA and starch can be seen flowing out of the mould. These PLA and PLA and starch blends are very sticky and they have high tendencies to stain on the surface area of the mould; thus, making the cleaning process of the mould to be very difficult.

After the PLA pellets and PLA and Starch blends gone through the cooling process, there are several differences that can be observed between PLA 100 %, PLA/Starch 80/20, and PLA/Starch 50/50 plates.

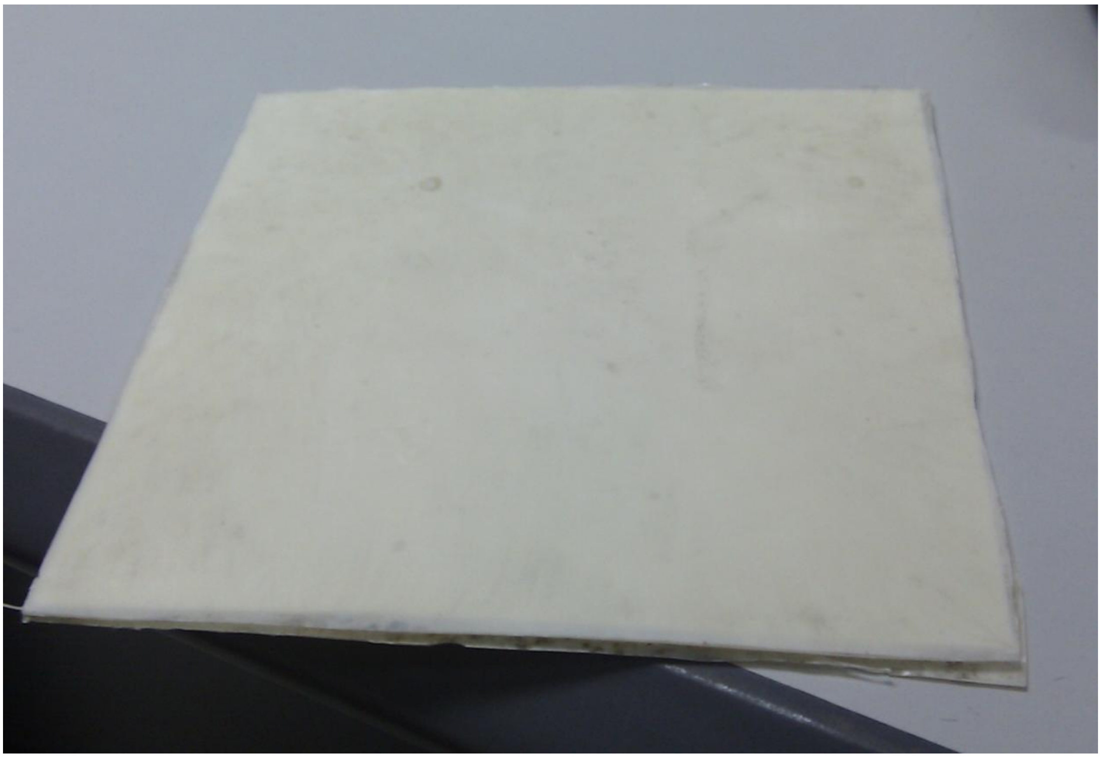


Figure 4.6: Appearance of PLA 100 % plate

For PLA 100 % as shown in Figure 4.6, the surface of the plate is relatively smooth and the colour of the plate is relatively dull in yellowish colour. This sample of PLA is considerably brittle and has small amount of ductility. However, it will crack or breaks into pieces if moderate pressure were applied forcefully.

Figure 4.7: Appearance of PLA/Starch 80/20 plate

For PLA/Starch 80/20 as shown in Figure 4.7, it is observed to be beige in colour and the surface of the plate is reflective and smooth but uneven due to the OHP transparencies being used to cover the sample that might have been distorted during the heating process in compression moulding. The outcome of this formulation is a very fragile, brittle and weak sample. It is so weak that with a small amount of pressure applied on it, will cause it to shatters into pieces.

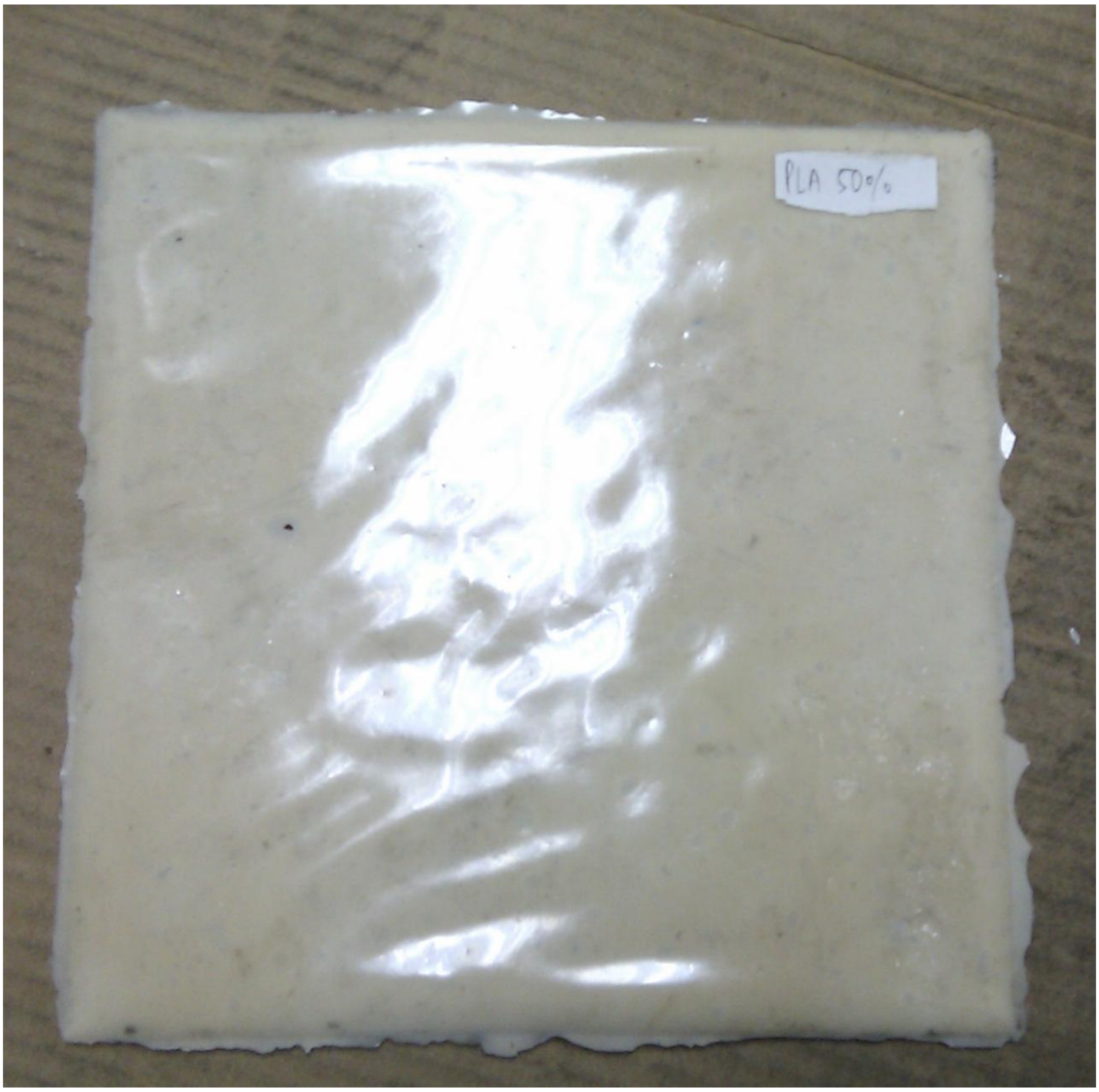


Figure 4.8: Appearance of PLA/Starch 50/50 plate

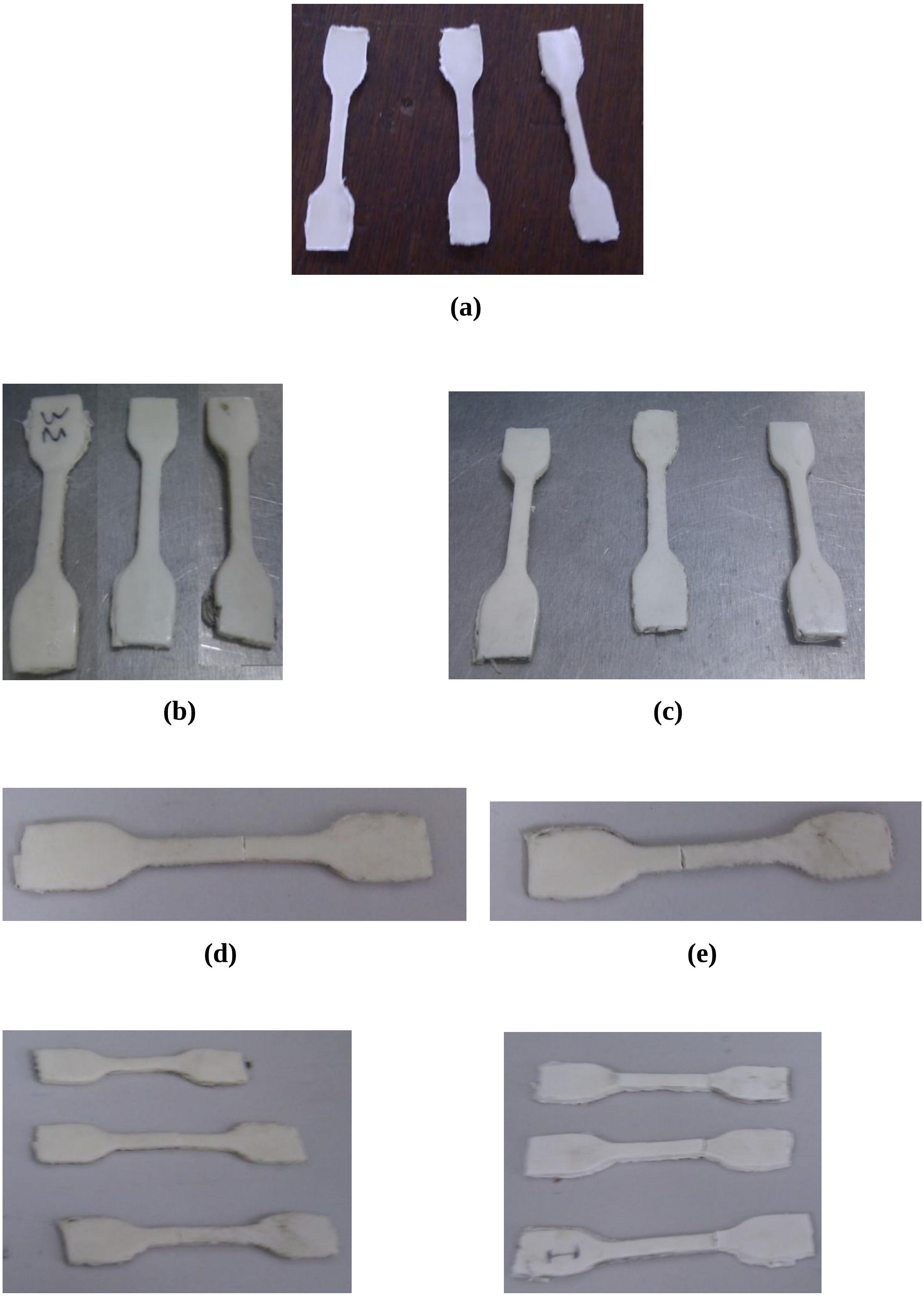
Figure 4.8 shows the PLA/Starch 50/50 sample, it has a similar appearance with PLA/Starch 80/20. However, this formulation is a lot weaker and more brittle then PLA/Starch 80/20. A slight pressure applied on it will cause it to fragmentize. Based on this observation, the relationship between the presence of starch and the amount of starch can be related with the integrity of the sample. As the amount of starch increases, the mechanical properties of the sample decreases.

4.2.2 Post-Degradation

The appearance of the PLA and PLA and starch blends are observed to have noticeable changes after being buried under the soil especially under the soil that contains microbes.

4.2.2.1 Appearance of PLA 100 %

Figure 4.9 shows the appearance of various samples of PLA 100 %. For the first 6 weeks no noticeable changes were observed in both samples either being buried under the soil with microbes and without microbes. However, at the 9th week, some changes in appearance are observed. The samples buried under the soil with microbes appear to be decolourized. This observation probably indicates degradation executed by the microbes. As for the samples buried under the soil without microbes, no noticeable differences were observed in compared with the previous samples.



(a)

(b) **(c)**

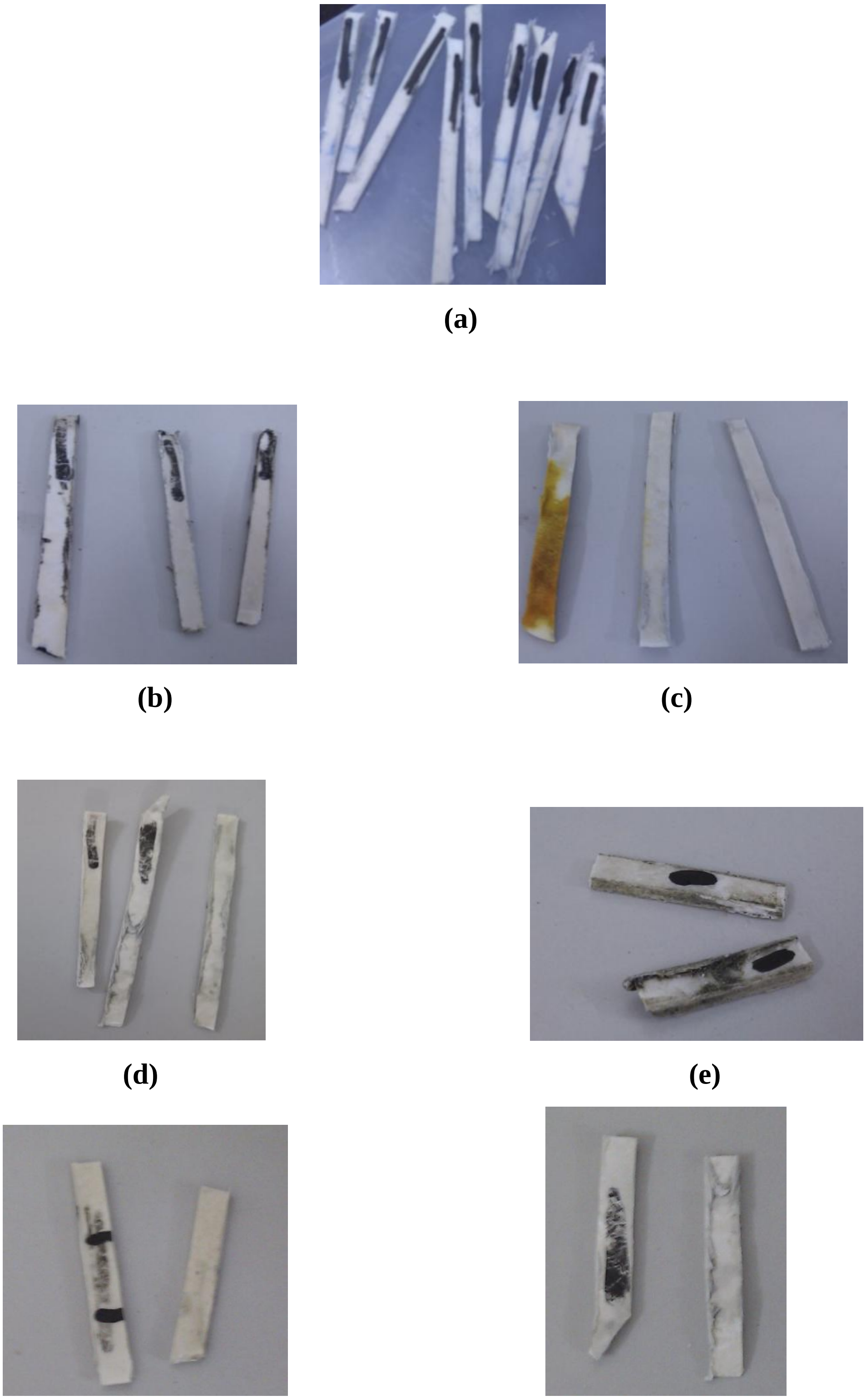
(d) **(e)**

(f) **(g)**

Figure 4.9: Appearance of PLA 100 % - (a) Initial; (b) Buried 3 weeks without microbes; (c) Buried 3 weeks with microbes; (d) Buried 6 weeks without microbes; (e) Buried 6 weeks with microbes; (f) Buried 9 weeks without microbes; (g) Buried 9 weeks with microbes

4.2.2.2 Appearance of PLA/Starch 80/20

Figure 4.10 shows the appearance of PLA/Starch 80/20 samples. For the first 3 week, samples buried under the soil without microbe shows no differences in appearance. However, for samples buried under the soil with microbes, it can be observed that one of the samples was distorted, displaying some brownish colour on its surface. The main reason this happens are due to the presence of starch and microbes. The starch composition in the sample becomes swollen and gelatinized due to rain water and heat from the sunlight (Yu *et al.*, 2006). This environment becomes favourable for the microbe to initiates its attack on the starch area. However, at this stage the attack are observed to occur on the surface area only. At the 6th and 9th week, observations on both samples are similar for samples buried under the soil without microbe. As for samples buried under the soil with microbes, it is observed that the sample becomes swollen.



(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 4.10: Appearance of PLA/Starch 80/20 - (a) Initial; (b) Buried 3 weeks without microbes; (c) Buried 3 weeks with microbes; (d) Buried 6 weeks without microbes; (e) Buried 6 weeks with microbes; (f) Buried 9 weeks without microbes; (g) Buried 9 weeks with microbes

4.2.2.3 Appearance of PLA/Starch 50/50

Figure 4.11 shows the appearance of PLA/Starch 50/50 samples. Observations for PLA/Starch 50/50 and 80/20 are similar. The only difference would be the characteristics of the sample. Samples of PLA/Starch 50/50 are softer due to the higher content of starch in the samples and the starch area becomes very moisture after being buried under the soil. At the 9th week, samples buried under the soil with microbe were observed to have crevice on its surface. This observation indicates the degradation due to microbial invasion after a period of time.

(a)

(b) (c)

(d) (e)

(f) (g)

Figure 4.11: Appearance of PLA/Starch 50/50 - (a) Initial; (b) Buried 3 weeks without microbes; (c) Buried 3 weeks with microbes; (d) Buried 6 weeks without microbes; (e) Buried 6 weeks with microbes; (f) Buried 9 weeks without microbes; (g) Buried 9 weeks with microbes

4.3 Tensile Testing

Tensile tests measures the force required to break a sample specimen and the extent to which the specimen stretches or elongates to that breaking point. In this project, the tensile testing that were carried out are Tensile Stress and Young Modulus. The result of this testing can help specify optimal materials, design parts to withstand application force, and provide key quality control for material checks.

4.3.1 Results of Tensile Tests of PLA 100 %

Initial result before degradation process

- Tensile stress: 66.51 MPa
- Young Modulus: 2.56 GPa

4.3.1.1 Buried under the soil without Microbes

Table 4.1, 4.2, and Figure 4.12 and 4.13 shows the tensile test results for PLA 100 % buried in soil without microbes.

Table 4.1: Tensile Stress of PLA 100 % without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Tensile Stress (MPa)	52.88120	53.83586	38.2677	41.93703
	66.76579	37.52092	31.08739	33.64185
	79.88710	17.39091	18.13572	49.23359
Average	66.51136	36.24923	29.1636	41.60416
Standard Deviation	13.50475	18.25572	10.20293	7.801198

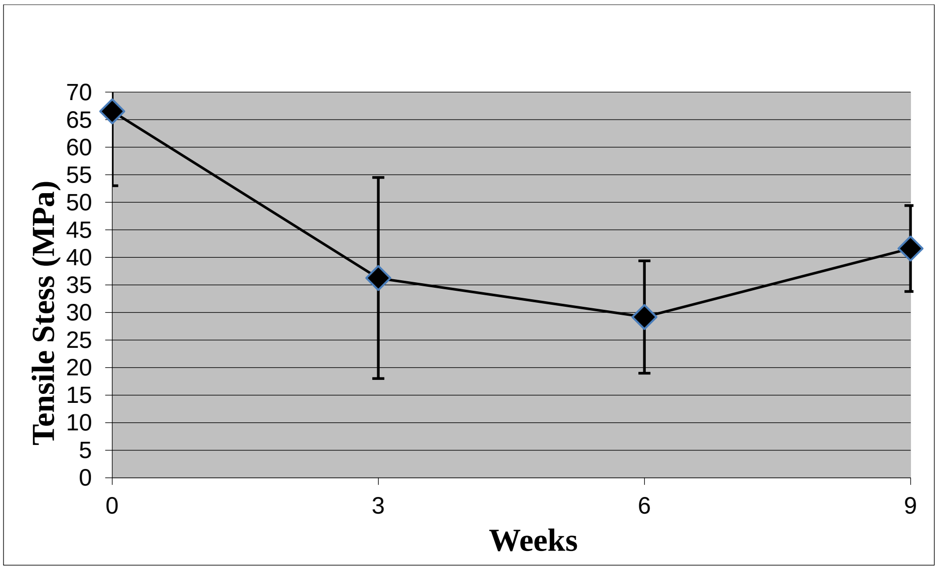


Figure 4.12: Tensile Stress versus buried time in soil without Microbes for PLA 100 %

Table 4.2: Young Modulus of PLA 100 % without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Young Modulus (GPa)	2.75	0.739	0.949	1.752
	2.55	2.786	0.932	1.643
	2.38	1.835	0.884	1.637
Average	2.56	1.786667	0.921667	1.677333
Standard Deviation	0.185203	1.024356	0.03371	0.064733

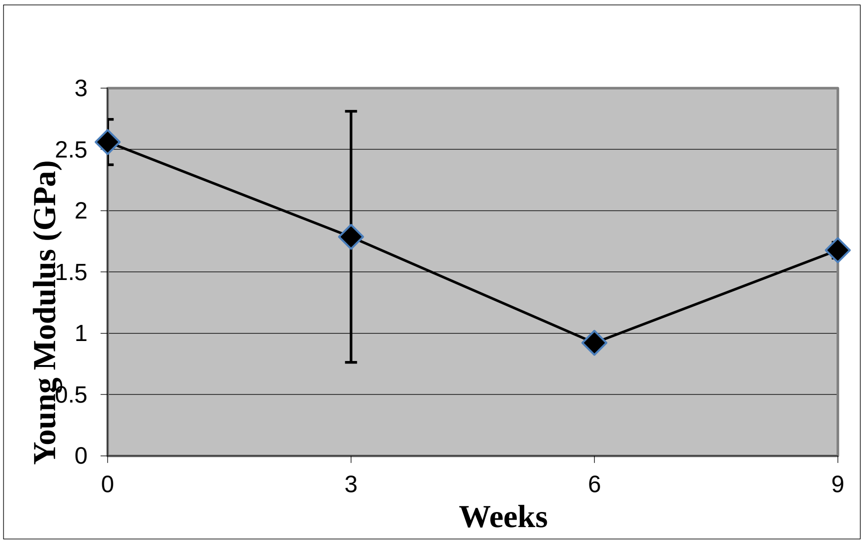


Figure 4.13: Young Modulus versus buried time in soil without Microbes for PLA 100 %

From the results above, the tensile strength of PLA 100 % at initial (Tensile stress: 66.51 MPa; Young Modulus: 2.56 GPa) shows a steep decline after 3 weeks and not much changes were observed in the following 6th and 9th weeks.

4.3.1.2 Buried under the soil with Microbes

Table 4.3, 4.4 and Figure 4.14 and 4.15 shows the tensile test results PLA 100 % buried in soil with microbes.

Table 4.3: Tensile Stress of PLA 100 % with Microbes

Weeks	**Initial**	**3**	**6**	**9**
Tensile Stress (MPa)	52.88120	25.24982	28.44394	27.06046
	66.76579	25.18982	21.85999	25.84748
	79.88710	13.23401	15.22723	17.27032
Average	66.51136	21.22455	21.84372	23.39275
Standard Deviation	13.50475	6.920076	6.60837	5.336757

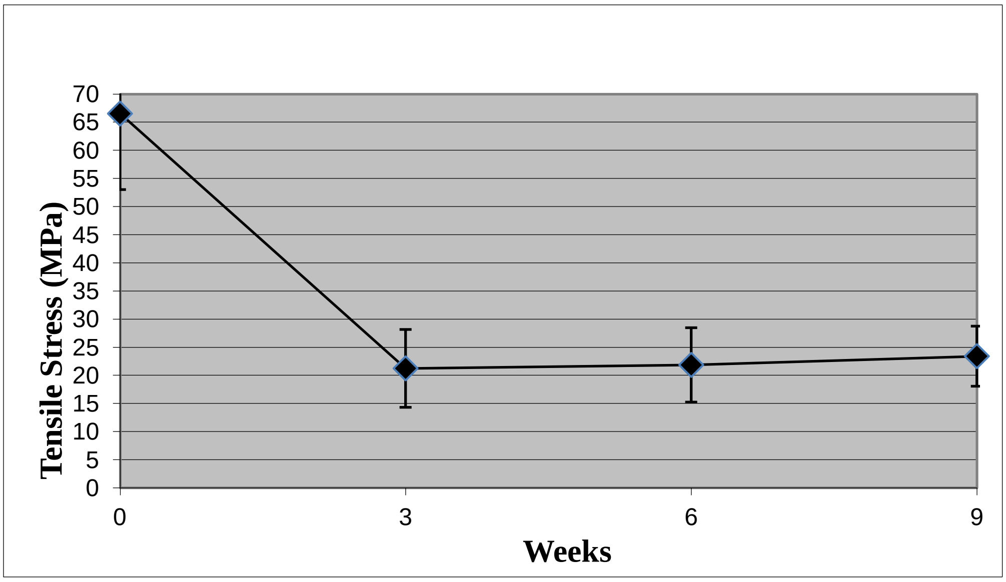


Figure 4.14: Tensile Stress versus buried time in soil with Microbes for PLA 100 %

Table 4.4: Young Modulus of PLA 100 % with Microbes

Weeks	Initial	3	6	9
Young Modulus (GPa)	2.75	0.741	0.78	1.128
	2.55	0.716	0.797	0.789
	2.38	0.445	0.866	0.855
Average	2.56	0.634	0.814333	0.924
Standard Deviation	0.185203	0.164155	0.045545	0.179725

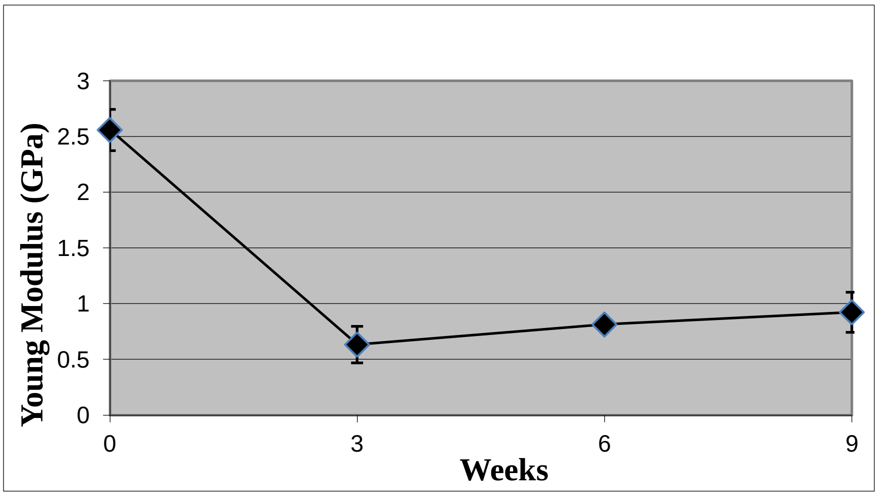


Figure 4.15: Young Modulus versus buried time in soil with Microbes for PLA 100 %

Based on this result, it is observed that the tensile strength of the PLA samples buried with microbe shows a steeper decline compare with the PLA samples buried without the microbe. However, similar traits of PLA samples buried in soil without microbe were observed on the PLA samples buried in soil with microbe on the 6th week and 9th week as it shows little changes on that period of time.

4.3.2 Results of Tensile Test of PLA/Starch 80/20

Initial result before degradation process

- Tensile stress: 22.18 MPa
- Young Modulus: 0.92 GPa

4.3.2.1 Buried under the soil without Microbes

Table 4.5, 4.6 and Figure 4.16 and 4.17 shows the tensile test result for PLA/Starch 80/20 buried in soil without microbes.

Table 4.5: Tensile Stress of PLA/Starch 80/20 without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Tensile Stress (MPa)	21.68247	13.98007	12.5667	9.0777
	30.33864	18.67474	16.2022	10.2678
	14.50498	17.851	14.56789	13.5567
Average	22.17536	16.83527	14.4456	10.9674
Standard Deviation	7.928329	2.506743	1.820833	2.320009

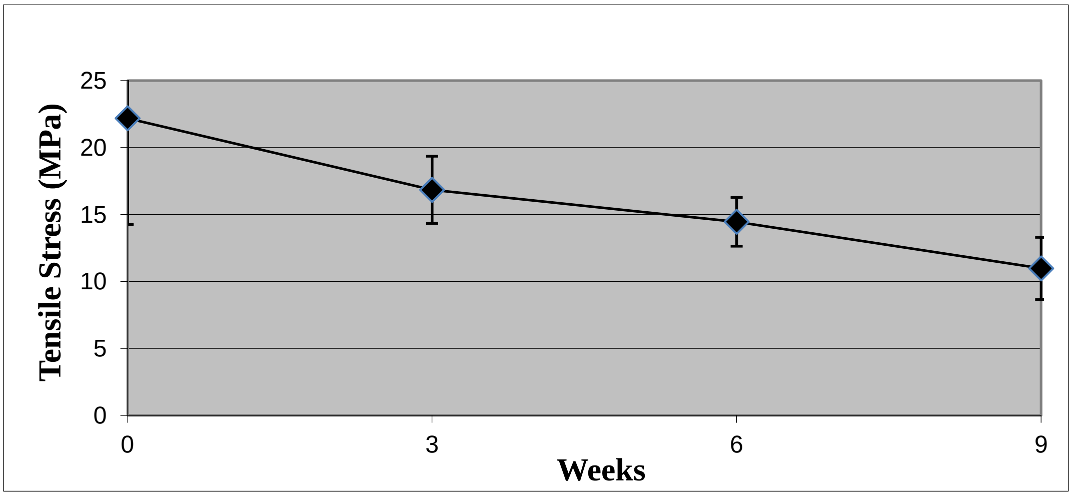


Figure 4.16: Tensile Stress versus buried time in soil without Microbes for PLA/Starch 80/20

Table 4.6: Young Modulus of PLA/Starch 80/20 without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Young Modulus (GPa)	0.579	0.581	0.552	0.322
	1.795	1.395	0.615	0.317
	0.370	0.754	0.456	0.309
Average	0.915	0.910	0.541	0.316
Standard Deviation	0.76952	0.428837	0.080069	0.006557

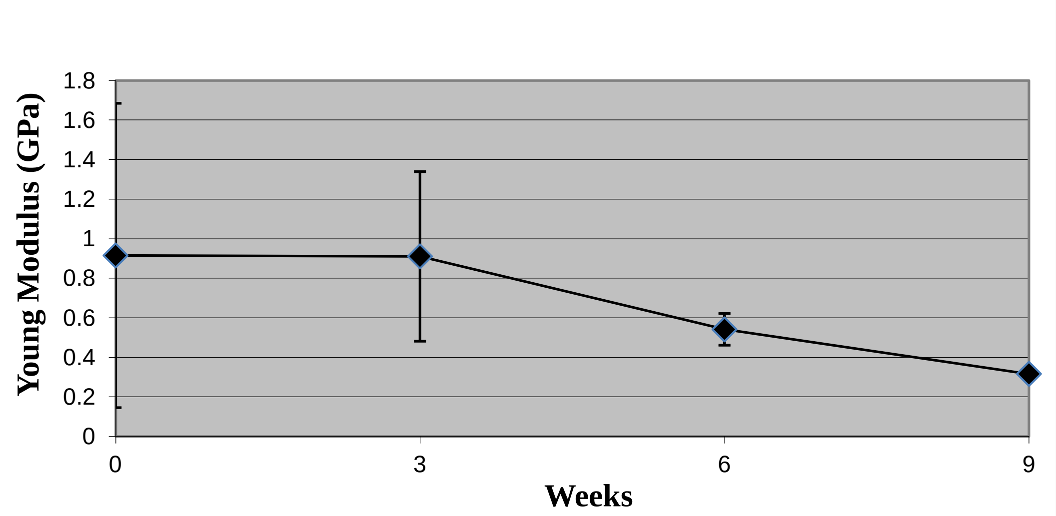


Figure 4.17: Young Modulus versus buried time in soil without Microbes for PLA/Starch 80/20

Refer to Figure 4.16, it is observed that the tensile strength of these samples are generally lower compare with pure PLA. However, the decrease in tensile strength was not as steep as compared with pure PLA as it was observed to decrease at a much more constant rate with time.

4.3.2.2 Buried under the soil with Microbes

Table 4.7, 4.8 and Figure 4.18 and 4.19 shows the tensile test result for PLA/Starch 80/20 buried in soil with microbes.

Table 4.7: Tensile Stress of PLA/Starch 80/20 with Microbes

Weeks	**Initial**	**3**	**6**	**9**
Tensile Stress (MPa)	21.68247	16.6052	12.4456	8.765
	30.33864	11.7865	14.2567	10.2525
	14.50498	9.7611	13.9888	11.6982
Average	22.17536	12.7176	13.5637	10.23857
Standard Deviation	7.928329	3.51577	0.977524	1.46665

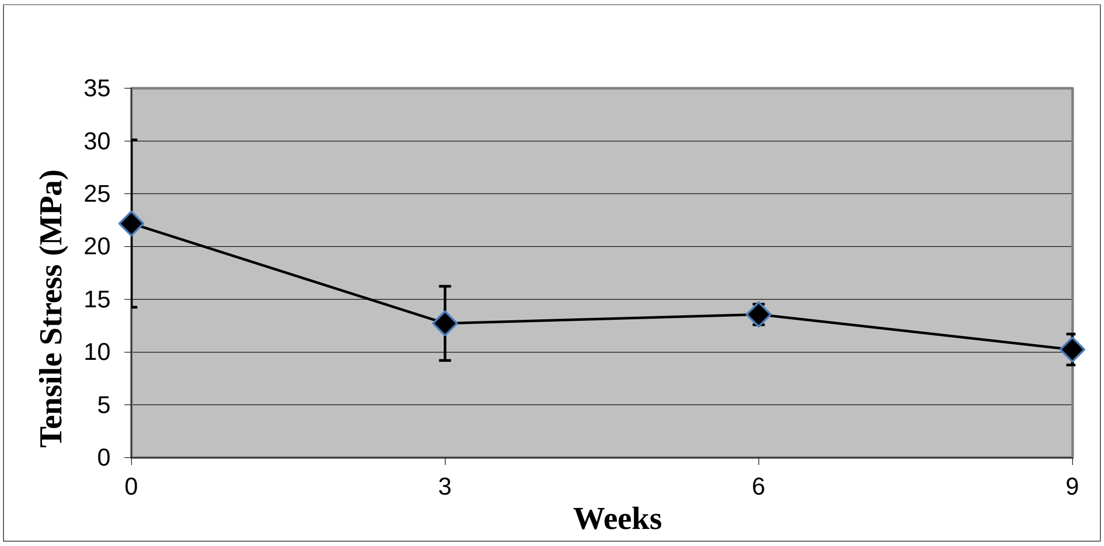


Figure 4.18: Tensile Stress versus buried time in soil with Microbes for PLA/Starch 80/20

Table 4.8: Young Modulus of PLA/Starch 80/20 with Microbes

Weeks	**Initial**	**3**	**6**	**9**
Young Modulus (GPa)	0.579	0.065	0.046	0.031
	1.795	0.057	0.052	0.044
	0.370	0.077	0.043	0.042
Average	0.915	0.066333	0.047	0.039
Standard Deviation	0.76952	0.010066	0.004583	0.007

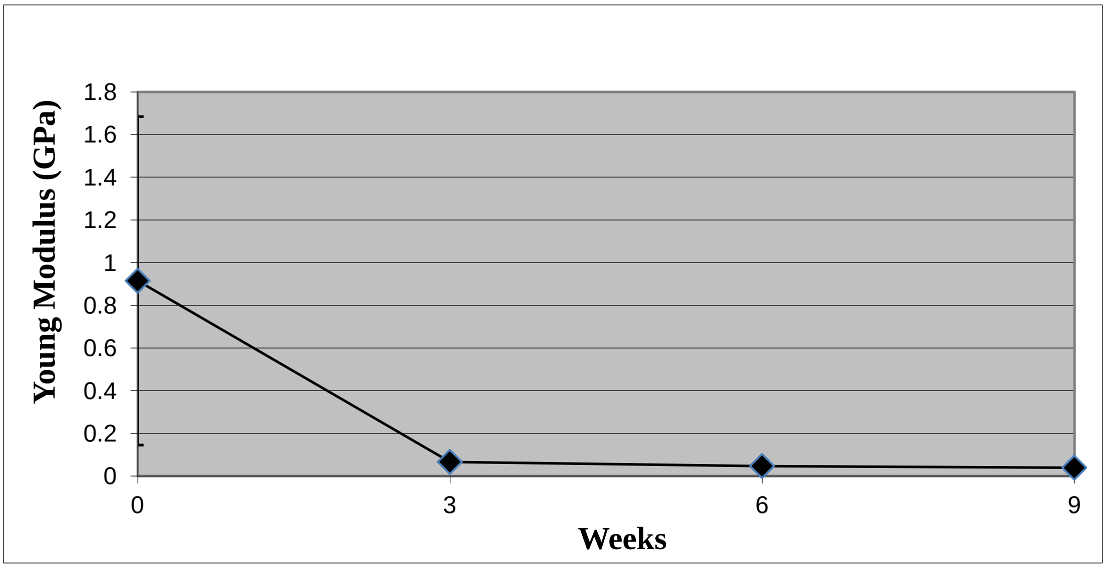


Figure 4.19: Young Modulus versus buried time in soil with Microbes for PLA/Starch 80/20

These samples however show a steep decrease in its tensile strength at the 3rd week under the soil. Based on this result, it clearly indicates that the presence of microbes plays an important role in degradation as the tensile strength are observed to be much lower compared with the sample buried without microbes.

4.3.3 Results of Tensile Test of PLA/Starch 50/50

Initial result before degradation process

- Tensile stress: 10.87 MPa
- Young Modulus: 0.27 GPa

4.3.3.1 Buried under the soil without Microbes

Table 4.9, 4.10 and Figure 4.20 and 4.21 shows the tensile test result for PLA/Starch 50/50 buried in soil without microbes.

Table 4.9: Tensile Stress of PLA/Starch 50/50 without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Tensile Stress (MPa)	7.91589	7.58318	6.2234	5.1257
	13.69790	5.10953	5.1257	5.8211
	10.98220	6.57181	6.3216	5.0766
Average	10.86533	6.421507	5.890233	5.341133
Standard Deviation	2.892776	1.243656	0.663923	0.416388

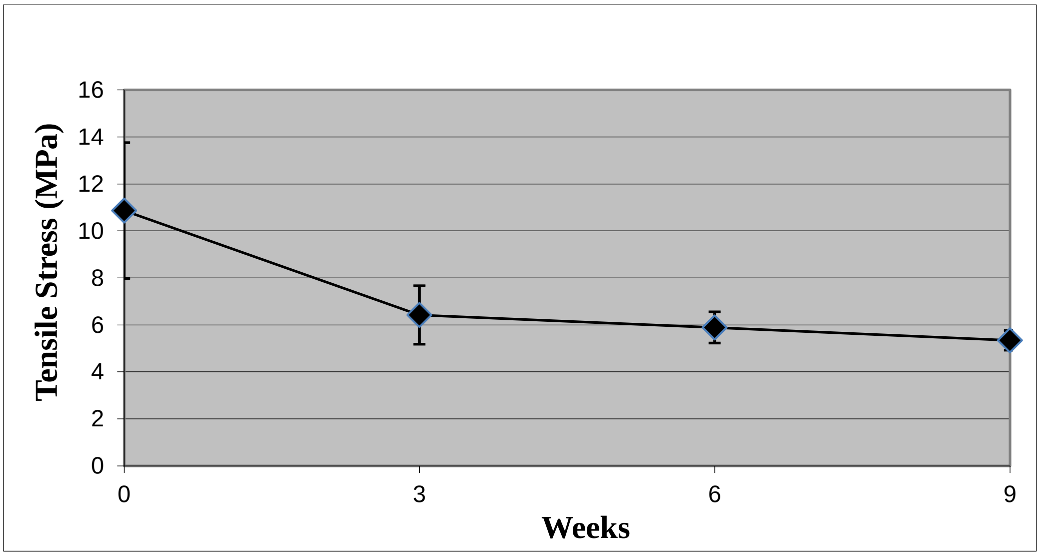


Figure 4.20: Tensile Stress versus buried time in soil without Microbes for PLA/Starch 50/50

Table 4.10: Young Modulus of PLA/Starch 50/50 without Microbes

Weeks	**Initial**	**3**	**6**	**9**
Young Modulus (GPa)	0.139	0.267	0.223	0.199
	0.298	0.157	0.253	0.1764
	0.377	0.319	0.255	0.155
Average	0.271	0.247667	0.243667	0.1768
Standard Deviation	0.121	0.082712	0.017926	0.022003

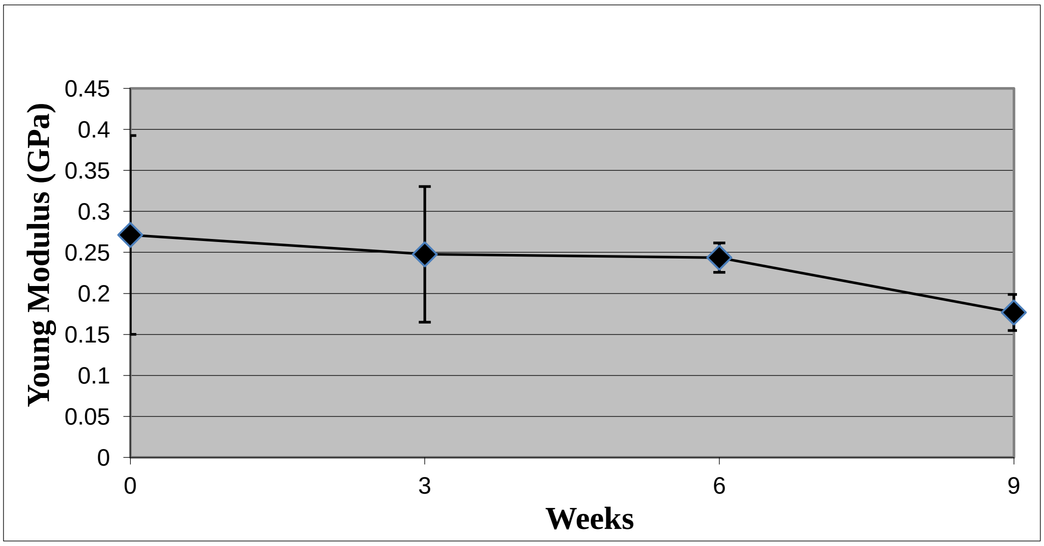


Figure 4.21: Effect of Young Modulus with time of PLA/Starch 50/50 without Microbes

Results from Figure 4.20 show that the tensile strength of these samples are lower compare with the PLA/Starch 80/20 and a lot lower than pure PLA. Based on this observation it can be seen that the relationship between the amount of starch and the strength of the blends are once again proven to be valid, where the higher the amount of starch in the sample gives a lower mechanical properties of blends.

4.3.3.2 Buried under the soil with Microbes

Table 4.11, 4.12 and Figure 4.22 and 4.23 shows the tensile test result for PLA/Starch 50/50 buried in soil with microbes.

Table 4.11: Tensile Stress of PLA/Starch 50/50 with Microbes

Weeks	Initial	3	6	9
Tensile Stress (MPa)	7.91589	5.16926	4.076	3.7777
	13.69790	5.11509	3.678	4.1224
	10.98220	5.13022	4.253	2.9763
Average	10.86533	5.13819	4.002333	3.625467
Standard Deviation	2.89278	0.027951	0.294493	0.58802

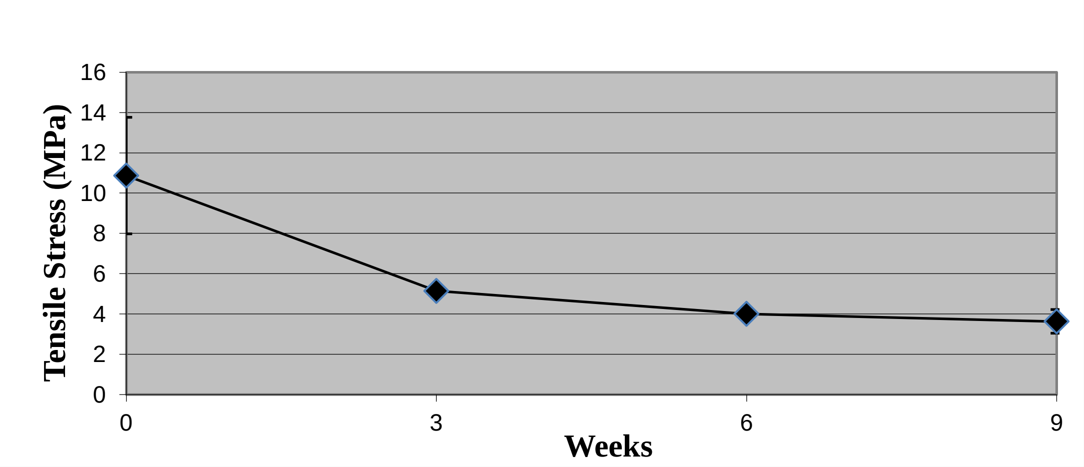


Figure 4.22: Tensile Stress versus buried time in soil with Microbes for PLA/Starch 50/50

Table 4.12: Young Modulus of PLA/Starch 50/50 with Microbes

Weeks	**Initial**	**3**	**6**	**9**
Young Modulus (GPa)	0.139	0.059	0.058	0.044
	0.298	0.067	0.0567	0.021
	0.377	0.055	0.059	0.0199
Average	0.271	0.060333	0.0579	0.0283
Standard Deviation	0.121	0.00611	0.001153	0.013608

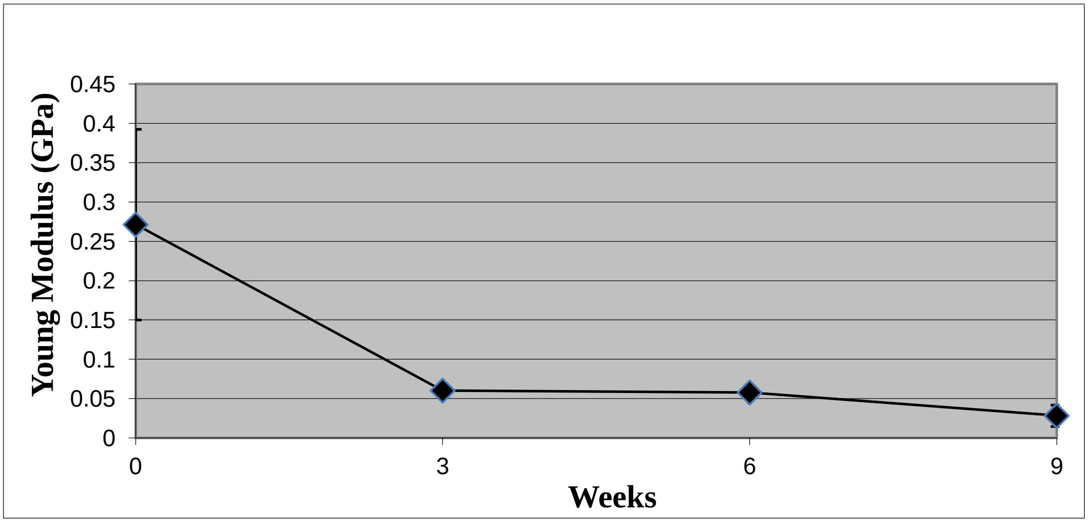


Figure 4.23: Young Modulus versus buried time in soil with Microbes for PLA/Starch 50/50

The tensile strength result of this sample is the lowest among all samples and tests being done in this project. This is due to the higher amount of starch presence in the sample and also the presence of microbe in the soil, thus making its biodegradation rate higher compare to other test conditions and formulations in this project.

Figure 4.24 to 4.27 shows the comparison of the test results.

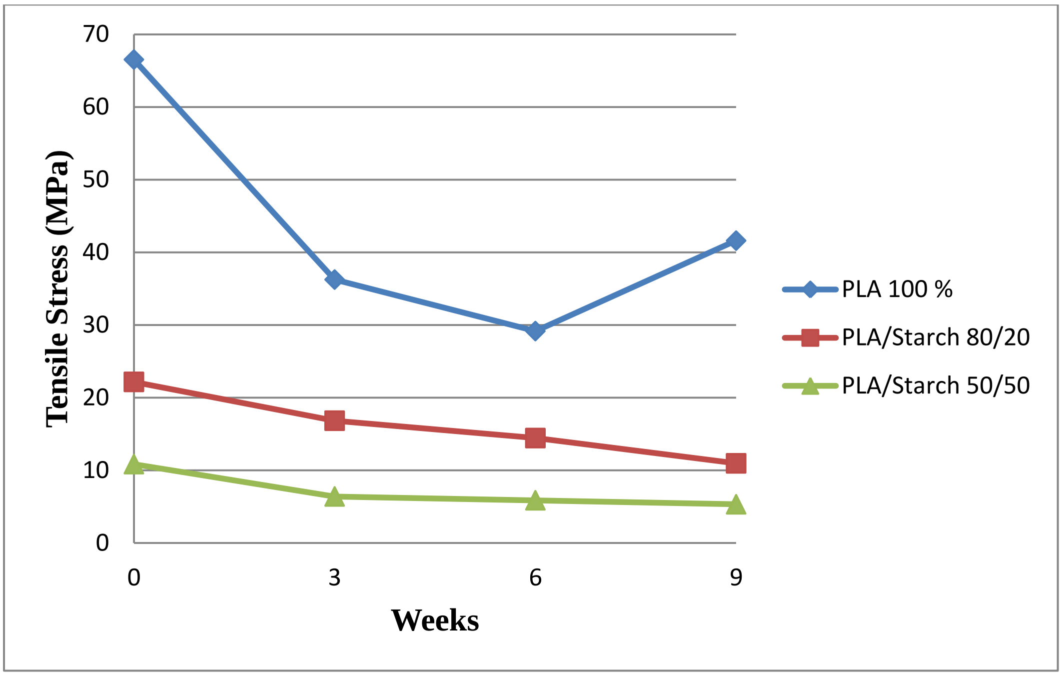


Figure 4.24: Tensile Stress of PLA and PLA and Starch Blends versus Time under the burial of soil without Microbes

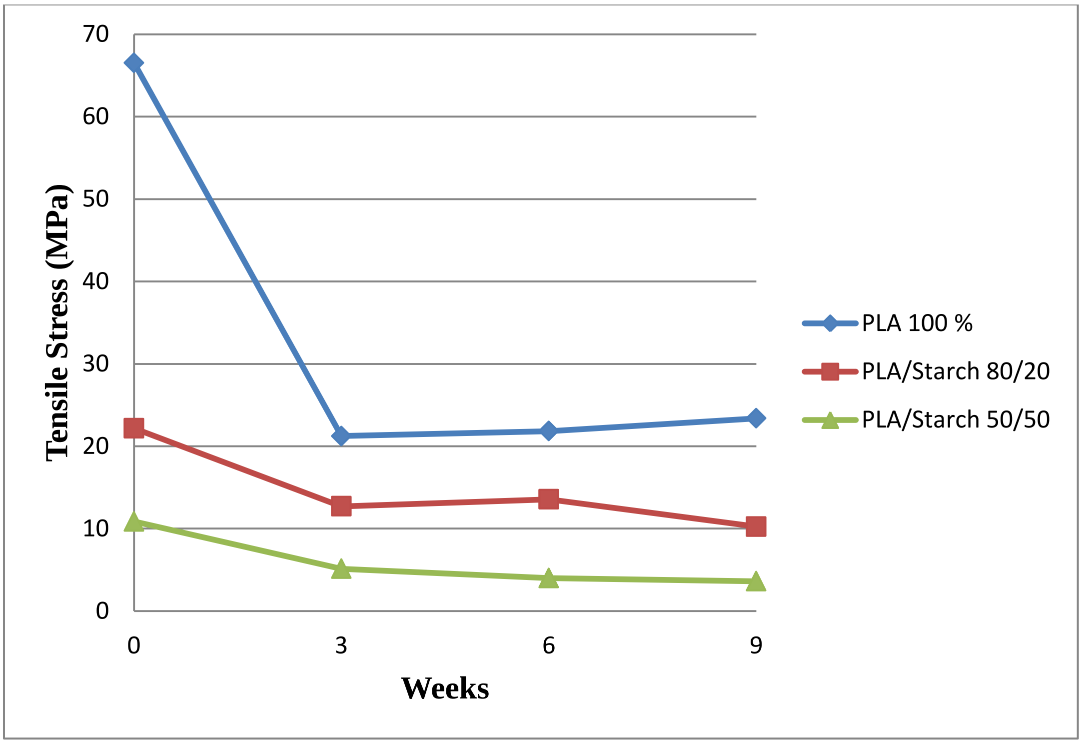


Figure 4.25: Tensile Stress of PLA and PLA and Starch Blends versus Time under the burial of soil with Microbe

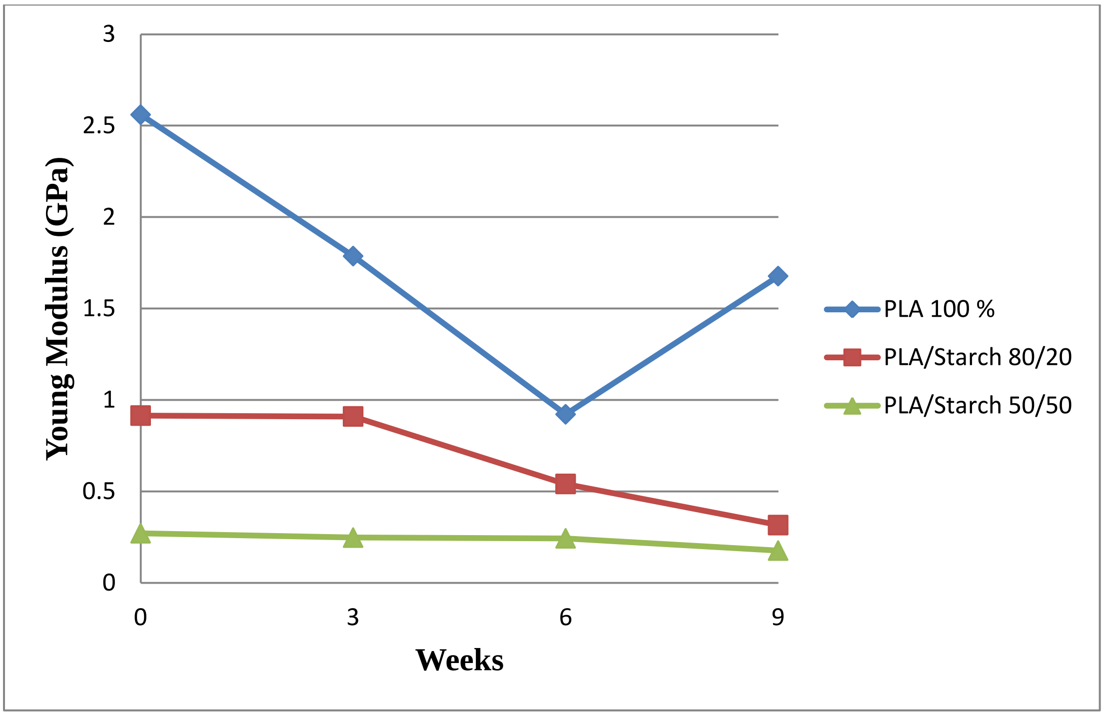


Figure 4.26: Young Modulus of PLA and PLA and Starch Blends versus Time under the burial of soil without Microbes

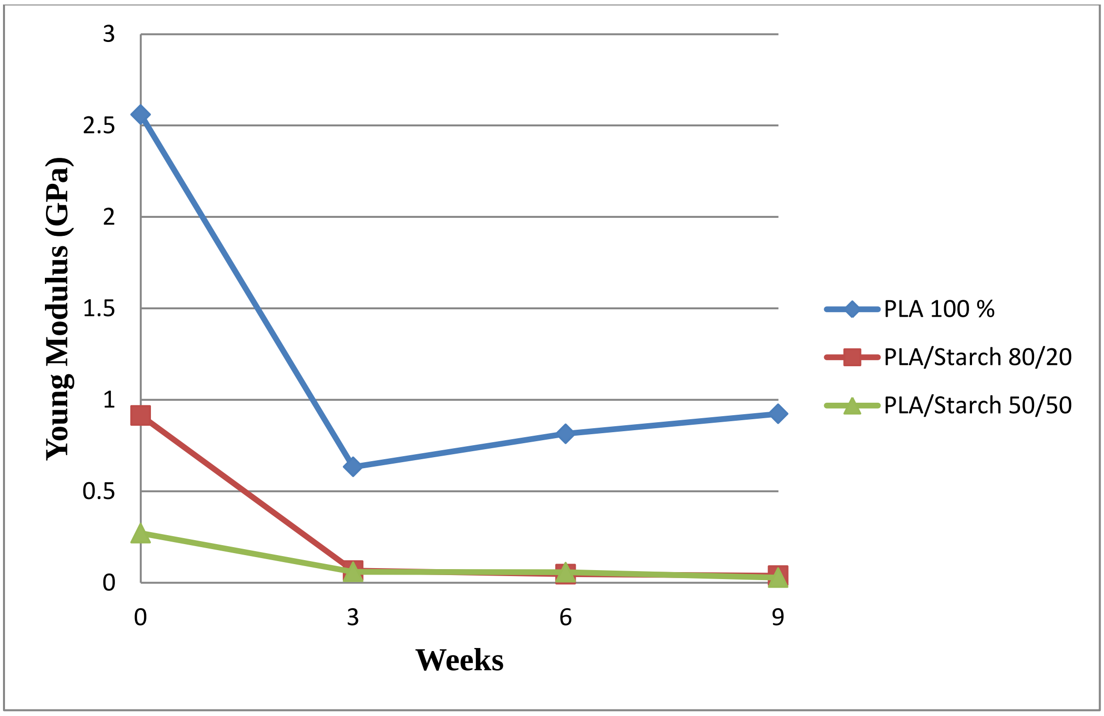


Figure 4.27: Young Modulus of PLA and PLA and Starch Blends versus Time under the burial of soil with Microbes

Biodegradation of PLA is generally slow in ambient temperature in soils. This case can be clearly evidenced by the little changes in tensile strength and modulus of pure PLA after a matter of time. Similar results were obtained in samples buried with microbe although a steep decline at initial and a generally lower tensile strength and modulus were observed. The slow degradation rates of PLA are due to its high molecular weight. For PLA to degrade and disintegrate quickly, it will need to be placed under high temperature and high humidity, as in active compost.

Tensile strength of PLA and starch blends also illustrated a steep decline at initial and than a fairly constant rate of declination for the remainder of the burial period. This is due to the absorption of water during soil burial with consequent weakening of the PLA and starch adhesion. The fairly constant rate of declination in tensile strength with concurrent loss of starch suggests that there was little or no adhesion of starch to the polymer matrix once moistened in soil.

From Figure 4.24 and 4.25, it can be observed that samples buried under the soil with the addition of microbes generally produces a lower tensile strength as time progresses compare to samples buried under the soil without the addition of microbes. In this study, all samples were placed under the conditions where they were exposed to sunlight, rain drops and the environment during the testing period. This exposure created an environment that enables the growth of microbes on both soil conditions. Presence of microbes in the soil is important. This is because without the presence of microbes to hydrolyse the PLA, biodegradation process will not occur. For soil mixed with microbes, these environmental conditions promoted the growth of microbes that was initially present in the soil. Thus, the concentration of microbes in the soil mixed with microbes will be higher than the microbes present in the soil without the addition of microbes.

Based on the results obtained, it can be observed that samples having a higher content of starch typically give a lower strength. This is because having a higher content of starch generally gives a relatively weak PLA and starch adhesion and it also provide a larger surface area for enzymatic degradation of microbes. As the starch content increases it also decreases the effective cross-section area of the continuous phase and the PLA matrix becomes discontinuous resulting in decreases in strength.

Biodegradation of the starch begins by hollowing out the polymer matrix. This is associated with the loss of mechanical properties, increased permeability and greater surface to volume ratio and this will facilitate further abiotic degradation process. Since this degradation was exposed to rain water, the starch particles swells and cause disruption to the polymer surface. Furthermore, the polymer surface were covered with a film of starch degradation products resulted from the enzymatic breakdown of starch particles and this will provide an intermediate carbon source for the invading microbes as well as overcoming the hydrophobic nature of the surface.

Similar testing have been carried out by Shogren, Doane, Garlotta, Lawton, & Willett (2002) where samples of PLA and PLA and starch blends were buried under the soil but without the initial mixing of microbes for over a year as shown in Figure 4.28

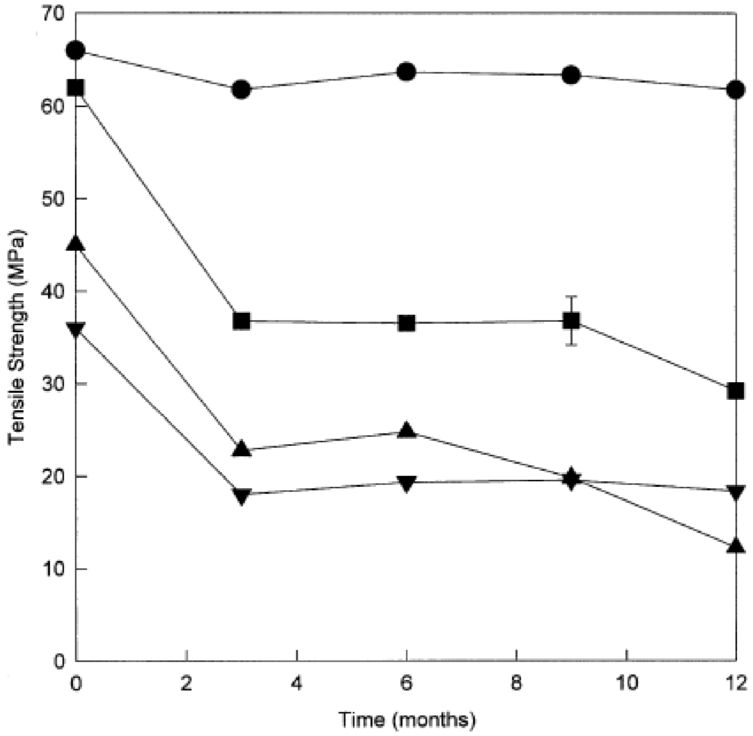


Figure 4.28: Effect of time of soil burial on tensile strength of moulded Starch/PLA bars by Shogren *et al* (2002). Where: ● denotes PLA 100 %; ■ denotes PLA/Starch 80/20; ▲ denotes PLA/Starch 60/40; ▼ denotes PLA/Starch 40/60

Based on the result obtained by Shogren *et al.* (2002), it can be observed that the tensile strength of the PLA and starch blends obtained by Shogren *et al.* are generally higher than the result obtained in this research. This is because samples prepared by Shogren *et al*. (2002) were done by injection moulding. This observation clearly evidenced that the increased in crystallinity due to compression moulding process will give a lower tensile strength than injection moulding as explained by Yu *et al*. (2006). A summary of Shogren *et a.l* (2002) results indicates that injection moulded PLA are slow to degrade in soil. Even with the addition of starch for up to 60 % by weight in the PLA and starch blends, it does not significantly accelerate the degradation of PLA and most of the starch remains intact after 1 year in soil.

The Young Modulus for PLA and starch blends decreases with time as the starch content increases as shown in Figure 4.26 and 4.27. Similar testing was done by Ke and Sun (2000) using corn starch and wheat starch and it shows that the modulus of the blends increases slightly as the starch content increases. However, in this study the starch used is tapioca starch and from Figure 4.26 and 4.27 it shows that the increased in starch content decreases the modulus of the blends. This is probably due to the increased in the discontinuous phase of PLA matrix which is stiffer then the tapioca starch granules.

In this study, no compatibilizers or additives were used in the PLA and starch blends thus resulting in a blend of high brittleness and low impact resistance. This is due to the hydrophobic PLA and hydrophilic starch that leads to a poor adhesion between two components. To improve the interfacial interactions of these blends, many types of compatibilizer and additives have been investigated. Additives such as methylenediphenyl diisocyanate (MDI) as proposed by Wang *et al.* (2001) or compatibilizer such as dioctyl maleate (DOM) as proposed by Zhang and Sun (2004) have shown to provide better interfacial interactions between the two components.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

PLA polymers have recently gained enormous attention as a replacement for conventional synthetic packaging materials. By being truly biodegradable and derived from renewable resources, this could provide customers with extra end-use benefits such as avoiding paying “green tax” in Germany or meeting environmental regulations in Japan, thus, making PLA a growing alternative for packaging material in numerous demanding markets (Yu *et al.*, 2006).

In terms of appearance and characteristics, neat PLA and PLA blends had slight variations due to the presence and amount of starch addition. The appearance of PLA 100 % samples was observed to have a relatively smooth surface and a relatively dull yellowish colour. As for PLA/Starch 80/20 and 50/50 samples, it is beige in colour and has a reflective and smooth surface but uneven due to the usage OHP transparencies during compression moulding. In terms of characteristics, PLA 100 % samples were observed to be considerably brittle and has small amount of ductility. PLA/Starch 80/20 samples were very fragile, brittle and weak. However, PLA/Starch 50/50 samples were observed to be even weaker and fragile then PLA/Starch 80/20. These observations clearly states that relationship between the presence of starch and the amount of starch are related with the integrity of the sample where the presence and increment of starch decreases the mechanical properties of the samples.

As for post-degradation appearance, generally no significant changes were observed in samples buried under the soil without addition of microbes. However, several changes were observed in the samples buried under the soil with addition of microbes. PLA 100 % samples appear to be decolourized after being buried under the soil mixed with microbes for 9 weeks. PLA/Starch 80/20 appears to be distorted and swollen, displaying some brownish colour on its surface due to rain water and heat from the sunlight that causes microbes to attack on its surface area. As for PLA/Starch 50/50 samples, similar observations with PLA/Starch 80/20 samples were observed for the first 6 weeks. However, crevices were observed to appear on the surface at the 9th week.

Based on this study, it can be summarised that neat PLA are generally slow to degrade in soil. It is observed to have steep decline in its tensile stress and elasticity at initial and than a fairly constant rate of declination for the remainder of the burial period. However, with the addition of microbes into the soil and tapioca starch into the PLA samples the degradation rates are higher so a significant decreased in tensile stress and elasticity were observed. Addition of microbes into the soil increases the hydrolysis rate to initiate the biodegradation process of PLA. Furthermore, addition of tapioca starch would give a weak adhesion against the PLA surface, a larger surface area for enzymatic degradation of microbes, and also decreased in the effective cross-section area of the PLA continuous phase, thus, resulting in decreases of tensile stress and elasticity. Other than the presence of tapioca starch, the increment in the amount of tapioca starch added in the samples were also observed to decrease the tensile stress and elasticity as it would give an weaker adhesion against the PLA surface.

5.2 Recommendations

Based on the results from this study, it appears that soil burial might not be an acceptable way to dispose of such materials either intentionally or by careless littering. This is because PLA materials may require years to fully degrade depending on the particular environment. Problems previously seen on the use of other types of biodegradable polymers such as partially degraded plastic bags or mulch blowing around and strangulation or intestinal blockage in animals could be potential problems for PLA as well. Thus, it is important to understand that PLA articles should not be randomly discarded in the environment although it would be compostable.

For proper disposal of PLA in the natural environment, alternatives such as copolymerization and blending in acidic compounds have been suggested. Other than that, addition of proteins which might induce the production of proteases by microorganisms that had been found to degrade PLA could also be considered. However, preferred methods of disposal would be composting or recycling or both.

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APPENDIX A

ESUN™ PLA Injection Grade

产品牌号（Product Mark）	PLA Injection Grade
样品外观（Sample Appearance）	白色粒子 white granule
报告日期（Report Date）	2010/04/16

项目 Parameter	测试标准 Test Method	单位 Unit	结果 Result
密度 density	Balance Cylinder Method	g/cm^3	1.31
熔融指数 Melt Index	GB/T 3682-2000	g /10min	10~11
热变形温度 Heat-Deflection-Temperature	GB/T 1633-2000	℃	55
屈服强度 Yield Strength	GB/T 1040-92 Test speed：10mm/min	MPa	38.9
断裂伸长率 Elongation at Break	GB/T 1040-92	%	18.3
弯曲强度 Flexural Strength	GB/T 9341-2000	MPa	53.3
弯曲模量 Flexural Modulus	GB/T 9341-2000	MPa	2908.0
冲击强度 Impact Strength	GB/T 1843-1996	KJ/m^2	3.2