

DEVELOPMENT OF LOW DENSITY POLYETHYLENE/SAGO BASED
BIOFILM VIA BLOW FILM MOLDING TECHNIQUE

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I hereby declare that this entitled “*Development of Low Density Polyethylene/Sago Based Biofilm via Blow Film Molding Technique*” is the result of my own research except as cited in the references. This report has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : _____

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ABSTRACT

The aim of this study is to develop degradable starch based packaging film with enhanced mechanical properties. A series of low density polyethylene (LDPE)/sago starch compounds with various sago starch contents were prepared by twin screw extrusion with the addition of maleic anhydride grafted polyethylene as compatibilizer. Palm cooking oil was used as processing aid to ease the blown film process, thus, degradable film can be processed via conventional blown film machine. Studies on their characteristics, mechanical properties and biodegradation were carried out by Fourier Transform Infrared (FTIR) spectroscopy and optical properties, tensile test and exposure to fungi environment and soil burial analysis respectively. The presence of high starch contents had an adverse effect on the tensile properties of LDPE/tapioca starch blends. However, the addition of compatibilizer to the blends improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the films. High content of starch also was found to increase the rate of biodegradability of LDPE/tapioca starch films. It can be proved by exposure of the film to fungi environment and weight loss in soil burial analysis. A growth of microbes colony can be seen on the surface of LDPE/tapioca starch film indicates that the granular starch present on the surface of the polymer film is attacked by microorganisms, until most of it is assimilated as a carbon source.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Synthetic polymers have become technologically significant since the 1940s and packaging is one industry that has been revolutionized by oil-based polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC). Plastics' versatility allows it to be used in everything from the simple part, for example plastic bags, bottles and dolls to the high-tech parts, cars, computer casing, electronic devices casing and many more. The reason behind multiuse of plastics is unique capability to be manufactured to meet very specific functional needs for consumers. Plastics have been found useful in applications ranging from transportation, packaging, building, medical appliances, agricultures and communication as shown in Figure 1.1 (Steven, 2002).

Worldwide production of plastics is more than 78 million tons per year and almost half of that is discarded within a short time, remaining in garbage deposits and landfills for decades (more than 30 years) (Volke-Sepulveda et al., 1999). Furthermore, major application of plastics is in packaging and this situation may contribute to serious environmental problems. Table 1.1 shows that thermoplastics are widely used in packaging and fabrication of bottles and films (Zheng and Yanful,

2005). Synthetic plastics accumulate in nature at a rate of 25 million tons per year and polyethylene represents 64% of the produced synthetic plastics. Petrochemical based plastics such as polyolefin, polyesters and polyamides have been increasingly used as packaging materials because of their availability in large quantities at low cost and favorable functionality characteristics such as good tensile and tear strength, good barrier properties to oxygen and aroma compounds and heat seal ability (Tharanathan, 2003).

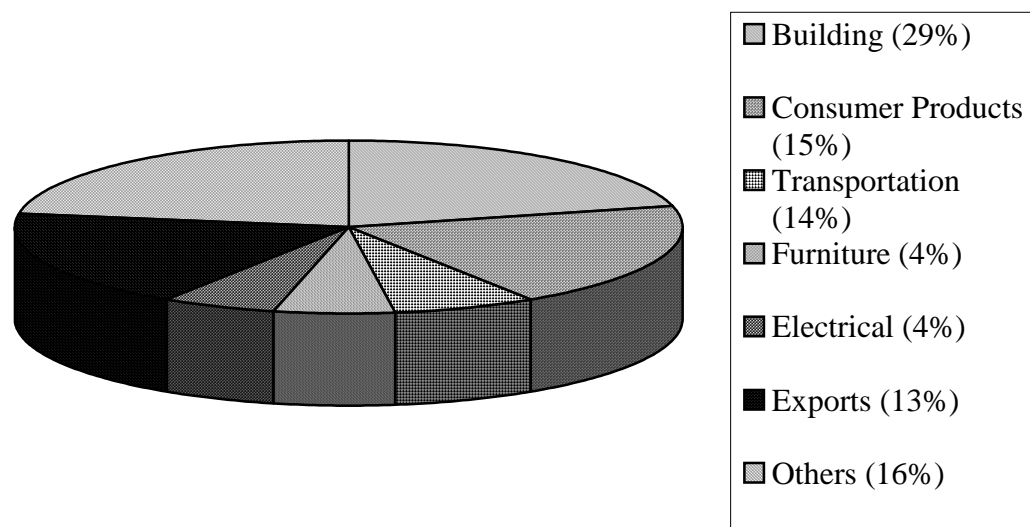


Figure 1.1 Major Uses of Plastics

However, these plastics are made of petroleum-based materials that are not readily biodegradable. Synthetic plastics such as polyethylene and polypropylene have a very low water vapor transmission rate and most importantly, so that, they are totally non-biodegradable, and therefore lead to environmental pollution, which pose serious ecological problems. Polyolefin are not degraded by microorganisms in the environment, which contributes to their long lifetime of hundred of years. There has been an increased interest in enhancing the biodegradability of synthetic plastics by blending them with low cost natural biopolymers.

Table 1.1 Main plastics and their applications

Plastics	Applications
Low density polyethylene (LDPE), linear low density polyethylene (LLDPE) polyvinylchloride (PVC)	Films and packaging
Polyethylene terephthalate (PET), PVC, high density polyethylene (HDPE)	Bottles, tubes, pipes, insulation molding
Polystyrene (PS) polypropylene (PP), PVC	Tanks, jugs, containers
LDPE, LLDPE	Bags
Polyurethane (PUR)	Coating, insulation, paints, packing

Most light weight plastic packaging material is used for a one-time application and discarded when its useful life is over. These materials are durable and inert in the presence of microbes thus leading to a long term performance (Arvanitoyannis, et al., 1998). Although there has been a lot of new technology and method in recycling and reducing plastics waste, the number of these materials is still increasing every year. Replacing plastics to other materials such as paper and metals is less attractive because of the special characteristics and economical factors. Recycle of products also has its limitation such as high cost of operation, besides, the technology of recycling are still under development. Many packaging materials do not lend themselves to recycling because of contamination, and the cleaning necessary prior to recycling can be very expensive.

Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation. They are defined as plastics with similar properties to conventional plastic but which can be decomposed after disposal to the environment by the activity of microorganism (Tharanathan, 2003; Raghavan, 1995). It is also defined as plastics with similar properties to conventional plastics, but it can be decomposed after disposal to the environment by the activity of microorganisms to produce end products of CO₂ and H₂O (Tharanathan, 2003). Biodegradable plastics provide opportunities for reducing municipal solid waste through biological recycling to the ecosystem and can replace the conventional synthetic plastic

products. In addition, it is desirable that these biodegradable polymers come primarily from agricultural or other renewable resources for a sustainable environment. Many synthetic materials like polyolefins are not degraded by microorganisms in the environment, which contributes to their long-life of hundreds of years (Chandra and Rutsgi, 1997; Sastry, et al. 1998). Biodegradation occurs when microorganism such as bacteria and fungi degrade a polymer in an aerobic and an anaerobic environment, carbon dioxide, methane and other natural products are derived from the degradation process. Hence, biodegradation can be stated as the conversion of the constituents of a polymer to carbon dioxide/methane, microbial cellular components and miscellaneous by-products, by microorganisms (Raghavan, 1995). Microorganisms break down the polymer chains and consume the material through several methods.

Polyethylene (PE) is one of the mass produced non-degradable polymers and various types of PE are used extensively in many fields, including agricultural and packaging films. Among the polyolefins, low density polyethylene (LDPE) is more susceptible to the attack of microorganisms in determined conditions (Ohtake, et al. 1998). LDPE had been a major use of plastics materials in packaging industries. Biodegradable polymers are considerably more expensive than competitive non-biodegradable polymers. New mechanisms for production and processing of synthetic polymer and natural polymer will be interesting alternatives to reduce the cost of biodegradable polymers in the market. Blending of low density polyethylene with a cheap natural biopolymer such as starch will enhancing the biodegradability of this material. Incorporation of starch will accelerate the attack of microorganisms to LDPE. Furthermore, starch is being a good choice since it is an abundant and low cost material in the market, so, it will reduce the cost of production of LDPE/starch biodegradable polymer.

Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Starch satisfies the requirements of having adequate thermal stability with minimum interference of melt properties and negligible disturbance of product quality and has been considered as a

material candidate in certain thermoplastic applications because it is known biodegradability, availability and low cost (Shah et al., 1995; Mani and Bhattacharya, 1998). The excellent physical properties of polyolefin make them suitable as packaging and film materials. Polyethylene (PE) blended with starch is already found to be a potential candidate to replace non-degradable thermoplastics in the areas of packaging. Starch is hydrophilic polymer, mainly due to the hydroxyls contains. In contrast, polyethylene is hydrophobic. Because of this totally different polar character of the polymers, they are immiscible.

Addition of glycerol as a plasticizer will improve the incorporation of starch in LDPE and also enhancing the biodegradability of the blends. Low molecular weight plastic additives like plasticizers and fillers are usually susceptible to microbial attack. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened the polymer (Sastry, et al. 1998). The microbes, in turn, release nonspecific oxidative enzymes that could attack synthetic polymers. Addition of palm oil based glycerin also can be function as a compatibilizer to the blend of starch and LDPE and it is also can reduce the cost of production. Films of polyethylene/starch blends with and without vegetable oils as a compatibilizer were prepared using blow film extrusion machine (Sastry et al., 1998). The degradation of the films under thermo oxidative treatment, ultraviolet light exposure, high temperature, high humidity and natural ambience (soil burial) were increased. It also can be seen that vegetable oil as an additive has a dual role; as a plasticizer, it improves the film quality; as a prooxidant, it accelerates degradation of the film.

Starches are polymers that naturally occur in a variety of botanical sources and it is a renewable resource widely available and can be obtained from different left over of harvesting and raw material industrialization. Sago starch is one of the potential starch can be used in the development of biodegradable polymers. The incorporation of starch, as naturally biodegradable polymers with synthetic polymers, such as polyethylene will produce a biodegradable film with excellent mechanical properties, can be easily process through polymer processing techniques and biodegradable. However, due to its poor melt processability, the properties of

LDPE/starch blends will be affected. The addition of plastifying agent, mainly glycols will enhance the compatibility of LDPE/sago based blend system an also usually susceptible to microbial attack (Mali et al., 2005). This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened the polymer. Plasticizers also reduce the brittleness of the film by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules and increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular volume (Tharanathan, 2003; Mali et al., 2005).

1.2 Problem Statement

With the growing concern about environmental pollution, the accumulation of plastics waste needs immediate resolution. Plastics packaging has become major contribution to accumulation of plastics waste in landfills. Increasing public concern over dwindling landfill space and accumulation of surface litter has promoted the development of degradable plastics. Biodegradable plastics offer one solution to managing packaging waste. Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation.

Thus, in the last 20-30 years, there has been an increased interest in the production and use of fully biodegradable polymers with the main goal being replacement of non-biodegradable plastics, especially those used in packaging materials. However, although these polymers possess the required properties and can be used for the production of blown film, there are not widely used due to their high cost. Biodegradable polymers are estimated to be four to six times more expensive than polyethylene and polypropylene, which are the most widely used plastics for packaging applications. Therefore, many research attempts have been focused on the use of natural biopolymers such as starch, cellulose, lignin and chitin, which are also fully biodegradable. In addition, these materials are also very cheap and they are produced from renewable, natural sources (Bikiaris and Panayiotou, 1998). However,

due to its poor properties, these materials are not suitable for most uses in the plastics industry.

Addition of starch as a filler in polyethylene blend will increase the biodegradability of the film and it is suitable for packaging industry. Many research have concentrate on the blending of corn, wheat, rice and whey starches with low density polyethylene to produced biodegradable polymers. Sago starch has become a potential use as a matrix for the development of biodegradable polymers because of its fully biodegradable properties and low cost of production. Sago starch had been widely studied by many researchers in edible films and coatings, being used to protect food products (Flores et al, 2007; Fama et al., 2005). Lawton (1996) has prepared starch-PVA films with the addition of glycerol and poly(ethylene-co-acrylic acid) (EAA) as processing aids to produced excellent biofilms. In this study, glycerol, palm oil based glycerol and maleic anhydride will be used as processing aids to improve the strength of the LDPE/sago starch biofilms.

High content of sago starch in the polyethylene blends will enhance the biodegradability of the LDPE/sago starch biofilms. Starch is susceptible to microorganisms, thus, when these blends are deposited in the environment, various microorganisms consume the starch, which leaves the polymer blend in a form which is full of holes. This form enables the easier disintegration of the material into small pieces. It also increases the total surface area accessible to oxygen. As a result, the oxidation of polyethylene becomes easier.

Increasing the amount of starch causes a decrease in both tensile strength and elongation at break. As a result, the produced materials lose their ability to produce blown films. This decrease arises from poor adhesion between starch and low density polyethylene (LDPE) due to different polar character of starch and LDPE (Bikiaris, 1998). The addition of processing aids will improve the compatibility between the two materials. Processing aids in LDPE/sago starch blending also improve the ability of the material to be process via blow film technique. Starch blended polyethylene films have been reported by many researchers, but there is lack of literature on their application in food packaging. Since sago starch containing plastic film has no adverse effects on food quality or food safety, it is suitable for use in food packaging.

1.3 Objectives of the Study

The main objective of this study is to develop biodegradable low density polyethylene (LDPE)/sago starch packaging film with enhanced mechanical properties via blow film extrusion process. This objective is divided into;

- (i) to determine the optimum loading of starch in LDPE/sago starch blends that can give good mechanical properties for packaging and can be processed using blow film machine.
- (ii) to characterize the mechanical, morphological, thermal properties of LDPE/sago starch films before and after they are subjected to biodegradation tests.
- (iii) to investigate the biodegradability of LDPE/sago starch films.

1.4 Scopes of the Study

Scopes of this study are;

- i. Compounding of LDPE/sago starch blends using twin screw extruder and processability studies on blow film machine.

Prior to compounding, all the ingredients will be mixed using high speed mixer. Then, the compounded samples will be blown using blow film machine to study the effect of it on the processability.

- ii. Mechanical properties study of LDPE/sago starch biodegradable films.
 - (a) Tensile strength and elongation at break
 - (b) Water absorption analysis

- iii. Characterization of LDPE/sagostarch biodegradable films
 - (a) Melt flow index analysis after compounding process to investigate its suitability for blown film process.
 - (b) Chemical structure analysis on Fourier Transform Infrared Spectroscopy
 - (c) Morphological analysis on optical microscopy and Scanning Electron Microscopy
 - (d) Thermal analysis on DSC and TGA

- iv. Biodegradation studies of LDPE/sago starch films
 - (a) Natural weathering studies
 - (b) Exposure to fungi environment

CHAPTER II

LITERATURE REVIEW

2.1 Plastics and Environment

Plastics are synthetic substances produced by chemical reactions. Almost all plastics are made from petroleum, save a few experimental resins derived from corn and other organic substances. "Plastics" earned their name because they can be molded, cast, extruded or processed into a variety of forms, including solid objects, films and filaments. These properties arise from their molecular structure. Plastics are polymers, very long chain molecules that consist of subunits (monomers) linked together by chemical bonds. Plastics, depending on their physical properties, may be classified as thermoplastic or thermosetting materials. Thermoplastic materials can be formed into desired shapes under heat and pressure and become solids on cooling. If they are subjected to the same conditions of heat and pressure, they can be remolded. Thermosetting materials acquire infallibility under heat and pressure and cannot be remolded.

Plastics are widely used, economical materials characterized by excellent all-round properties, easy molding and manufacturing. Approximately 140 million tones of synthetic polymers are produced worldwide each year to replace more traditional materials, particularly in packaging. Table 2.1 that is shows the word and USA production of plastics materials (Brydson, 1995). Over 60% of post consumer

plastics waste is produced by households and most of it as single use packaging (Zheng and Yanful, 2005). Plastics are manufactured and designed to resist the environmental degradation and also more economical than metal, woods and glasses in term of manufacturing costs and energy required. Due to these issues, plastics resins have become one of the most popular materials used in packaging. Plastics packaging has a cycle less than a year and continuously enter the waste stream on a short turnout of time. The continuous growing of plastics industries has lead to the increase volume of plastics waste in the landfill.

Table 2.1 World and USA production of plastics materials (Brydson, 1995).

Year	World	USA
1939	300 000	90 000
1951	2 000 000	810 000
1957	4 600 000	1 920 000
1960	6 200 000	2 480 000
1963	8 500 000	3 730 000
1967	18 000 000	5 567 000
1973	-	13 182 000
1980	50 000 000	16 117 000
1986	-	22 522 000*
1992	91 237 000	29 890 000*
1993	-	31 315 000*

*These figures are based on sales figures, not the production.

(Much of the earlier data are based on long tons; later data are in tones. The USA figure are based on estimates published in Modern Plastics, apart from those for 1967, which are from the US government sources. The global figures are from various sources, with the 1992 figure being based on RAPRA statistics.)

The principal worldwide problem is solid waste disposal, with billions of tones of waste created every year. Landfill used to be one of the main routes of disposal in everywhere but landfill capacity is now diminishing (Moore and Saunders, 1997). In the early stages, reduce; reuse and recycle have become

alternatives to overcome waste problems. Source reduction refers to the reduction of the amount of materials entering the waste stream by redesigning patterns of production or consumption. For example, the wall thickness of many plastic and metal containers has been reduced in recent years, and some European countries have proposed to eliminate packaging that cannot be easily recycled (Richardson, 2006). However, the durability, strength, low cost, water and chemicals resistance, welding properties, lesser energy and heavy chemicals requirements in manufacture, fewer atmosphere emissions and light weight are advantages of plastic materials, cause these material most preferable especially in packaging industries.

Reuse strategy also has its limitation. Many plastics applications are not designed to reuse because of the impurities and contamination. Food packaging, disposable diapers, medical appliances and agricultural mulch bags and covers are the most common plastics products that not suitable for reusing it. These are examples why plastics waste could be in the waste streams very fast.

Recycling of plastics after final use is possible, but plastic bags, in particular, are rarely recycled. Furthermore, the technology of sorting, collecting and recycling the plastics waste is still being developed and will cost a lot of money. Collecting and sorting used plastics is an expensive and time-consuming process. While about 27 percent of aluminum products, 45 percent of paper products and 23 percent of glass products are recycled in the United States, only about 5 percent of plastics are currently recovered and recycled (Richardson, 2006). Once plastic products are thrown away, they must be collected and then separated by plastic type. Most modern automated plastic sorting systems are not capable of differentiating between many different types of plastics. If plastic types are not segregated, the recycled plastic cannot achieve high remolding performance, which results in decreased market value of the recycled plastics (Richardson, 2006).

Other factors can adversely affect the quality of recycled plastics. These factors include the possible degradation of the plastic during the recycling process.

Furthermore, plastics wastes that enter the waste stream were normally contaminated by dirt, food scraps and waste. Cleaning of the plastics has become one of the major problems in plastics recycling. The high volume to weight ratio of plastic means that the collection and transport of this waste is difficult and expensive also caused a problem in plastics recycling. Finally, the plastics waste will be ended up in the landfill again.

Composting is the desirable method because it can be used to degrade 70% of solid waste created. However, in landfills the conditions are anaerobic and dry, not conducive to any degradation. In comparison, composting creates the optimum conditions for waste degradation; humidity, aeration and high temperatures. Plastics constitute high volume of solid waste and it is in this area that biodegradable polymers can play a major role (Moore and Sounders, 1997).

2.2 Polymers Used in Packaging

With the growing concern about environmental pollution, the accumulation of plastic waste needs immediate resolution. Biodegradable plastics have been intensively studied in recent years (Khabbaz et al., 1998; Erlandsson et al, 1997; Akaranta and Oku, 1997; Arvanitoyannis et al, 1997; Manzur et al, 2004) and have been commercialized into various products such as garbage bags, composting yard waste bags, grocery bags and agriculture mulches. Plastic packaging demand will increase more rapidly based on good opportunity for both flexible and rigid packaging. Flexible packaging advances will be fueled by rapid growth for pouches and protective packaging. The rapidly expanding stand-up pouch segment will enable flexible packaging to gain share in a number of rigid packaging applications. In rigid plastics packaging, best opportunities are anticipated for trays, tubs and cups. Table 2.2 shows total sales and captive use of selected thermoplastic resins by major market from 2001 to 2005.

Table 2.2 Total sales and captive use of selected thermoplastic resins by major market from 2001 to 2005.

Major Market	2001	2002	2003	2004	2005
Transportation	4,207	4,738	4,732	4,899	4,711
Packaging	22,847	24,170	24,087	25,952	25,144
Building & Construction	13,988	14,729	14,495	15,676	15,483
Electrical/Electronic	2,501	3,037	2,862	3,096	2,917
Furniture & Furnishings	3,226	3,507	3,361	3,458	3,406
Consumer & Institutional	16,510	17,649	17,571	18,714	17,400
Industrial/Machinery	968	998	962	1,042	1,087
Adhesives/Inks/Coatings	1,143	1,165	1,170	1,196	1,160
All Other	2,705	2,283	2,021	2,168	2,133
Exports	9,295	10,048	9,009	9,900	9,790

(Source: APC Plastics Industry Producers Statistics Group, as compiled by Veris Consulting, LLC. © 2006 American Plastics Council, part of the American Chemistry Council, as compiled by Veris Consulting, LLC.)

The two major applications of synthetic polymers fall in the field of food packaging (wrapping materials) and other uses, such as mulch films, seedling pots and binding twine. Plastics have gained a unique position in food packaging technology for a number of quite different reasons including;

- (a) higher strength , elongation and barrier properties against waterborne organisms responsible for food spoilage
- (b) lower cost and higher energy effectiveness
- (c) lightness and water resistance

The continuous growth of polymer materials for food packaging applications in conjunction with their recalcitrance toward degradation and their visibility in the environment when discarded have stimulated further research in the field of food packaging (Psomiadou et al., 1997). It has been estimated that 2% of all plastics eventually reach the environment, thus contributing considerably to a currently acute ecological problem.

2.3 Development in Biodegradable Packaging Materials

Over the last thirty years, there has been a growing interest in biodegradable polymers. Initial interests were in the fields of medicine, such as producing degradable fibers for sutures, and agriculture, for mulch films and controlled pesticide release (Moore and Saunders, 1997). In more recent years attention has been focused on the rising concern for the environment. Biodegradable plastics are plastics that can undergo a degradation process known as biodegradation. According to Moore and Saunders (1997), biodegradation of a plastic materials leading to a change in its chemical structure caused by biological activity leading to naturally occurring metabolic end products. A plastic material is called biodegradable if all its organic components undergo a total biodegradation. Rates of biodegradation are to be determined in standardized test systems.

Biodegradable plastics also defined as plastics with similar properties to conventional plastics, but it can be decomposed after disposal to the environment by the activity of microorganisms to produce end products of CO₂ and H₂O (Tharanathan, 2003). It is also an alternative to the petroleum based non-biodegradable polymers. Biodegradable plastics can be used in hygiene products, household goods, horticultural products, agriculture, medical products and many more. It decreases the solid waste problems created by plastics waste. Biodegradable polymers can be divided to two main categories, which are naturally occurring biodegradable polymers and synthetic biodegradable polymers (Danjaji, 2002).

Naturally occurring biodegradable polymers including polysaccharides such as starch, cellulose, chitin/chitosan, pullulan, levan, konjac and elsinan. In this compound, simple sugar such as glucose, fructose and maltose are the basic units (Danjaji, 2002). The various naturally occurring biopolymeric materials of use in composite film making and coating formulation are shown in Figure 2.2. Some polyester such as polyhydroxyalkanoates is also naturally occurring biodegradable polymers.

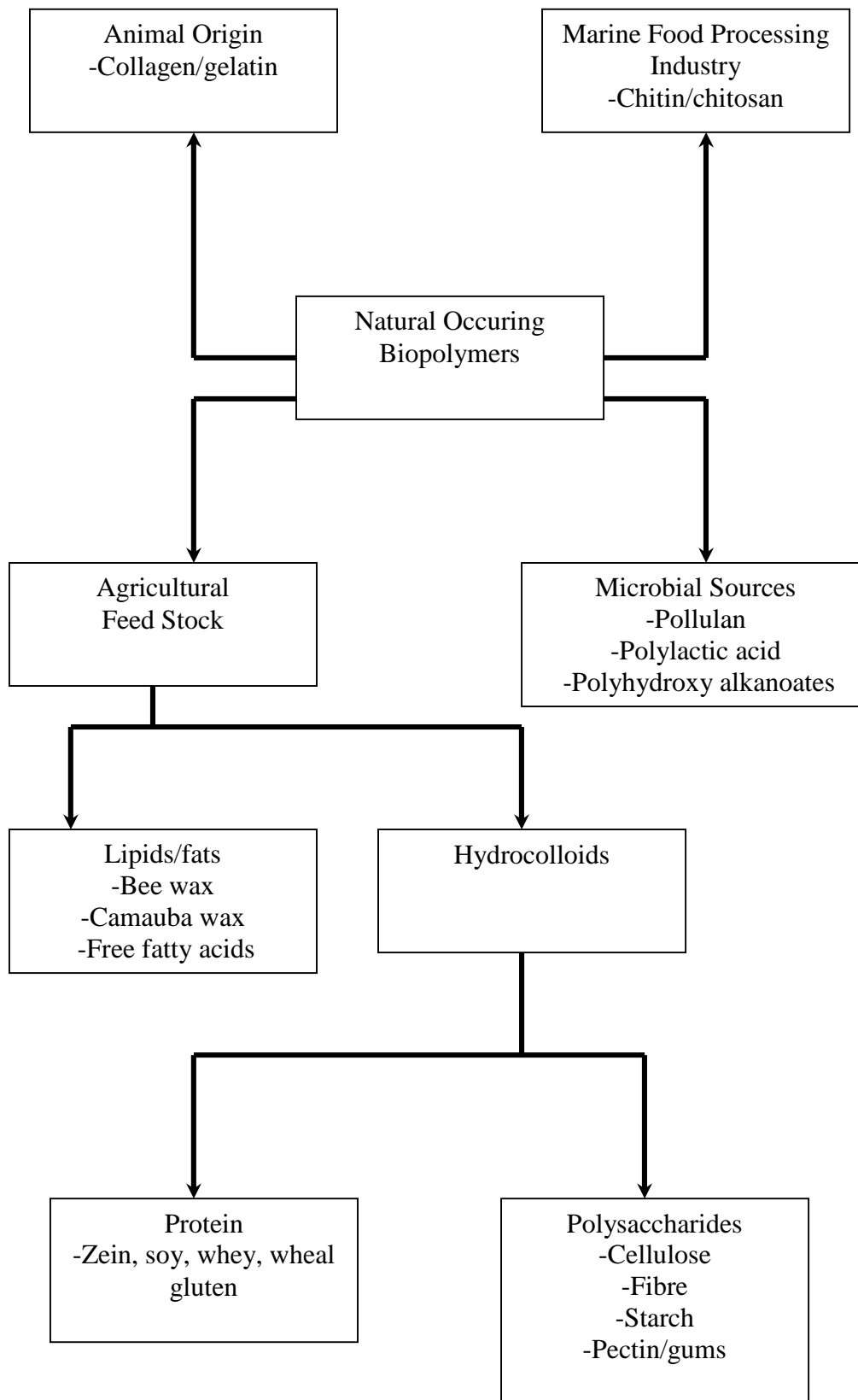


Figure 2.2 Naturally occurring biopolymers of se in biodegradable packaging and composites (Tharanathan, 2003)

Synthetic biodegradable polymers are normally polymers with hydrolysable backbone or polymers that are sensitive to photodegradation. Polyester is the polymer with hydrosable backbone. Examples of polymers that in the family of polyesters are poly(glycolic acid), poly(glycolic acid-co-lactic acid), polycaprolactone, polyether-polyurethane and poly(amide-enamide)s. Some common synthetic biodegradable and its descriptions are listed in Table 2.3.

Table 2.3 Common synthetic biodegradable plastics (Garthe and Kowal, 1994)

Plastic Type	Name	Description
Polyester	Polyglycolic acid (PGA)	Hydrolizable polyhydroxy acid
	Polylactic acid (PLA)	Hydrolyzable polyhydroxy acid; polymers derived from fermenting crops and dairy products; compostable
	Polycaprolactone (PCL)	Hydrolyzable; low softening and melting points; compostable; long time to degrade
	Polyhydroxybutyrate (PHB)	Hydrolyzable; produced as storage material by microorganisms; possibly degrades in aerobic and anaerobic conditions; stiff; brittle; poor solvent resistance
	Polyhydroxyvalerate (PHBV)	Hydrolyzable copolymer; processed similar to PHB; contains a substance to increase degradability; melting point; toughness; compostable; low volume and costly production
Vinyl	Polyvinyl alcohol (PVOH)	Water soluble; dissolves during composting
	Polyvinyl acetate (PVAC)	Water soluble; predecessor to PVOH; has shown no significant property loss during composting tests
	Polyethylketone (PEK)	Water soluble; derived from PVOH; possibly degrades in aerobic and anaerobic conditions

The most attractive feature of the biopolymer-based materials is their total biodegradability. As a result they fit perfectly well in the ecosystem and save the world from growing ecological pollution caused by non-biodegradable plastics, which are essentially petroleum-based. A number of aerobic and anaerobic microorganisms have been identified for biodegradation (Hooi, 2005). The carbon cycle involving the biopolymer degradation is shown in Figure 2.3.

2.3.1 Starch Based Biodegradable Polymers

Polymeric materials are generally durable and inert towards microbes, thus offering long term performance. According to the emphasis on environmental pollution problems and land shortage problem for solid waste management, such as nonavailability of landfills, public perception, and reduction of fertility of lands by accumulation of surface litter, environmentally degradable and ‘environmentally friendly’ polymers are of interest (Arvanitoyannis et al., 1998). Biodegradable polymers can be further broken down into two main areas; renewable and non-renewable biodegradable polymers. Essentially renewable biodegradable polymers utilize a renewable resource, for example, a plant by-product, in development of the polymer, rather than a non-renewable, for example, petroleum based resource (Halley, 2005). There is wide variety of biodegradable polymer platforms being developed. Summarises of various biodegradable polymers, along with their generic advantages, disadvantages, potential applications and some current suppliers are shown in Table 2.4.

Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Technologies have been developed for continues production of extrusion films and injection-moulded plastics containing 50% or more of starch (Tharanathan, 2003). Starch satisfies the requirements of adequate thermal stability, minimum interference with melt properties and disturbance of product quality (Shah et al., 1995).

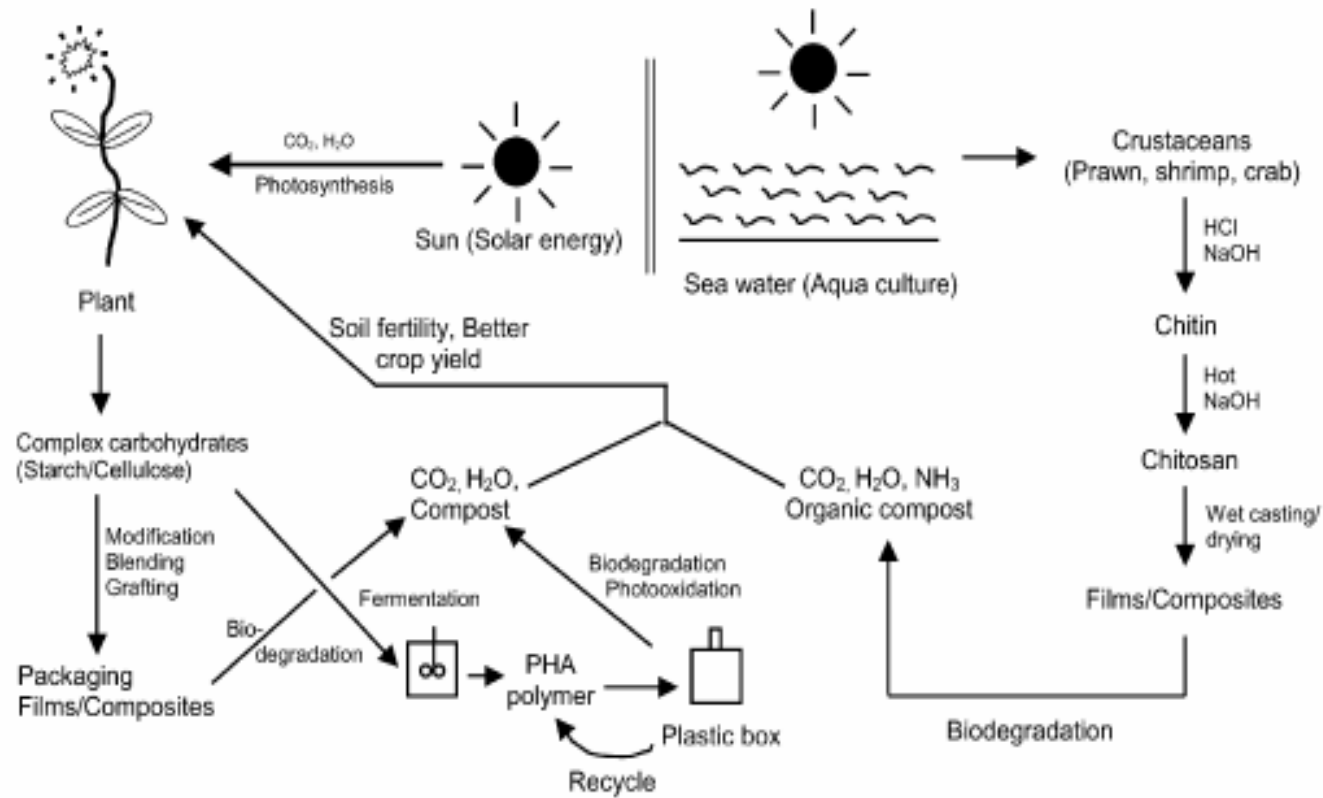


Figure 2.3. The carbon cycle involving the biopolymer degradation (Tharanathan, 2003)

Table 2.4 Summarizes of various biodegradable polymers, along with their generic advantages, disadvantages and potential applications (Halley, 2005)

Base polymer	Source type	Advantages	Disadvantages	Potential applications	Suppliers
Starch	Renewable	Low cost Fast biodegradation	Poor mechanical properties Hydrophilicity	Foams Films and bags Moulded items	Novamont (Materbi) Plantic Technologies (Plantic) Rodenberg (Solanyl) Biotec (Bioplast) National Starch (ECOFOAM)
Polyhydroxyalkanoates (PHA)	Renewable	Rapid biodegradation Water stable	High cost	Moulded items	Biomer (Biomer) Metabolix P&G
Cellulose and cellulose acetates	Renewable	High strength Water stable	Difficult to process Very low biodegradability	Composites Fibre board	UCB (Natureflex) Mazzucchelli (Bioceta)
Fatty acid (triglyceride oil based) polymers	Renewable	High strength	Brittle Low biodegradability	Composites Adhesives Compatibilisers	Dow UDelaware (research)

Continued...

Lignin polymers	Renewable	High strength	Brittle Low biodegradability	Composites Adhesives Compatibilisers	Borregard (Lignopol)
Collagen/Gelatine polymers	Renewable	High strength	Non-reproducible properties	Films	No information
Polylactic acid (PLA)	Non-renewable	High strength	Brittle	Injection moulding Fibres	Cargill-Dow (Natureworks) Boehringer
Polyglycolic acid (PGA)	Non-renewable	High strength	Brittle Soluble in water	Fibres Sutures	Davis and Greck Ethicon
PCL	Non-renewable	Water stable Hydrolysable	Low melting point	Compost bags Cold packaging	Solvay (Capa)
PVOH	Non-renewable	Good barriers properties	Low biodegradability Solubility in water	No information	No information
Synthetic polyesters	Non-renewable	High strength Good processing	Relatively high cost	Films Moulded items	BASF (Ecoflex) Showa (Bionolle) DuPont (Biomax) IRE Polymers Eastman (Easter Bio)

Incorporation of starch into the synthetic polymer will increase the biodegradability of synthetic polymer when starch is consumed by microorganisms. It is believed that under a rapid enzymatic hydrolysis, starch will be degraded leading to a void containing matrix, reduced the mechanical properties of the plastics and might be promote the biodegradation of synthetic polymer due to the increased surface area available for interaction with microorganisms (Chandra & Rutsgi, 1999).

2.3.1.1 Starch Based Low Density Polyethylene Biodegradable Polymers

One of the most important polymers, both in usage and in volume of production is polyethylene. As the polymer with the greatest annual production worldwide, PE is the main component in plastic waste worldwide (Bikiaris et al., 1997). Polyethylene is one of common synthetic polymers of high hydrophobic level and high molecular weight (Abd El-Rahim et al., 2004). In natural form, it is not biodegradable. Thus, their use in the production of disposal or packing materials causes dangers environmental problems.

Many solutions have been proposed for soil waste management of plastics, like recycling, incineration, landfill disposal and degradable plastics. Recycling will not yield quality products due to heterogeneous nature of the plastics. Incineration of plastics will release toxic gases and vapors, which could prove to be a serious health hazard and use of plastic in landfill operations is least preferred because of space constraints (Sastry et al., 1998). It is increasingly felt that the best alternative would be making the plastics degradable. The importance of studying low density polyethylene (LDPE) biodegradable formulations is motivating many researchers in this area.

2.4 Processing of Biodegradable Packaging Materials

There are three main classes of biodegradable polymers. The first class of material is synthetic polymers, with vulnerable groups susceptible to hydrolysis attack by microbes, such as polyesters, polyanhydrides, polyamides, polyurethanes and many more. The second class of materials is composed of naturally occurring processible bacterial polymers, such as polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). PHB and PHV are truly biodegradable, being attacked by a wide variety of bacteria. The third class of is blends of polymers and additives that are readily consumed by microorganisms, The classic example of this class of materials is biodegradable polyethylene and starch blends (Chandra and Rutsgi, 1997; Chandra and Rutsgi, 1999).

The most popular method in preparation of starch and polyethylene blends was the conventional extrusion with the addition of processing aid to enhance the compatibility of the two materials. Shah et al. (1995) have prepared detailed experimental approach for blending modified starch with LDPE. LDPE was compounded with well dried, modified granular starch using a two roll mill and a single screw Brabender to obtain starch filled LDPE strips. Arvanitoyannis et al. (1998) and Psomiadou et al., (1997) also extruded the LDPE/rice and potato starch blends using twin screw extruder in the presence of 15-20% water content. For the mechanical studies, specimens were obtained by injection molding (Nakamura et al., 2005). Chandra and Rutsgi (1997) prepared a reactive blending of LLDPE/corn starch with an anhydride functional polymer. Maleic anhydride (MA) was grafted onto LLDPE in xylene using dicumyl peroxide, and blending of MA-g-LLDPE/corn starch was carried out in a torque rheometer.

A series of LDPE/corn starch blends were processed into film by two different processes, namely, solution casting followed by thermo pressing and extrusion process have been prepared by Raj et al. (2004). LDPE/corn starch biofilms for food packaging were prepared using solution blending procedure, which is LDPE resins were dissolved in tetrachloride under reflux conditions for two hours,

followed by thermo pressing technique to form films. They also prepared different composition of LDPE/cornstarch blends by extrusion technique using twin screw extruder. Sastry et al. (1998) have compounded LDPE/starch blends using twin screw extruder with and without the addition of vegetable oil during the processing. Then, samples were fabricated in a blow film machine to produce LDPE/starch biofilm. Erlandsson et al. (1997) had also prepared LDPE/starch blends made by conventional extrusion blowing to investigate the properties and biodegradability of the films with a thickness of 80 μ m.

2.5 Properties of Biodegradable Packaging Materials

Nakamura et al. (2005) have investigated the incorporation of different starches, such as native, adipate, acetylated and cassava starch in low density polyethylene matrix to verify the possibility to obtain partially product with the aim to decrease the plastics waste in the environment. However, LDPE/starch compounds generally present poor thermal-mechanical properties when compared with those of pure LDPE. They have studied the interfacial properties between starch and polyolefins to improve the hydrophilic and hydrophobic character respectively, responsible for the poor mechanical properties. For that, the introduction of ethylene-acrylic acid (EAA) and PE-g-MA copolymers in the LDPE/starch formulations improved the thermal-mechanical properties of the blends. Bikiaris et al. (1997) also study the effect EAA and plastisized starch in LDPE/starch blends to improve the interfacial properties of the two polymers. Legislative threats and increasing demand in agricultural applications have generated much interest in degradable plastics. However, most of the cheap synthetic plastics have fairly good resistance to microorganisms due to low surface area, relative impermeability and high molecular weight.

Shah et al. (1995) found that, various fungi and bacteria through starch hydrolysis study, have consumed the starch granules present on the surface of the polymer. Holes and cracks were also observed on the surface of the hydrolyzed polymer in the SEM micrographs. Akaranta and Oku (1999) also confirmed that, the incorporation of starch in LDPE/starch blends promotes the growth of microbes on the surface of the films. The growth of the colony also increased with increase in the starch content of the films.

The continues growth of polymer materials for food packaging applications in conjunction with their recalcitrance toward degradation and their visibility in the environment when discarded have stimulated further research in the field of food packaging. Blends of LDPE/wheat or soluble starch have been prepared to study their properties and biodegradation rate (Psomiadou et al., 1997). The current practice of disposing most plastics consists of landfills, composting and incineration. They have prepared an anaerobic bioreactor to stimulate those of a representative landfill. The first stage of degradation consists of partial starch removal and only at a later stage does slow rate degradation of LDPE occur as shown in Figure 2.4 and Figure 2.5 (Psomiadou et al., 1997). Blends of LDPE with wheat and soluble starch were prepared and their mechanical properties were recorded. In general, the higher the starch content the worse the performance of the composite but the higher their biodegradability.

A series of LDPE and rice or potato starch have been prepared, varying in starch and water content, to investigate their mechanical properties, gas/water permeability and biodegradability (Arvanitoyannis et al., 1998). The presence of high starch content (above 30% w/w) had an adverse effect on the mechanical properties of LDPE/starch blends. Gas permeability and water vapour transmission rate increased proportionally to the starch content in the blend. The biodegradability rate of the blends was enhanced when the starch content exceeded 10% w/w. They also proposed that the kinetics of LDPE/rice starch blends degradation can be visualized as following three phase process;

(i) **First phase**

Amorphous starch chain, easily accessible, by the microbes is normally those located near the surface. Further progress of the microbes to the interior of the LDPE/starch blend should be rather interpreted with the help of the percolation theory.

(ii) **Second Phase**

This phase consists of a further, even deeper, invasion of microbes, which, however, cannot be considered yet a through one because of the persisting physically unaccessed 'starch islets'. The resulting holes or voids mainly due to vacation of starch sites, are occupied by either microbes or water thus leading to extensive degradation of the blend.

(iii) **Third phase**

The more the degradation approaches its final stage, the available microbes decrease in number because of lack of nutrients. The very high surface area generated by removal of starch from the polymer blends enhances considerably the chemical degradation process, which, in turn, promotes further biodegradation.

Raj et al. (2004) have prepared a series of low density polyethylene-starch blends films with starch content ranging from 2.5 to 50% by two methods, namely, solution blending followed by thermopress and extrusion methods. The films were studied for various properties like physicochemical, optical, morphological, thermal and biodegradation for packaging application. The extruded films had shown better mechanical properties compared to those of solution cast thermo-pressed films due to unidirectional molecular alignment. Contat-Rodrigo and Greus (2002) studied the effect of the degradation in soil in the samples morphology by differential scanning calorimetry (DSC) on LDPE samples filled with three commercial biodegradable additives (Mater-Bi, Cornplast and Bioeffect).

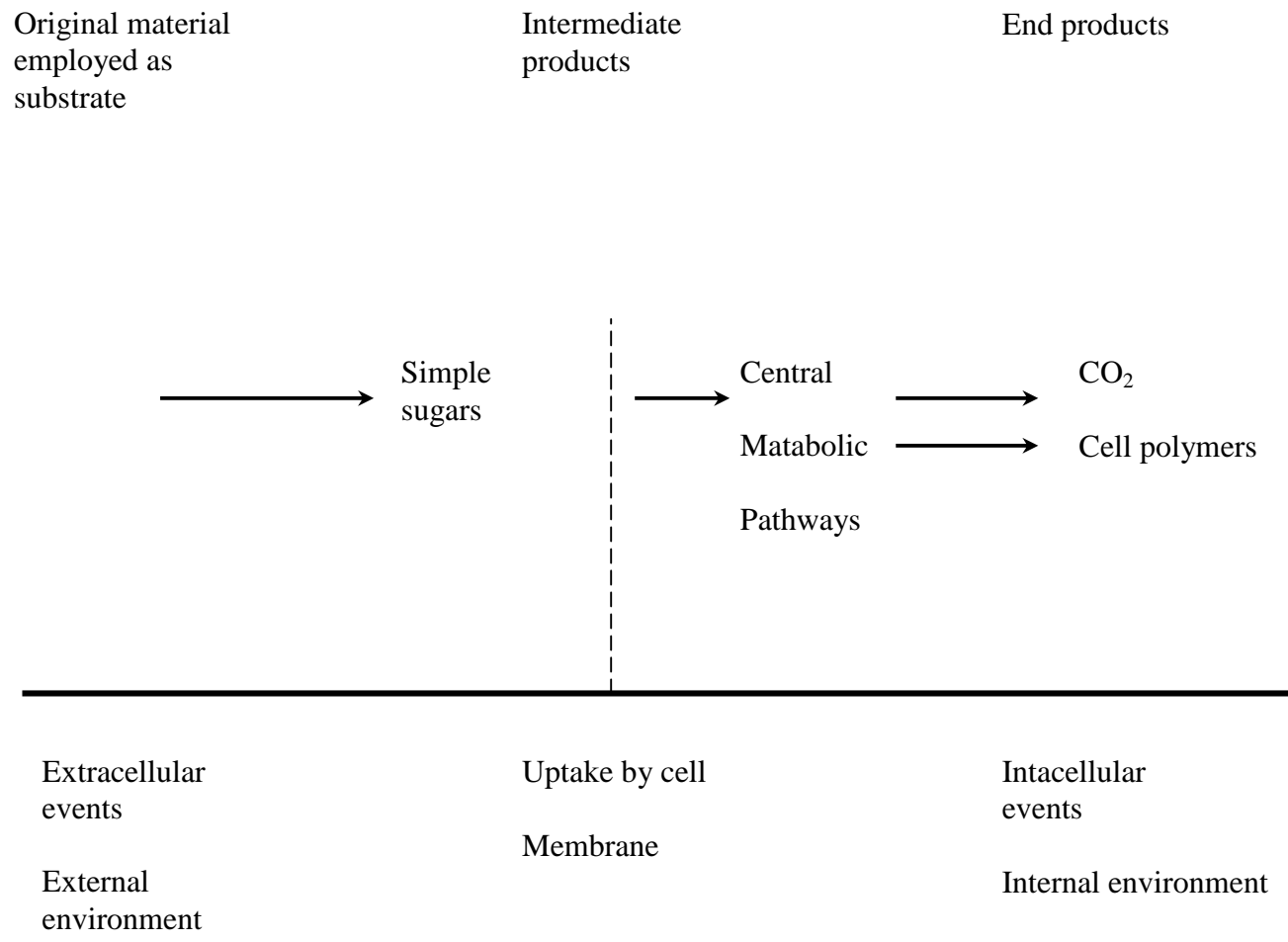


Figure 2.4 Descriptive model for starch degradation

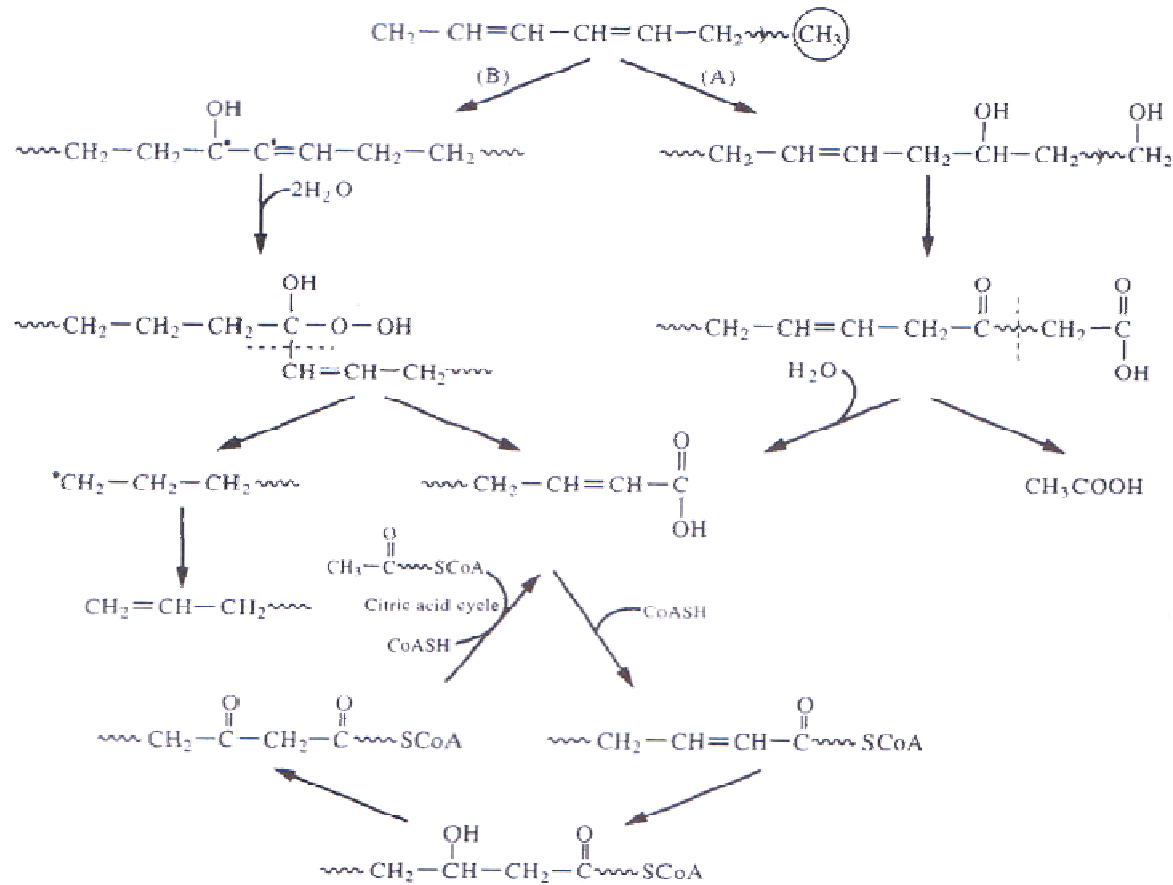


Figure 2.5 Tentative model for the biodegradation mechanism of LDPE: (A) via oxidation of both main chains and end groups; (B) via oxidation of exclusively main chain ends.

2.6 Modification of Biodegradable Packaging Materials

Erlandson et al. (1997) have studied the comparison of the susceptibility of pure LDPE, LDPE mixed with starch and LDPE mixed with starch and a prooxidant, manganese stearate (MB) to thermo and photooxidation. They have found that, the LDPE-MB (with prooxidant) is more susceptible to thermal degradation and photodegradation than the other two materials. The prooxidant system enhances the thermal degradation and not the starch part, which might even retard the degradation. Prooxidant can promote photooxidation to polyethylene chain, thus reduces the molecular weight of polyethylene chain. A reduction in molecular weight needs to take place before the material biodegrades at any appreciable rate. The oxidation is followed by cleavage of the chain (Khabbaz et al., 1998).

Thermoplastics are widely used due to their mechanical strength, low cost, easy processability and resistance to chemical and biological attack (Kim et al., 2001). As possible candidates to reduce pollution problems cause by plastic wastes are desired, various biodegradable polymers have been extensively investigated. Biodegradable polymers are desirable for a variety of applications, such as in packaging, agriculture and medicine. Polyethylene blended with starch is already found to be a potential candidate to replace nonbiodegradable thermoplastics in the areas of packaging. Films of polyethylene-starch blends with and without vegetable oil as compatibilizer were prepared by Sastry et al. (1998). Low molecular weight plastic additives like plasticizers and fillers are usually susceptible to microbial attack. This will leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened the polymer. The microbes in turn, release nonspecific oxidative enzymes that could attack the synthetic polymer. Also, the gradual degradation of the natural polymer leads to increased surface area by erosion and pitting. This will accelerate the degradation of the synthetic polymer by diffusion of O₂, moisture and enzymes into the porous polymer matrix.

In order to enhance the compatibility between two immiscible polymers, a reactive functional group can be introduced into synthetic polymers, being capable of hydrogen bonding with starch hydrolysis. The chemical modification of the hydroxyl groups of starch with a hydrophobic compound in LDPE-starch blends also can improve miscibility and adhesion of phases of starch-LDPE blends. Thiebaud et al. (1997) prepared the esterification of native starch with fatty acid chlorides. These starch esters were mixed with low density polyethylene at various proportions by melt blending. The blends show better thermal stability and higher elongation, but lower tensile strength and water absorption.

More recently, an increased interest has appeared in the use of polymers containing reactive groups, such as, maleic anhydride as compatibilizers to improve their compatibility (starch and LDPE). It was discovered that anhydride groups could react with hydroxyl groups in starch to produce chemical bonding, thus improving the dispersion of starch, the interfacial adhesion, and subsequently, the mechanical properties of the resultant blends. Liu et al. (2003) have investigated the effect of polyethylene-grafted-maleic anhydride (PE-g-MA) on the thermal properties, morphological and tensile properties of blends of low density polyethylene and corn starch. They have found that, the miscibility between granular corn starch and LDPE was improved by the addition of a commercially available compatibilizer, PE-g-MA attributed to a chemical reaction between hydroxyl groups in starch and anhydride groups in PE-g-MA and the physical interaction between the PE in PE-g-MA and LDPE. It is also possible to blend a high percentage of a granular corn starch with LDPE while keeping comparable tensile properties (Liu et al., 2003).

Natural starch exhibits a pronounced macro-molecular structure, which is suitable for the production of bioplastics. However, prior to production of such materials, the structure of native starch should be suitably modified. This is necessary, because starch degradation starts at a temperature lower than its melting point, and thus native starch cannot be processed by conventional plastics technology without any modification. Blends of low density polyethylene and corn starch with addition of an ethylene-g-maleic anhydride (PE-g-MA) also can modified the

structure of native starch (Matzinos et al., 2001) and this blends can be process by conventional thermoplastics processing, such as, extrusion, injection moulding and film blowing.

Great deals of works have been reported for the preparation of biodegradable polyethylene using various methods. However, very little information is available on grafting of naturally occurring biodegradable polymers like starch and gelatin on commonly used synthetic polymers like PVC and PE. Mahara and Singh (2006) have prepared graft copolymerization of low density polyethylene onto starch, carried out with glucosecerium(IV) redox initiator in an aqueous sulfuric acid medium under nitrogen atmosphere. According to them, chemical grafting is a useful technique for carrying out modifications of polymers easily and inexpensively with very thin stable coatings that outlast and outperform the expensive conventional methods. Grafting of biodegradable starch moieties on synthetic polymers has also induced biodegradability, and the percentage of biodegradation has increased with the increase in percentage graft yields of starch on polyethylene.

Some studies have been done on the effect of treated starch to the LDPE/starch blends. Thakore et al. (1999) studied the degradability of LDPE/starch and LDPE/starch/starch acetate (STAc) blends and the effect of STAc content on mechanical and degradability effect. Mechanical properties such as tensile strength, elongation at break and izod impact test decreased with increased of native starch content. However, when STAc was added to the blends, the mechanical properties improved particularly on toughness and elongation at break. Cell growth was observed to increase with increasing of (starch + STAc) content in the composite blends. Kim and Lee (2002) have studied the cast film of starch filled LLDPE using crosslinked potato starch. Potato starch was crosslinked by using various amount of epichlorohydrine. Mechanical properties of these films were measured and compare with native potato starch. Mechanical properties, such as, tensile strength and elongation at break were generally higher in crosslinked potato starch compared with the native starch.

2.7 Others Starch Based Biodegradable Polymers

Polycaprolactone (PCL) is one of the commercial available biodegradable polymers. It has a high flexibility and biodegradability due to its hydrophilic behavior. The idea of adding starch to the PCL is to increase the biodegradability and lower the cost of production as PCL is much more expensive compared to commodity plastics. Various types of starch were blend with PCL to produce biodegradable plastics with good mechanical and thermal properties, also can reduce the cost of production of these materials. Properties of PCL/starch and maleic anhydride-grafted-PCL/starch (PCL-g-MAH/starch) was studied by Wu (2003) using FTIR spectroscopy, NMR, DSC and mechanical testing. Poor compatibility of starch and PCL leading to phase separation between the two components were the main cause of the poor thermal and mechanical properties. Incorporation of PCL-g-MAH as a matrix shows better compatibility and homogeneity dispersion due to the formation of ester carbonyl groups. The thermal analysis results revealed that PCL-g-MAH has a lower melting temperature and better processability. Soil burial test showed some weight loss of the samples indicate that all the samples are biodegradable. However, the mechanical properties show decreased in tensile strength and elongation at break of the blends. PCL-g-MAH showed higher water resistance compared to PCL/starch blends.

Comparison of the performance of PCL/high amylase starch blends with and without compatibilizer was done by Avella et al. (2000). The influence of the compatibilizer in the degradability of the blends in compost stimulation study also has been done. Incorporation of compatibilizer (PCL-co-pyromellitic anhydride) in composites of PCL/starch improved the performances in mechanical properties without changing its biodegradability. Rosa et al. (2005) studied the effect of addition of different proportions of azodicarbonamide(ADC) as an expander to the blends of PCL with corn starch. A blend of PCL with cornstarch has reduced the mechanical properties of the composite. However, addition of ADC to the blends increased the mechanical properties of the composite, such as tensile strength and elongation at break. PCL/corn starch composite with 50% w/w starch content in the blends showed higher biodegradability compared to PCL itself. Addition of ADC to

the blends does not show any significant changes to the biodegradability.

Park et al. (2005) have prepared a polycaprolactone grafted to poly(ethylene-co-vinyl alcohol) (EVOH) through ring opening polymerization of ϵ -caprolactone (CL) with EVOH as a macroinitiator. The elongation at break of the LDPE/PCL blend remained almost invariable even after the soil burial test because the tensile properties depended mostly on the LDPE phase on account of the poor interaction between the continuous LDPE matrix and the dispersed PCL phase. For EVOH-g-PCL, the elongation at break decreased drastically as a result of the soil burial test, and the reduction of the elongation at break was more pronounced for EVOH-g-PCL with a higher PCL content.

2.8 Degradation

All natural phenomenon can cause materials degradation. Heat, light, short-wavelength electromagnetic radiation, radioactive emissions, chemicals and interaction with bacteria, fungi can damage materials. Degradation is defined as a process that results in change in the properties of materials, which reduces the ability of the material to perform its intended function (Charlesby, 1987). Degradation processes are categorized into several groups, such as, chemical, mechanical/physical and biological. Figure 2.6 summarizes the various modes of environmental polymer degradation (Matsumura, 2005). Materials degradation such as thermal damage or chemical reactions, which are either entirely physical or chemical in nature coexist with combined forms of materials degradation such as corrosive wear. Environmental conditions also exert a strong effect on materials degradation and there are three basic degradation mechanisms that can be identified which are scission of intermonomer linkages in the backbone, scission of side chain linkages in the backbones, and ionically catalysed attack on side chains (Battacharya et al, 2005).

The degradation of polymers may proceed by one or more mechanisms, including biodegradation, photo degradation or thermal degradation, depending on the polymer environment and desired application. Table 2.5 shows the possible degradation process or agent for polymers and elastomers. The combination of different factor from the environment such as sunlight, heat and humidity also has synergistic effects on the degradation (Shah, et al., 1995).

Photodegradation of polymers is a natural phenomenon, involving mainly sunlight and oxygen, which cause deterioration of physical properties and appearance of the material. Some of the atoms within the polymer chain will absorb the energy of the photons from the sunlight and become excited, thus cause chain scission in polymer chain. Thermal effects are a major cause of deterioration of physical properties of polymers. Relatively high temperatures are often encountered in polymer processing may result in breaking chemical bonds. Polymers are sensitive to high temperature and will progressively decompose.

Table 2.5 Degradation process for polymers and elastomers (Bever, 1986)

Chemical	Mechanical	Physical	Biological
<ul style="list-style-type: none"> • Oxidative degradation • Reaction with air pollutants • Reaction of olefinic double bonds • Ozonization and ozone cracking • Ionic degradation 	<ul style="list-style-type: none"> • Fracture • Fatigue • Wear abrasion • Erosion 	<ul style="list-style-type: none"> • Photo oxidation by uv • Thermal degradation • Ultrasonic degradation • Radiation damage • Radiolysis 	<ul style="list-style-type: none"> • Enzymatic attack by microorganism • Attack by mammals and insects

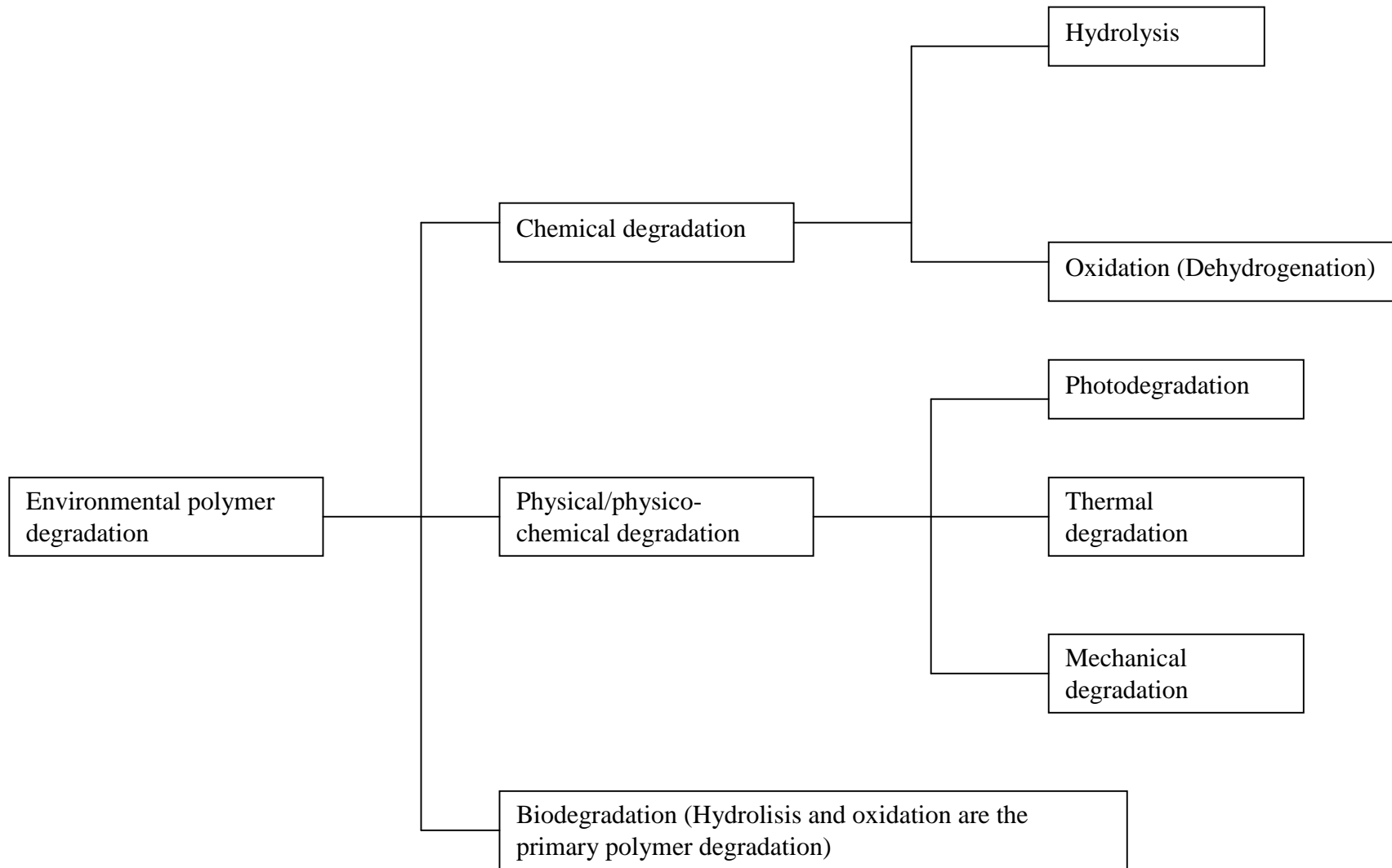


Figure 2.6 Environmental polymer degradation

2.9 Biodegradation

Biodegradation is one of the several ways of polymer may degrade in the environment. This process are also interpreted by the general public as the same sa other proprocesses of polymer degradation such, as photodegrdation, oxidation and hydriilisis, thoug they lead to very different end products. It is often conceived that the breakdown of a plastic into small, invisible fragments is biodegradation, when in reality these fragments may remain in the environment over a significant period.

Biodegradable polymers when placed in bioactive environments, such as compost, will break down to carbon dioxide and water under the action of bacteria and fungi. There are two major steps in the biodegradation process. The first one involves the depolymerization or chain cleavage of the polymer to oligomers, and the second step is the resulting mineralization of these oligomers (Bhattacharya et al., 2005). The depolymerization step normally occurs outside the microorganism and involves both endo and exo-enzymes. Endo-enzymes cause random scission on the main chain, while exo-enzymes causes sequential cleavage of the terminal monomer in the polymer main chain. Once depolymerized, sufficiently small-sized oligomeric fragments are formed. These fragments are transported into the cell where they are mineralized (Bhattacharya et al., 2005). Mineralization is defined as the conversion of the polymers into biomass, minerals, water, CO_2 , CH_4 and N^2 .

There are several standard test methods available to evaluate the biodegradability of plastics as listed in Table 2.6. Most of these test methods measure the percent conversion of the carbon from the designed biodegradable plastics to CO_2 and CH_4 (plus some CO_2) in aerobic and anaerobic environments, respectively. The absence of polymer and residue in the environment indicates complete biodegradation process, whereas incomplete biodegradation may leave polymer and/or residue as a result of polymer fragmentation or metabolism in the biodegradation process (Bhattacharya et al., 2005).

Table 2.6 Standard methods for estimating biodegradation of plastic materials (Bhattacharya et al., 2005).

Test	Environment	Property Measured
ASTM D 5209-92	Aerobic sewage sludge	CO ₂
ASTM D 5210-92	Anaerobic sewage sludge	CO ₂ /CH ₄
ASTM D 5247-92	Aerobic specific microorganism	Molecular weight
ASTM D 5271-93	Activated sewage sludge	O ₂ /CO ₂
ASTM D 5338-92	Controlled composting	CO ₂
ASTM D 5509-94	Simulated compost	Physical properties
ASTM D 5511-94	High solids anaerobic digestion	CO ₂ /CH ₄
ASTM D 5512-94	Simulated compost using external heated reactor	Physical properties
ASTM D 5525-94	Simulated landfill	Physical properties
ASTM D 5526-94	Accelerated landfill	CO ₂ /CH ₄
MITI Test	Mixed microbial	O ₂

2.10 Factors Affecting Biodegradation

Polymeric materials were subjected to degradation by biological, chemical and/or physical actions in the environment. Generally, biodegradation involves successive chemical reactions, such as hydrolysis, oxidation with/without the aid of enzymes in living organisms. The rate of biodegradation was found to be affected by several factors. Polymer's environment, organisms utilized and the nature of the polymeric materials are three main factors affecting biodegradation.

All microorganisms have an optimum temperature, at which maximum growth rate occurs and thus highest enzyme kinetics exist. Gilmore et al. (1993)

discovered that an increase in the temperature of sewage in a waste water treatment plant, correlated with the increase in the rate of biodegradation of poly(hydroxylalkanoates) being tested. However, if the temperature in the environment becomes higher than the optimum temperature of a microorganism, then the denaturing of enzymes and other proteins in the microorganism takes place. In this case, the rate of biodegradation is reduced (Moore and Saunders, 1997). An optimum pH value also will affect the rate of biodegradation. A microorganism also needs a certain amount of nutrients from its environment to allow it to grow. Therefore, the concentration of nutrients is essential to the rate of biodegradation. Oxygen and moisture concentration also have considerable effect on rates of biodegradation in terrestrial environments (Moore and Saunders, 1997). One of the main problems in landfill sites is that there is lack of oxygen and moisture in the environment. If there is not enough moisture and oxygen in the environment, the microorganisms cannot growth.

Nature of polymer substrate also affects the rate of biodegradation. Increased branching in polymeric materials will reduce the rate of degradation. Maximizing the linearity of the molecule reduces steric hindrance facilitates the maximum susceptibility of the molecule to enzymatic attack and promotes microorganism assimilation. Low molecular plastics are susceptible to degradation, due to the ability to transport into a microbial cell (Chandra and Rutsgi, 1998). List of factors that affecting the rate of biodegradation are shown in Figure 2.7.

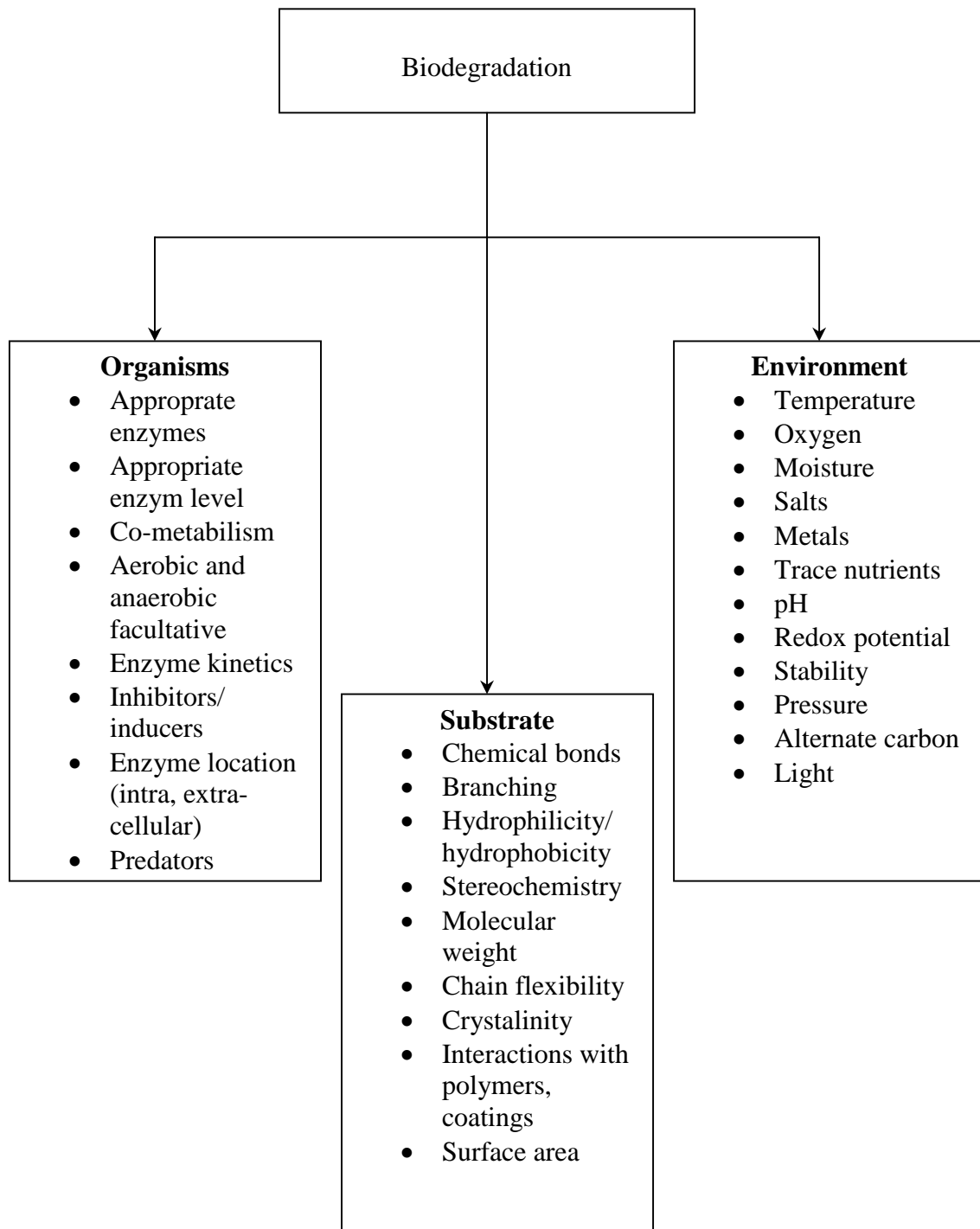


Figure 2.7 List of factors that affecting the rate of biodegradation

2.11 Mechanism of Biodegradation

The production of biodegradable polymers is now rapidly increasing, and new biodegradable polymeric materials have been developed based on various factors, such as polymer structure, chemical/enzymatic modification, blending and mechanical treatments. Polymeric materials were subjected to degradation by biological, chemical and/or physical (mechanical) actions in the environment. Polymeric materials generally undergo these factors concurrently in the environment.

Typical examples related to biodegradation are biological hydrolysis by hydrolase enzymes and oxidation by oxidoreductase enzymes. The hydrolase enzyme is responsible for the hydrolysis of ester, carbonate, amide and glycosidic linkages of the hydrolysable polymers producing the corresponding low molecular weight oligomers. The oxidoreductase enzyme is responsible for the oxidation and reduction of ethylenic, carbonate, amide, urethane, etc (Matsumura, 2005). Hydrocarbons such as polyethylene, natural and polyisoprene rubbers, lignin and coal are first subjected to biological oxidation by oxidoreductase, such as oxygenases, hydroxylases, monooxygenases, peroxydases and oxidases in the biodegradation process (Matsumura, 2005). However, the degradation process proceeds both by abiotic and biotic actions in the environment. Structure of the main chain polymer and the specific example of the related enzyme are shown in Table 2.7.

Biodegradable polymers are generally degraded through two steps of primary degradation and ultimate biodegradation as shown in Figure 2.8. Primary degradation is the main chain cleavage forming low molecular weight fragments (oligomers) that can be assimilated by the microbes. Molecular weight reduction is mainly caused by hydrolysis or oxidative chain scission. Hydrolysis occurs using environmental water with the aid of an enzyme or under non-enzymatic conditions (abiotics). Oxidative scission occurs mainly by oxygen, a catalytic metal, UV light or an enzyme (Matsumura, 2005).

Table 2.7 Structure of the main chain polymer and the specific example of the related enzyme (Matsumura, 2005).

Main chain structure		Polymer	Corresponding enzyme responsible to the primary degradation
-C-C- -C=C-	C-C linkage	polyethylene natural rubber polyisoprene lignin	<u>Oxidoreductase</u> peroxidase oxidase lignin peroxidase dehydrogenase
-C-C-C- OH OH	β -Hydroxy group	poly(vinyl alcohol)	dehydrogenase oxidase peroxidase
-C-O-C-	Ether linkage	polyethylene glycol polypropylene glycol	
-C-O- O	Ester linkage	Polyesters PHA, PCL, PLLA	<u>Hydrolase</u> PHA depolymerase Lipase, esterase protease
-O-C-O- O	Carbonate linkage	polycarbonate	Lipase esterase
-C-N- H O	Amide linkage	Protein Polylysine Polyglutamic acid Polyaspartic acid	protease
-N-C-O H O	Urethane linkage	polyurethane	

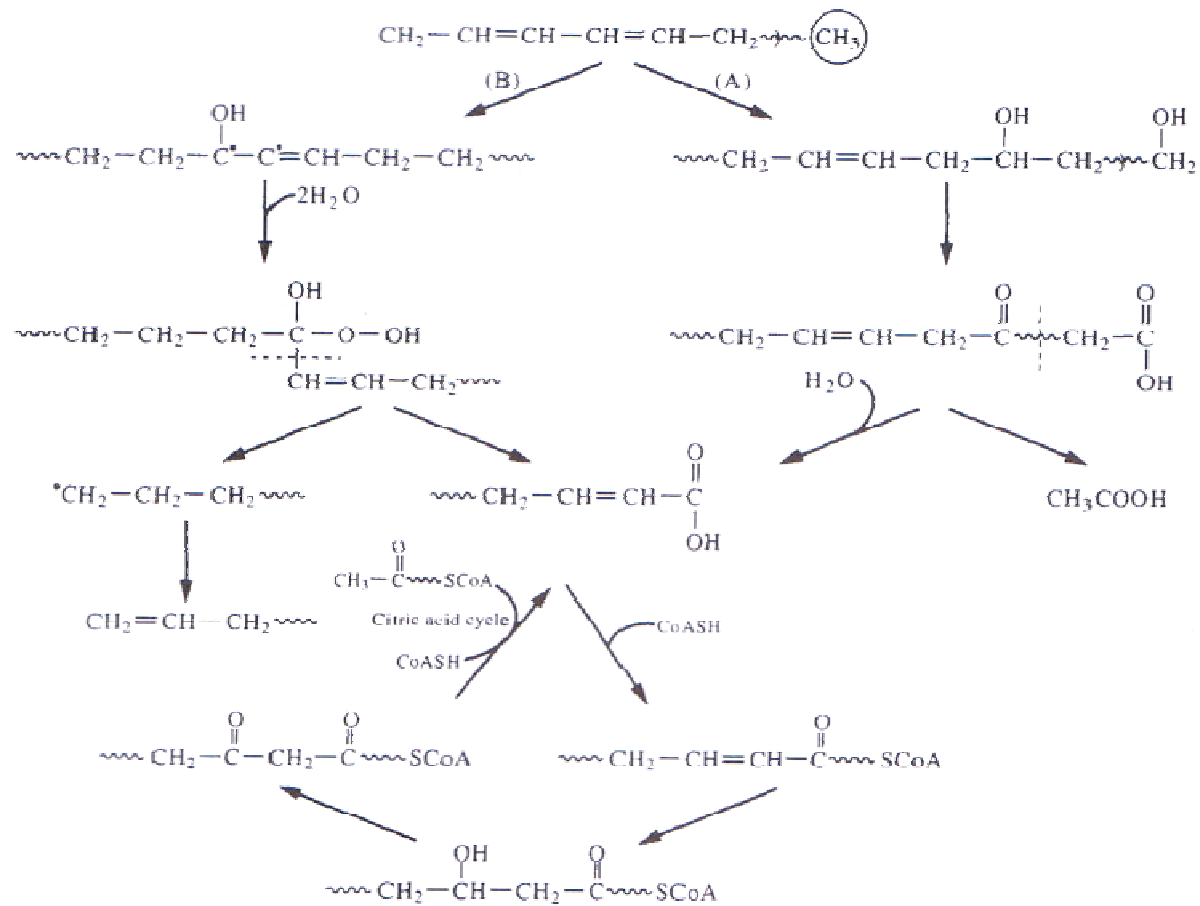


Figure 2.8 Biodegradation processes of biodegradable polymers.

Polymer chain can also be cleaved by mechanical strain such as bending, pressing or elongation. The low molecular weight fragments produced were incorporated into microbial cells for further assimilation to produce carbon dioxide and microbial cells, metabolic products under aerobic conditions. Under anaerobic conditions, methane is mainly produced in place of carbon dioxide and water (Matsumura, 2005).

Polymer chain scission is one of the degradation phenomena in biodegradable. This process occurs in two ways, depolymerization (exogeneous) scission and random (endogeneous) scission. In the former the polymer chain is cleaved from the terminal of the chain. A water soluble oligomer is generally liberated into the reaction media and the rate of the molecular weight reduction of the residual polymer is small. In the latter way the polymer chain is randomly cleaved. In this case, the molecular weight of the remaining polymer quickly decreased. At the same time, the mechanical properties of the remaining polymer are also quickly decreased. The addition of these two types of polymer chain scission causes degradation at the weak link. The polymer chain is cleaved at the relatively weak bond by the various physico-chemical actions.

Polyesters, polyanhydrides, polycarbonates and polyamides are mainly degraded by hydrolysis into low molecular weight oligomers at the primary degradation with subsequent microbial assimilation in the biodegradation process. Some other degradation mechanisms include oxidative cleavage by a radical mechanism. Oxidative degradation is the main mechanism for non-hydrolyzable polymers, such as polyolefins, natural rubber, lignins and polyurethanes. For many polymers, hydrolysis and oxidation occur simultaneously in the environment. Surface degradation and bulk degradation are examples of polymer degradation mechanisms depending on the main degradation site.

The C-C polyvinyl type polymer containing side groups, such as short alkyl Groups and phenolic groups are generally resistant to biodegradation. PVA is readily biodegradable by environmentally occurring microbes. Polyethylene (PE) with a low molecular weight of less than 1,000 is biodegradable (Albertsson and Banhidi, 1980; Cornell et al., 1984). Biodegradation of the low molecular weight PE involves oxygenase elimination (ω -oxidation) by the action of oxidoreductases, such as oxygenase, dehydrogenase and oxydase, forming a fatty acid with subsequent β -oxidation.

The mechanism shows similarities with the typical β -oxidation of fatty acids and n-alkanes. For PE degradation, an initial abiotic oxidation of the polymer chain is also a necessary step. Once hydroperoxides have been introduced, a gradual increase in the ketone groups of the polymers is followed by a decrease in the ketone groups when short chain carboxylic acids are release as degradation products. The combined effect of an abiotic oxidative step with consequent biotic action will be a slow but definite and progressive mineralization (Albertsson et al., 1897; Albertsson and Karlsson, 1990). Figure 2.9 shows the proposed biodegradation mechanism of polyethylene and n-alkane.

2.12 Sago Starch

Sago starch, unlike the other starches, is derived from the pith of numerous kinds of palm trees, namely *Metroxylon sago*. The sago palm is 6-14 m tall and hapaxantic- that is; it flowers once and dies shortly thereafter. Just before flowering, the plant converts its stored nutrients into starch, which fills the trunk. Desiccated products made from sago starch can be stored for exceptionally long periods (Abd-Aziz, 2002). Before the emergence of rice, sago (*Metroxylon sago Rottboll*) was the main source of sustenance for the inhabitants of the Malay Archipelago. The dried provision enable earl inhabitants of the Malay Archipelago to travel far and wide, and made the colonization of the many island possible (Abd-Aziz, 2002).

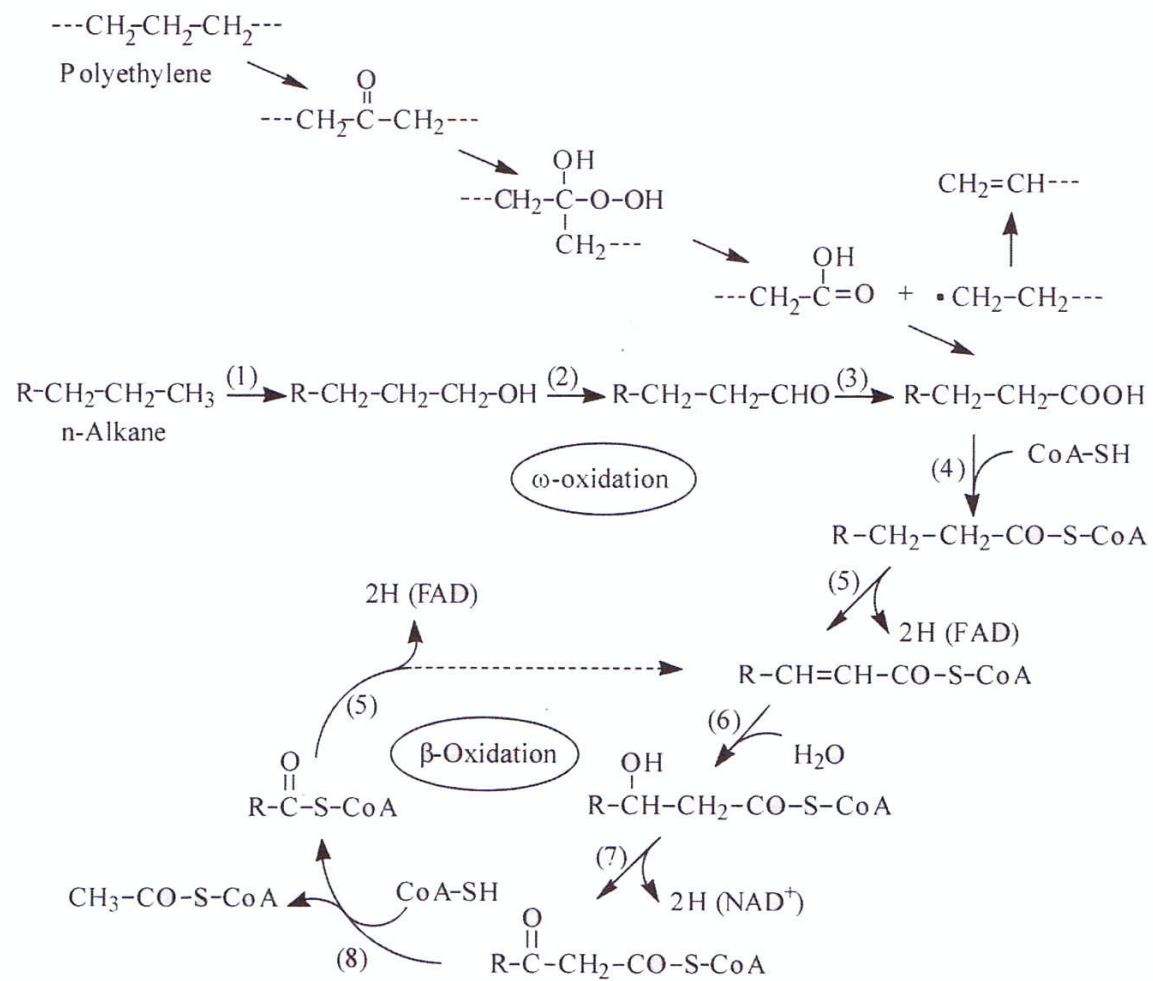


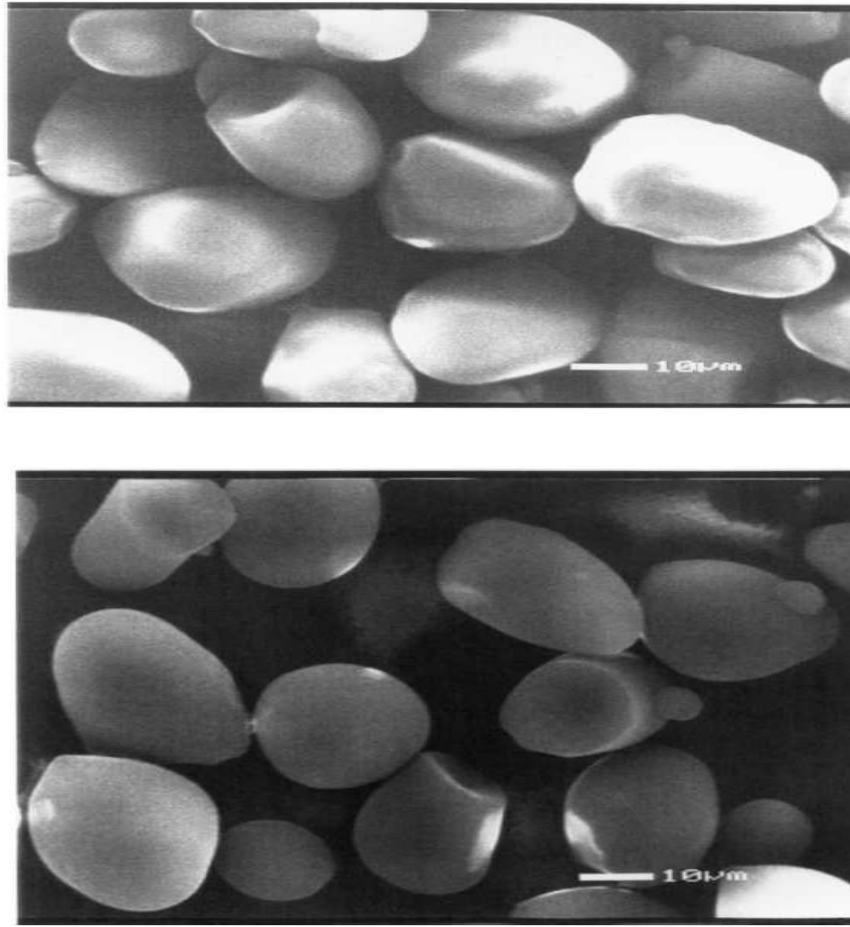
Figure 2.9 Proposed biodegradation mechanism of polyethylene and n-alkane (Matsumura, 2005).

The major area of cultivation of sago starch in Malaysia is Sarawak, where up to 25 tonnes of the starch can be produced per hectare. Sago starch is mainly used as a food and in food formulations. In the food industry, it is used in the production of monosodium glutamate, glucose, custard powder, sauce mixes, etc., while in the pharmaceutical and petroleum industries it is used as digest able filler for drugs and medications and as additives to coolants and lubricants used in oil drilling operations, respectively. The use of starch as a filler opens up another avenue for the large-scale utilization of sago starch (Danjaji *et al.*, 2002). Besides its use as a foodstuff, sago starch can also be utilized to produce adhesives for paper, textiles, and plywood. New uses for sago starch include in biodegradable plastics, fuel alcohol, and ethanol. Table 2.5 summarized the utilization of sago starch and its residues.

Table 2.8: Utilization of sago starch (Abd-Aziz, 2002)

Sago palm part	Usage/Utilization
Refined sago starch	An ingredient of noodles, vermicelli (beehoon), Kuah-Tiau, biscuits, and many other foods Used industrially in products such as monosodium glutamate, glucose, caramel (color milk), fructose, syrups, etc
Sago fiber	Provides bulk for rumen fermentation.
Sago pitch	Used as an animal feedstuff and in the live-stock industry
Sago fronds	Used in the pulp and paper industries

Compared to the cassava starch, sago starch has higher ash content and the contents of fat, protein, and fiber are similar. Arbakariya (1990) also reported the chemical composition of commercial sago starch originated from Malaysia, and compared it with commercial corn starch, the sago starch has a higher content of ash and moisture, but similar contents of fiber, fat and protein. The size of sago starch granules varies between 15-65 micron but mostly ranges between 20-60 micron. The shape of the granule is oval and some truncated (Swinkels, 1985; Akaranta *et al.*, 1999).



**Figure 2.10: SEM for sago starches (top picture sago 6, bottom picture sago 3)
(Fasihuddin *et al.*, 1999)**

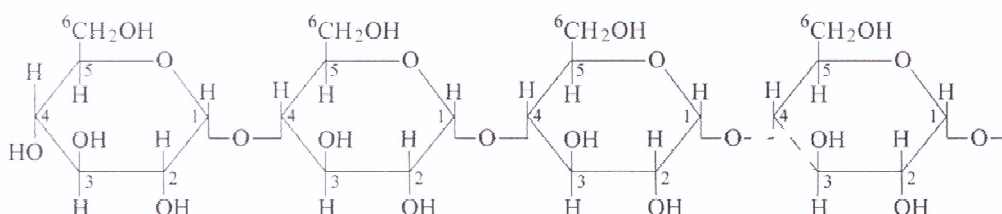
2.4.1.1 Sago waste

Sago waste or sago ‘hampas’ is the fibrous residue left behind after most of the starch has been washed out of the rasped pith of the sago palm. Microscopic examination reveals that a large number of starch granules are trapped within the lignocellulosic matrix. Dried ‘hampas’ contains about 60-70 % starch on a dry weight basis. Studies by Vicky and Shim (1996) showed the approximate residues of sago ‘hampas’ obtained from nine major factories in Sibul, Sarawak as shown in Table 2.6 (Abd-Aziz, 2002).

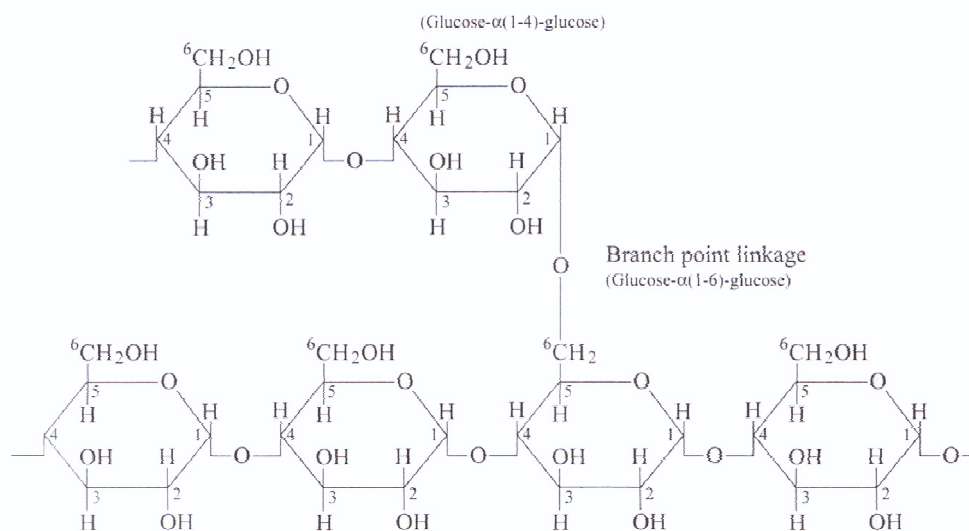
Table 2.9: Component analysis of sago ‘hampas’ (Abd-Aziz, 2002).

Component	Percentage
Apparent starch	65.7
Crude fiber	14.8
Crude protein	1.0
Fat	n.d.
Ash	4.1
Moisture	59.1

n.d., Not detectable



(a)



(b)

Figure 2.11 Major macromolecular components of starch; (a) amylose and (b) amylopectin (Halley, 2005)

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Matrix

Low-density polyethylene (LDPE) resin grade (TITANLENE® LOW-DENSITY POLYETHYLENE, 71009A, LDF 260GG) supplied by Titan Polyethylene (M) Sdn. Bhd. was used in this research. The density of the polymer was 0.922 g/cm^3 according to ASTM D1505. It had a melt flow of 5 g/10 min according to ASTM D 1238 and a melting temperature (T_m) of 110°C . Representative properties of LDPE are shown in Table 3.1.

3.1.2 Filler

Sago starch, food grade was used as filler in this research. The particle size of those starches ranged from $9.73 \text{ }\mu\text{m}$ to $83 \text{ }\mu\text{m}$ with an average particle size of $32.97 \text{ }\mu\text{m}$. The moisture content of starch is average of 11.5%.

Table 3.1 Representative Properties of LDPE

Properties	Range
Density, g/cc	0.91-0.925
Melting point, °C	110
Tensile strength, kg/cm ²	80-240
Elongation at break, %	200-800
Elmendorf tear strength, g/mil	100-400
Bursting strength, kg/cm ²	0.70
Haze, %	4-10
Light transmission, %	65
Glass transition temperature, °C	60-70

3.1.3 Processing Aids

Glycerol (glycerin, C₃H₈O₃) from Fisher Chemicals (Molecular weight = 92g mol⁻¹ and palm oil based glycerin were used as a processing aids to this blends. Varying the amount of this processing aids to the blending will be done to get the optimum composition.

3.1.4 Compatibilizer

Maleic anhydride –grafted– polyethylene from DuPont was used as a compatibilizer of LDPE/starch blends.

3.2 Sample Preparation

3.2.1 Pre-mixing

Low-density polyethylene (LDPE) will be mixed with starch (Bikiaris et al., 1997) and its compatibilizer using high-speed mixer (Chyau Long, model: CL-FC-10), made in Taiwan, before undergo compounding process. The mixing process will took 12 minutes of mixing time with a speed of 30 rpm at room temperature.

3.2.2 Compounding

Low-density polyethylene and starch will be dried in an oven for 24 hours at 80°C before pre-mixing and compounding to dry the moisture especially for starch. The compounding of LDPE/starch will be done using twin screw Brabender Plasticoder. The compounding process will be carried out at a speed of 80 rpm and the temperature will be set at 150°C/150°C/140°C/140°C (Shah et al., 1995). The extrudates will be palletized using a pelletizer machine for each formulation.

Extrusion is a continuous process, as opposed to all other plastic production processes, which start over at the beginning of the process after each new part is removed from the mold. In the extrusion process, plastic pellets are first heated in a long barrel. A rotating screw then forces the heated plastics through a die opening of the desired shape. As the continuous plastic form emerges from die opening, it is cooled and solidified, and the continuous plastic form is then cut to the desired length. Technical specifications of twin screw extruder are listed in Table 3.2.

Table 3.2 Technical specifications of twin screw extruder

Screw diameter	25 mm
Core diameter	17 mm
Center distance	21.5 mm
Screw Shaft	Square polygon 14/11 mm
Dynamic load	14 400 N
Nominal voltage	32 A, 50/60 Hz
Barrel temperature	400 °C max
Melt pressure	300 bar max
Nominal torque	360 Nm
Driving speed	275 min ⁻¹ max
Weights	Approx 400 kg
Dimension	W: approx. 780 mm H: approx. 1200 mm L: approx. 1300 mm

3.2.3 Blown Film

The compounded samples will be blown using blow film machine (Tai King, model: TK/HD-40M, Tai King Machinery Factory Co. Ltd., Taiwan) to produce LDPE/starch plastic bags. This process will be carried out at temperature of 165°C/160°C/150°C/140°C/130°C/120°C with drawer and screw speed of 50 rpm and 600 rpm respectively.

Blow film extrusion is the process used to make plastic continuous sheets. This process works by extruding a hollow, sealed-end thermoplastic tube through a die opening. As flattened plastic tube emerges from die opening, air is blown inside the hollow tube to stretch and thin the tube to the desired size and wall thickness. The plastic is then air-cooled and pulled away on take up rollers.

3.2.4 Compound Formulation

Table 3.3 Samples formulation for effect of glycerol as processing aid

Samples	LDPE (w/w %)	Starch (w/w %)	Glycerol (w/w %)
LDPE/TS:90/10-1	90	10	1
LDPE/TS:80/20-1	80	20	1
LDPE/TS:90/10-3	90	10	3
LDPE/TS:80/20-3	80	20	3
LDPE/TS:90/10-5	90	10	5
LDPE/TS:80/20-5	80	20	5

However, the entire sample cannot be process using blow film machine. The amount of glycerol in the blends has to be increase.

Table 3.4 Samples formulation

Samples	LDPE (wt %)	Tapioca starch (TS)(wt%)
LDPE	100	0
LDPE/TS:90/10	90	10
LDPE/TS:80/20	80	20
LDPE/TS:70/30	70	30
LDPE/TS:60/40	60	40
LDPE/TS:50/50	40	50

The compounding of LDPE/starch with various blends ratio were done using twin screw extruder with the addition of palm cooking oil (PCO) (5 wt%) as processing aids and PE-g-MA (5, 10, 15 and 20 wt%) as compatibilizer.

3.3 Melt Flow Index Determination

Melt flow index will be determined using Melt flow Indexer (S. A Associates) according to ASTM D1238. The temperature of 190°C and load of 2.16

kg will be used. The time taken for the interval is one minute. The weight of extrudates will be measured and the melt flow of the samples will be calculated. The MFI corresponds to the mass of polymers that passes through a standard capillary, in an interval of 10 min, at a given applied pressure (load).

3.4 Film Characterization

3.4.1 Fourier-transform Infrared Spectroscopy

Fourier-transform spectroscopy (FTIR) (Perkin Elmer System 2000) will be used to obtain some qualitative information about the functional groups and chemical characteristics of the LDPE/starch blends after the addition of processing aid, prooxidant and comatibilizer. About 5 mg of samples as mix with about 95 mg potassium bromide (KBr) prior to compacting into thin pellets using a hydraulic press for about 3 minutes. The pellets will be scanned and interpreted by OMNIC software.

3.4.2 Morphological studies

3.4.2.1 Optical Microscopy

Electron microscope (Leica equipment) will be used to show the interface LDPE/tapioca starch before and after biodegradation studies. The specimens will be cut using a microtome to approximately 10 μm thickness at room temperature. The specimens will be then mounted and viewed under the bright field mode with the light microscopy fitted with surface imaging analysis system.

3.4.3 Thermal Analysis

3.4.3.1 Thermogravimetry Analysis

Thermogravimetry analysis (TGA) will be used to determine the degradation temperature of the samples. The LDPE/starch blends will be scanned at a heating

rate of 20°C/min from 30°C to 700°C and the analysis will be carried out in the presence of nitrogen flowing of a rate of 200 ml/min.

3.5 Mechanical Testing

3.5.1 Tensile Test

Tensile test will be carried out using an Instron machine Lloyd. The test will be done according to ASTM D 638. Gauge length will be set at 50 mm and the crosshead speed of testing will be fixed at 5 mm/min. Samples for tensile measurements will be conditioned at 30±2% relative humidity for 24 hours before testing and ten samples will be tested for each formulation. The conditioning of tensile specimens will be followed accordingly as stated by the standard. Tensile modulus, tensile strength and elongation at break will be evaluated from stress-strain data.

3.5.2 Water Absorption test

This test is carried out to study the water resistance of LDPE/tapioca starch films. Samples will be dried at 80°C in a vacuum oven until a constant weight will be attained prior to immersion in water in a thermostated stainless steel water bath at 30°C. Weight gain of the samples will be recorded by periodic removal of the specimens from the water bath and weighing on a balance with a precision of 1 mg. The percentage of weight gain at any time, t , M_t , as a result of moisture absorption will be determined by equation 3.1;

$$M_t(\%) = \frac{(W_w - W_d)}{W_d} \times 100 \quad [3.1]$$

where W_d and W_w are weight of dry material (the initial weight samples prior to exposure to the water absorption) and weight of samples after exposure to water

absorption respectively. The percentage equilibrium or maximum moisture absorption M_m will be calculated as an average value of several consecutive measurements that show no appreciable additional absorption. The weight gain resulting from moisture absorption can be expressed in terms of two parameters, the diffusion coefficient or diffusivity, D , and the maximum moisture content, M_m , as given by equation 3.2 (Mohd Ishak and Berry, 1994);

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right] \quad [3.2]$$

where h is the thickness of the sample and D can be calculated from the initial linear portion of the absorption curve (slope M_t versus $t^{1/2}$).

3.6 Biodegradability Studies

3.6.1 Natural Weathering Test

The weathering test will be conducted according to ASTM D1435. Specimens will be attached to a rack complete with a specimen holder. The rack will be adjusted to face the equator at an angle of 45° and the rack is situated at an open area whereby it is free from being overshadowed by other objects. The specimens will be exposed to all environmental effects such as rain, sunlight and wind. Samples will be collected every two weeks for a total of two months to determine the degree of degradation. Moisture at the surface of the samples will be removed with a clean towel and the samples will be left in air for 24 hours at room temperature before mechanical test will be conducted.

3.6.2 Exposure to Fungi Environment

Degradation of the blend will be determined according to ASTM G21-70, which is method to evaluate the resistance of polymeric materials to fungi. Samples

will be placed in sterile Petri dishes containing solidified nutrient salt agar. A fungi spore solution, *Aspergillus Niger* will be prepared. The surfaces including the surface of the test specimens will be inoculated with the fungi spore suspension by spraying the suspension from a sterilized atomizer with 110 kPa of the air pressure so that the entire surface will be moistened with the spore suspension. Covered Petri dishes will incubated at 28-30°C and 85-90% relative humidity for a minimum of 28 days. Petri dish covers will be sealed by wax to a void any kind of contamination. The only carbon source for the growth of the fungi will be from the samples. The fungi growth will be followed by visual observation. The specimens after 28 days will be washed free of growth, immersed in an aqueous solution of mercuric chloride for 5 min, rinse in tap water and air-dried overnight at room temperature.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Melt Flow Index (MFI) Measurement

Table 4.1 shows the melt flow index (MFI) values of LDPE/S composites decreased as the content of starch increased. Reduction in MFI values indicate the viscosity of composite increased. This finding is similar to most filled thermoplastic and agrees that reported by Thakore *et al.* (1999) and Rosa *et al.* (2004) whereby the MFI of starch composite decreased as the filler loading increased

Results show the MFI value of LDPE is 2.664 and increased to 3.1576 when glycerol is added. But, the value of the MFI become lower reaching 1.9236 when starch at 10% loading is added, compared to neat LDPE. The combination of LDPE, glycerol and starch at 10% loading, gives MFI value of 2.5787. This shows that both glycerol and starch influenced the MFI values. Glycerol as plasticizer decreased the intermolecular forces between polymer coils and increased the molecular spaces (Audic *et al.*, 2005; Mali^b *et al.*, 2005) and mobility of polymers.

Table 4.1: MFI value of materials

Materials	Weight percent (wt%)	MFI value (g/10min)	
		Sago starch	Sago waste
LDPE	100	2.664	-
LDPE/S*10	90/10	2.5787	2.0688
LDPE/S*20	80/20	1.8029	1.3571
LDPE/S*30	70/30	1.5937	0.5465
LDPE/S*40	60/40	1.1816	-
LDPE/S*50	50/50	0.9197	-

*S = Starch loading in formulation that refer to sago starch and sago waste

Rosa *et al.* (2004) reported the MFI value of polymer-filled starch is lower than MFI value of neat polymer. This is similar to the obtained results shown in Table 4.1. The reduction may probably due to the starch granules can still retained their shape and functioned as rigid particulate fillers when processed. The flows of matrix LDPE were restricted by the starch particles and thus, increased the viscosity of composite. In addition, decreasing of MFI also due to the fact the starch particles are more viscous than LDPE (Nawang *et al.*, 2001). This can be observed from the data illustrating MFI of neat LDPE is higher than LDPE/SS10. Starch granules are partially crystalline and have higher molecular weight than LDPE.

As the content of starch is increased, the interaction among the granules was increased and contributes to the higher viscosity. For higher loading of starch, the spaces between particle-particle were small. If the particle-particle interactions are stronger than particle-matrix interaction, agglomeration of particles may occur and result in the immobilization of more matrix molecules. The matrix molecules become trapped in filler particles as the size of agglomerates rise and flows have been confined. The same trend also can be observed for the LDPE filled with sago waste as shown in Table 4.1.

At 10% loading of starch, sago waste shows the lower MFI (i.e. 2.0688) compared to sago starch at the same level (i.e. 2.5787). The possible reason for this phenomenon may be due to the starch content in the sago waste (i.e. 60-70%) is

lower than sago starch that has low content of crude fiber (Abd-Aziz, 2002). The fibers present in the sago waste act as rigid particulate that inhibit flow, thus increases the viscosity. Nevertheless, MFI values i.e. 1.3571 and 0.5465 for composite contains 20% and 30% are lower than sago starch at the same level i.e. 1.8029 and 1.5937. The possibility is because of the content of starch and crude fiber increased. The fillers particles crowded the composite and restricted the flow of matrix.

4.2 Fourier Transformed Infrared Analysis

Figure 1 shows representative FTIR spectra for LDPE, tapioca starch and LDPE/tapioca starch (90/10) films. The existence of peaks at 2650 cm^{-1} , 2018 cm^{-1} , 1902 cm^{-1} and $1265 - 1400\text{ cm}^{-1}$ show the characteristics bands of LDPE. LDPE/tapioca starch films showed a broad O-H stretching absorbance in the $3600 - 3000\text{ cm}^{-1}$ region and strong set of C-O stretching in the $1190 - 960\text{ cm}^{-1}$ region indicated the characteristic bands of starch (Chandra and Rutsgi, 1998). The result indicated that the starch is distributed uniformly in LDPE matrix. There is no shift in starch peaks in LDPE/tapioca starch blends, inferring that the LDPE/tapioca starch systems were immiscible blends.

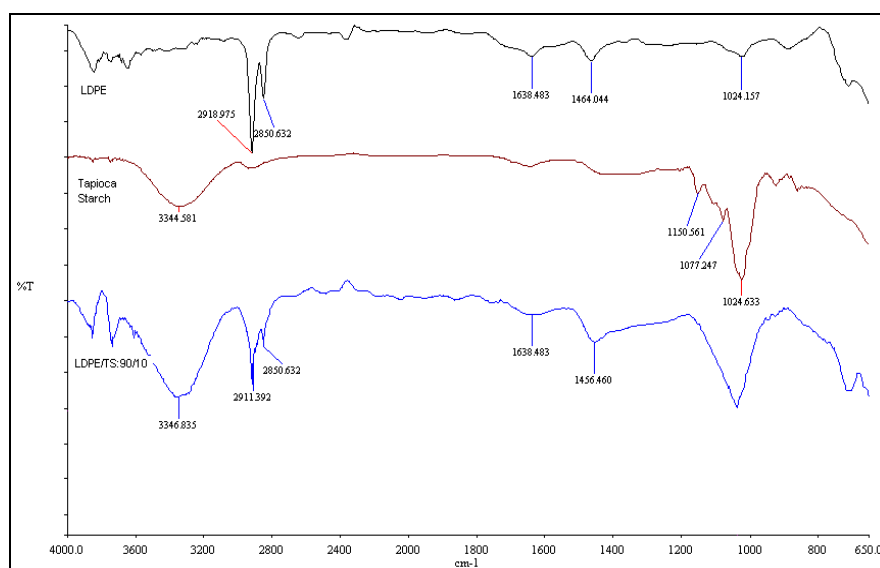


Figure 4.1: FTIR spectra for LDPE, tapioca starch and LDPE/tapioca starch (90/10) films

4.3 Gloss test

Table 4.2 shows the glossiness level for each formulation in LDPE/S blends in this study. The control of surfaces gloss is very important in order to achieve the desired visual effect. The gloss level is determined by the degree of specular reflection. In this study, all of the formulations were in range of 20-44 percent gloss unit i.e. leveled as semi gloss and egg shell with reference to Table 4.3. Although LDPE film was semi gloss, but with incorporation of glycerol increased slightly the reading. Incorporation of starch into films attributed the decreased of glossiness. Glossiness reading for LDPE/SS10 was lower than LDPE, indicated that the starch granules influenced the glossiness effect. As the starch content increased, the glossiness reduced, whereas at 50% of starch loading, the samples categorizes as egg shell. As more starch is added the more ordered will be the packing in the blend thus reduced the amount of the reflected light; glossiness reduced.

Table 4.2: Measurement level of glossiness

Materials	Angle, 60°	Gloss level
LDPE	41.1 ± 2.92	Semi gloss
LDPE /SS10	32.6 ± 5.02	Semi gloss
LDPE/ SS10	31.8 ± 7.59	Semi gloss
LDPE/ SS20	30.1 ± 3.65	Semi gloss
LDPE/ SS30	28.8 ± 2.19	Semi gloss
LDPE/ SS40	27.0 ± 2.77	Semi gloss
LDPE/ SS50	22.8 ± 1.06	Egg shell
LDPE/ SW10	41.5 ± 2.82	Semi gloss
LDPE/ SW20	42.1 ± 1.74	Semi gloss
LDPE/ SW30	32.5 ± 2.33	Semi gloss

However, the glossiness readings for LDPE blends containing sago waste were higher than LDPE/sago starch blends wherein at 10% of sago waste contents, glossiness readings was same as LDPE glossiness. The reading increased slightly at 20% starch contents and reduced a lot at 30% loading. Probably, the higher glossiness readings of films containing sago waste were due to less of apparent starch

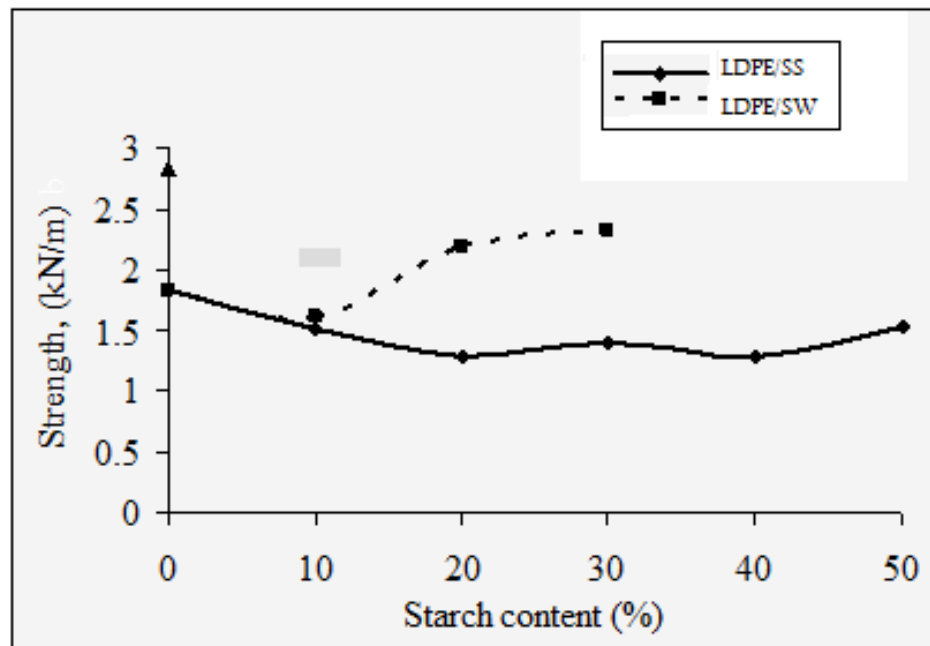
in sago waste. The higher amount of particulate fibers disturb the packing in the blend system making it more disordered and rough or uneven with higher free volume, thus more light can diffuse back or reflected. LDPE with sago starch is less glossy due to its better packing as a result of smaller starch particles size compared to sago waste with uneven and bigger particles size allowing more light being reflected.

Table 4.3: Reference of gloss level measurement by Saias (1986)

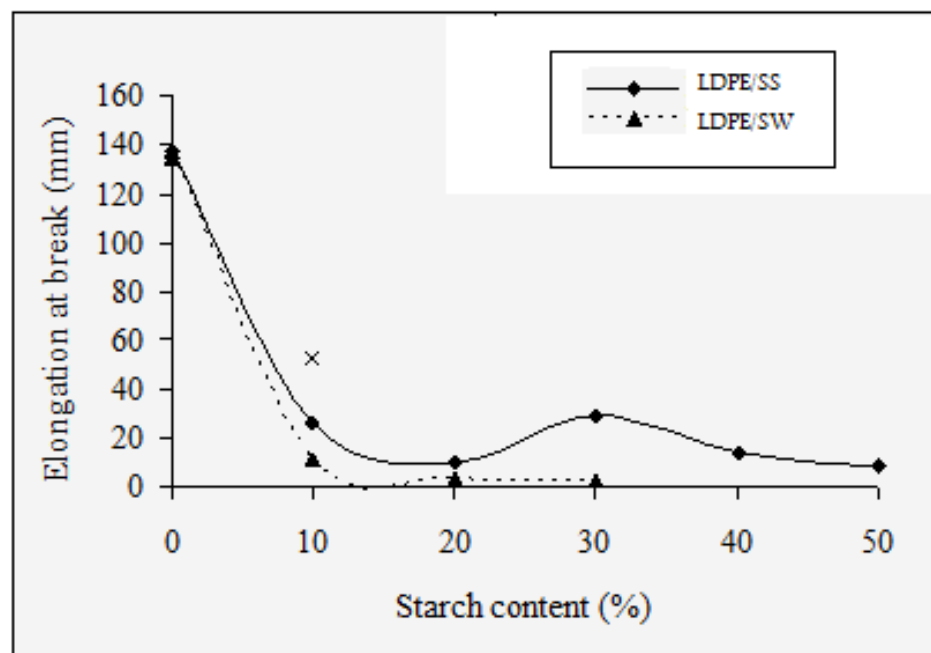
Gloss level	60° Gloss (percent)
High gloss	70-95
Semi gloss	30-70
Egg shell	10-25
Matte	2-10

4.4 Mechanical Test

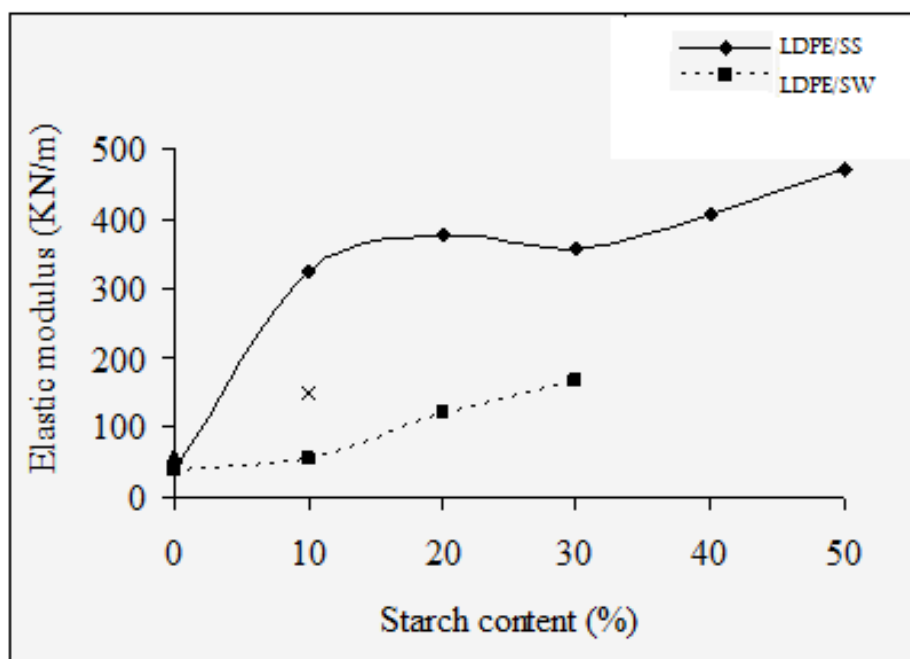
Variations of tensile strength, elastic modulus and elongation at break of LDPE/starch composite films had been observed and reported in the Figure 4.2(a), 4.2(b) and 4.2(c). As expected, tensile strength and elongation at break of LDPE/SS blends decreased as the starch content increased. While the elastic modulus of the composites increased as the starch content rose. Similarity trend was also observed in composite films loaded with sago waste except for the tensile strength, that showed an increased as the filler content increased. This was expected due to sago waste behaves as reinforcing fillers through the existence of crude fiber. Reduction of tensile strength and elongation at break was probably caused by less effective cross sectional area of LDPE matrix (i.e. continuous phase) toward spherical particulates starch granules as the starch contents rose. Subsequently resulting in reduce of tensile strength.



(a)



(b)



(c)

Figure 4.2: Variations of mechanical properties for LDPE/starch blends: (a) tensile strength, (b) elongation at break (c) elastic modulus.

Low tensile strength of LDPE/S composite also occurred because of the weakness of interfacial adhesion in which probably attributed to hydrophilic nature of starch, which was not compatible with hydrophobic polymers. This is in agreement with the results presented by Thakore *et al.* (1999) and Ahamed *et al.* (1996). According to Thakore *et al.* (1999), the decreasing of tensile strength occurred due to weakness of interfacial adhesion between starch-polymer. Besides, it was observed the presence of bubbles in the samples. It showed the possibility of reduction of tensile strength was also due to the presence of moisture at the LDPE-starch interface. Danjaji *et al.* (2002) reported that tensile strength and elongation at break decreased with time of immersion and starch content. This was due to the presence of moisture at the LDPE-starch interface, which weakens the already weak interfacial adhesion. The decreasing of tensile strength also indicated that sago starch granules behaved as non-reinforcing filler. At higher starch loading, filler-filler interaction becomes more pronounced than filler-matrix interaction.

Similar to tensile strength, decreasing of elongation at break occurred because of the weakness of interfacial adhesion between starch-LDPE. In synthetic polymer blends, the addition of the immiscible component to a ductile matrix generally decreased the elongation properties at break. The elongation will therefore depend on the state of the interface (Rosa *et al.*, 2004; Thakore *et al.*, 1999). In cases such as when 20% of the dispersed minor phase has been added, highly deformable matrix materials are transformed into fragile materials (Rosa *et al.*, 2004). In this study, the optimum was at 10% loading.

During processing, the starch granules did not melt and retained their shape as rigid filler. As the starch contents increased, particles were crowded among them, resulted in increasing the particles-particles interaction. The films became more rigid and reduced the elongation at break. Rosa *et al.*, (2004) reported that the addition of dry granules to PCL follows the general trend for filler effects on polymer properties; i.e., the modulus increases through stiffening of the granules and elongation decreases as the starch content increased. In recent study by Raymond and Charles (1981), they concluded that the fillers accumulate in adjacent polymeric chains, thus reducing the mobility of the chains. Subsequently, the fillers increase adhesion to one another through Van der Waals forces and hydrogen bonds. These researchers further suggested that if perfect adhesion between the filler and polymer matrix is assumed, the polymer matrix confined between two particles would undergo a larger strain than macroscopic strain. This would be due to the fact that rigid filler particles do not elongate. Thus, this material will give a higher macroscopic strain than the polymer with no fillers (Herald *et al.*, 2002)

In contrast, elastic moduli increases as the starch loading is increased. Starch incorporated into LDPE still retained their granular shape after processing. These granules are stiff and act as rigid fillers. This is in harmony with the resulted presented by Nawang *et al.*, (2001). These researchers reported that the incorporation of sago starch into LLDPE has led to an increase in the modulus of the composites because of the starch granules are stiffer than the LLDPE matrix in which they are dispersed. In general, modulus is closely related to the hard domain of the material. As the starch content increases, the hard domain content increases, as does the tensile

modulus of the blend. As starch is partially crystalline, there was possibility of increasing modulus attributed to crystalline. Crystallinity brings about an increase in modulus. Incorporation of crystalline starch into binary PE-starch blend shows an increasing in modulus with increasing starch contents (Thakore *et al.*, 1999).

Apart of influences by the incorporation of starch, addition of glycerol enhances the mechanical properties where the films become more flexible. At this state, although the tensile strength was lower than the pure LDPE films, but elongation at break and elastic modulus were not affected. This results might be because of low concentration of glycerol was added. Hence, starch granules solely induced the results of elongation and modulus.

In order to enhance the compatibility between two immiscible polymers, an increased interest has appeared in the use of polymers containing reactive groups, such as, maleic anhydride as compatibilizer. Addition of PE-g-MA to this blends, showed a significant changes in tensile strength of LDPE/tapioca starch blends (Figure 4.3). Tensile strength of LDPE/Starch:70/30 (30 wt% of tapioca starch content in the blends) film increased as the compatibilizer contents rose. It was discovered that anhydride groups could react with hydroxyl groups in starch to produce chemical bonding, thus improving the dispersion of starch, the interfacial adhesion, and subsequently the mechanical properties of the blends (Liu *et al.*, 2003).

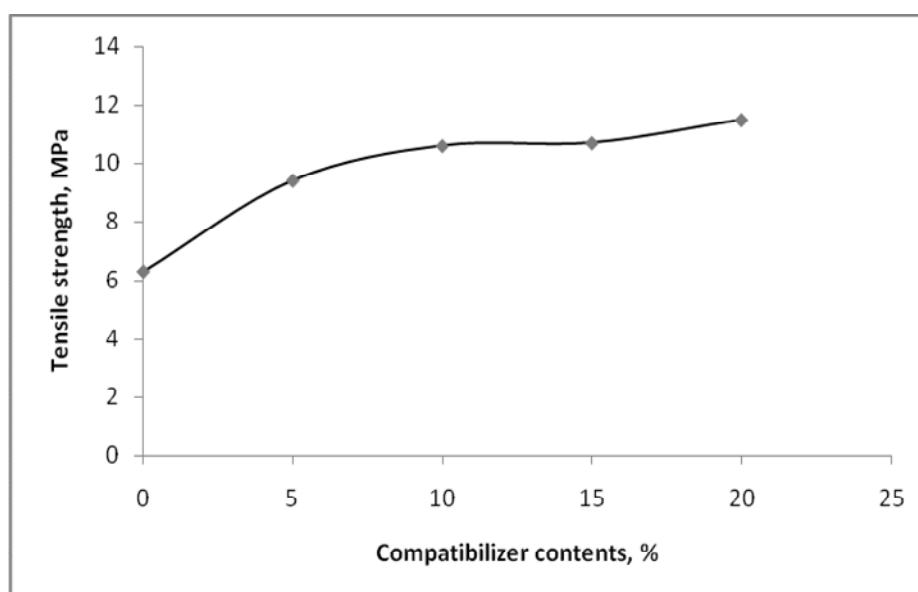
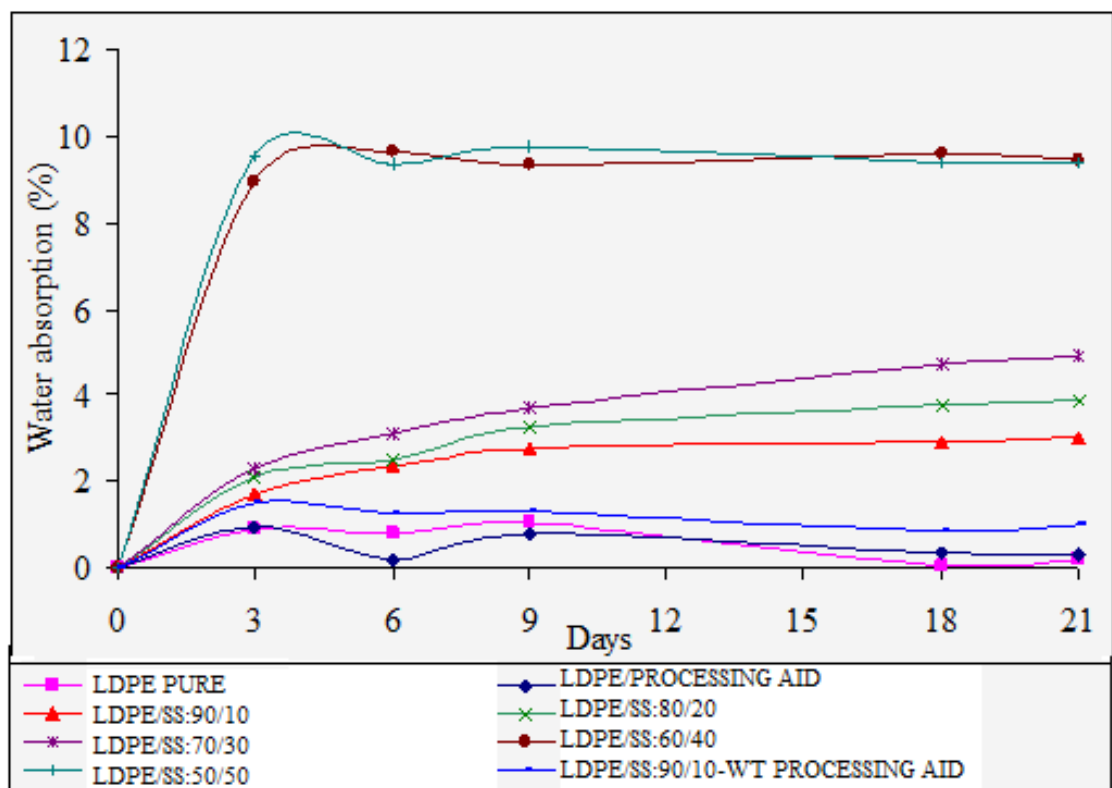


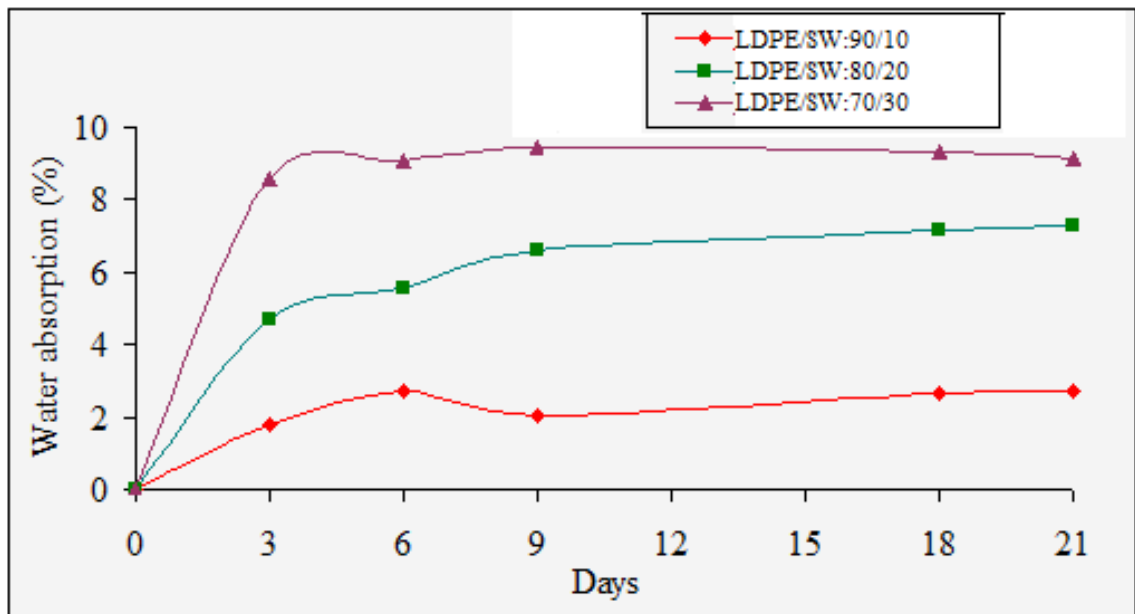
Figure 4.3: Tensile strength of LDPE/tapioca starch based films with various compatibilizer contents

4.5 Water Absorption Test

Starch content influences the water absorption of LDPE/S composites films. This phenomenon can be observed through Figure 4.4(a) and 4.4(b) that shows the moisture uptakes of composites increased with starch contents and immersion times. Thus, in agreement with that reported by Danjaji *et al.* (2002), Mani *et al.* (1998) and Mali^b *et al.* (2005) that moisture uptake increased with immersion time and increasing filler concentrations.



(a) LDPE/Sago starch blends



(b) LDPE/Sago waste blends

Figure 4.4: Percentages of water absorption for LDPE/Starch composites with time of immersion.

For neat LDPE films, a little water uptake can be observed similar to LDPE containing glycerol. The fact that three-hydroxyl group in molecules, glycerol is hydrophilic in nature. However, since there is low concentration of glycerol in composite films, the water uptakes was not significantly different from neat LDPE. The water diffusion was strongly affected by starch content as showed by higher percentage water absorption of LDPE/SS10.

Starch based synthetic materials tend to absorb water because the hydroxyl group in starch can form a hydrogen bond with water (Mani *et al.*, 1998). Since the starch is hydrophilic, it has a highly tendency to attract water molecules. Therefore, as starch content increased, the tendency increases. There are also high amylopectin in sago starch (73%) that influenced the water absorption. Mani *et al.* (1998) reported that the starch blends containing high amylopectin content absorbed more water compared to other starch blends possessing low amylopectin due to the gelatinization and degradation of starch blends.

Danjaji *et al.* (2002) also reported that a rapid moisture uptake was observed within the first few days of immersion, but this decreased slowly with time. The similarity can be figured over first 3 days in which the percentage of water absorption increased progressively and consecutively slowed. The decreased in the rate of moisture uptake with time of immersion could be due to a concentration gradient across the two materials. Initial water molecules added to starch particles have been found to be strongly bonded as in a hydrate (Danjaji *et al.*, 2002). The absorption of water is related to its rate of diffusion into the composites. Willet reported that the starch content exerted a strong influence on the diffusion coefficient and the differences in diffusion coefficient between starch blends decreased as the starch content increased (Mani *et al.*, 1998). Probably, water penetrated into the films and bonded to the hydroxyl group of starch caused the starch granules swelled and reduced the gap between their molecules and space to the matrix molecules. As the starch content rose, the particles crowded and gap became smaller and narrowed. Thus, water difficult to diffuse and rate of water uptake reduced.

Composite films contain 40% and 50% of starch show high water uptake. Meanwhile, composite films containing 10%, 20% and 30% of starch content differ slightly from each other. This was expected due to the low concentration of starch particles near to the composite surfaces while the rest were positioned inter the matrix. The interior starch particles were not available to form hydrogen bonding with water molecules as they are trapped in LDPE matrix. For higher loading of starch, starch particles filled and crowded the composites and resulted in higher concentration of starch near the composite surface. Moisture uptakes in starch-LLDPE composites is mainly due to the starch particles, exposed starch granules or those at or near the surface absorb moisture faster than those interior. Starch-PE composites take months to equilibrate even completely immersed in water (Danjaji *et al.*, 2002). In contrast, some formulation of composite films in this study showed equilibrium achievable over 21 days.

Based on Figure 4.4(b) similar water resistance properties were observed for LDPE/starch composite film filled with sago waste. These films also exhibited the same behaviors of water absorption as sago starch filled composite films. The water

absorption increased as the sago waste content increased. Sago waste contains an abundance of hydroxyl group that are available to interact with the water molecules. Abd-Aziz, (2002) reported that, sago waste contains around 65.7% of apparent starch and moisture content about 59.1%. Hence, this suggested the high water uptake of sago waste composite films compared to sago starch composites films at same level content.

Figure 4.4(a) and 4.4(b) also shows some reduction in water absorption of composite films over period of immersion. It was expected that some starch particles were leached away form the samples. According to Mani *et al.* (1998), a possible drawback in the starch blend is the possibility of material leaching into the liquid. It was suggested that upon water uptake, resulted in the starch granules swelled up, increased in size and being forced out. LDPE does not swell proportionately with starch, because it is a poor moisture absorber.

4.6 Biodegradability

4.6.1 Exposure to Fungi Environment

Starch is a biopolymer that is degradable when exposed to the environment. Table 4.4 shows the rating of visual assessment of *Aspergillus Niger* growth after 21 days. Based on table above, there was no evidence of fungi growth on the surface of LDPE and LDPE/GLY specimens (Figure 4.6(a) and 4.6(b)). This was due to microbial resistance behavior belongs to LDPE. LDPE is formed by carbon-carbon (C-C) linkages in which these linkages are not susceptible to microbial attack. In additional, there was no nitrogen source support the fungal growth in the LDPE.

Table 4.4: Visual assessment of fungi growth for each formulations of LDPE/starch blends

Materials	Rating* of fungal growth
LDPE	0
LDPE/SS10	1
LDPE/SS20	1
LDPE/SS30	2
LDPE/SS40	3
LDPE/SS50	3
LDPE/SW10	1
LDPE/SW20	2
LDPE/SW30	2

*Rating (see Appendix II):

0- no growth apparent,

1-growth clearly visible under microscope,

2-growth covering less than 25% of specimen surface,

3-growth covering more than 25% of the specimen surface

In contrast, *Aspergillus Niger* grew on the LDPE containing starch. After 21 days, the fungi growth was clearly visible under microscope as shown in Figure 4.6 (c), Figure 4.7 and Figure 4.8. Furthermore, the growth were visible to the naked eye at the sago starch loading 30% and 40% with growth covering less than 25% (Figure 4.7(c) and 4.7(d)). At 50% sago starch contents (Figure 4.7(e)), almost whole of the specimen surface was covered by fungi growth. This indicated that the growth of *Aspergillus Niger* colony increased as the starch content increased. This evident is consistent with the results presented by Akaranta & Oku, (1999). They reported that the growth of colony increased with the increase in the filler content of the films. Pure polyethylene films showed no evidence of biodegradation. Same with LDPE/SS blends, composites films containing sago waste also susceptible to the fungi attack and the growth increased as the starch loaded increased that shown in Figure 4.8.

Aspergillus Niger assimilated the starch and caused the specimen loss of weight. Figure 4.7 shows the weight loss of specimen over 21 days of inoculation. There was a slight weight drop for 10% and 20% of starch content, but decreased progressively at starch loading of 30% and more. The same trend was observed with films containing sago waste, but weight loss rate was more linear and higher than LDPE/sago starch. Therefore, LDPE/ sago waste undergoes biodegradation at a faster rate compared to LDPE/sago starch, that is probably due to the higher fiber content in the LDPE/sago waste. Thus fiber seems to initiate and promote biodegradation or easily attack by Aspergillus Niger. The degree of microbial growth increased with the increasing degradation of polyethylene. Some weight loss occurred within the first 7 weeks of the 1-year incubation and this was due to the removal of additives (Aminabhavi *et al.*, 1990).

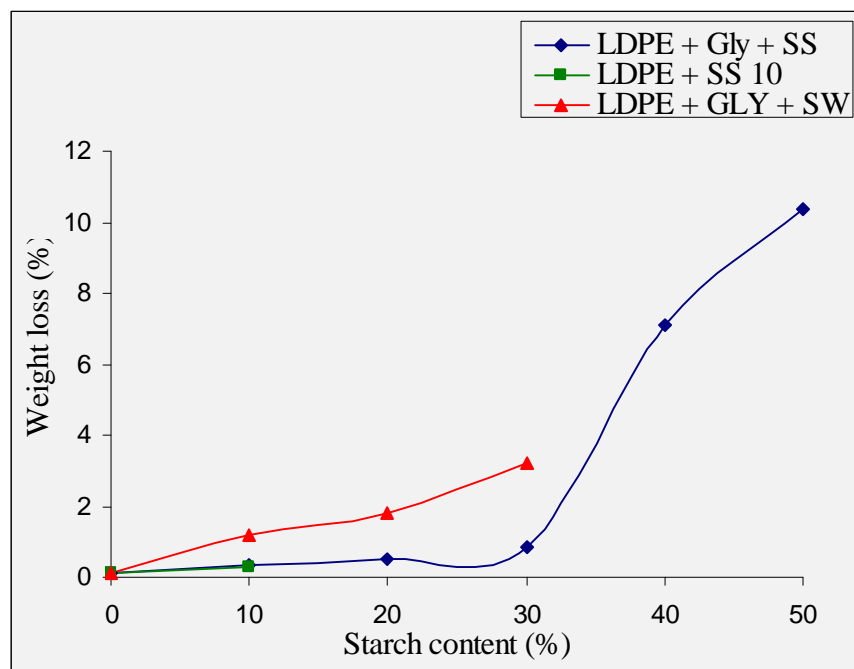
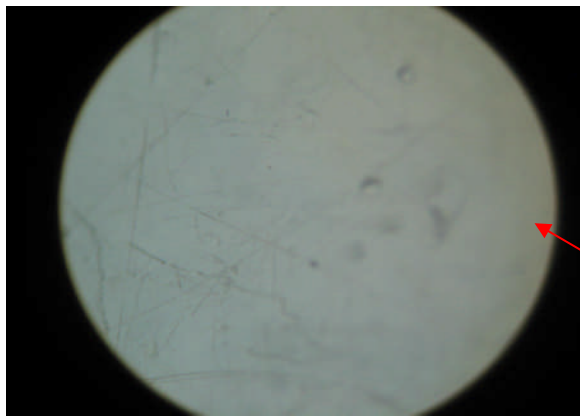
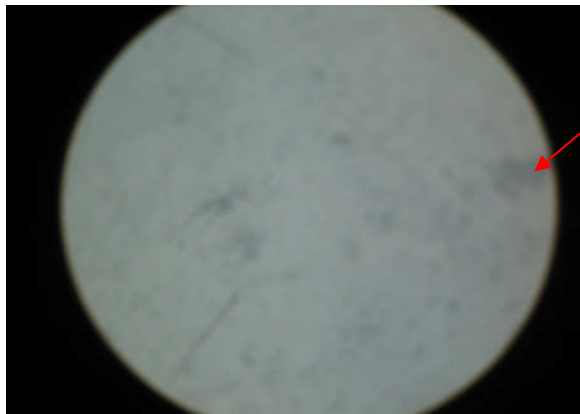


Figure 4.5: Percentage of weight loss over 21 days of inoculated with Aspergillus Niger



(a) Pure LDPE



(b) LDPE/Processing aid

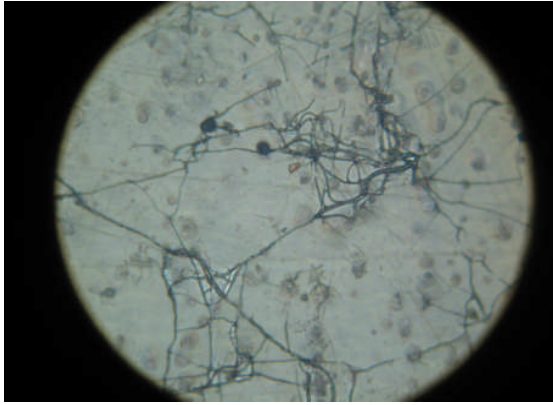


(c) LDPE/SS10

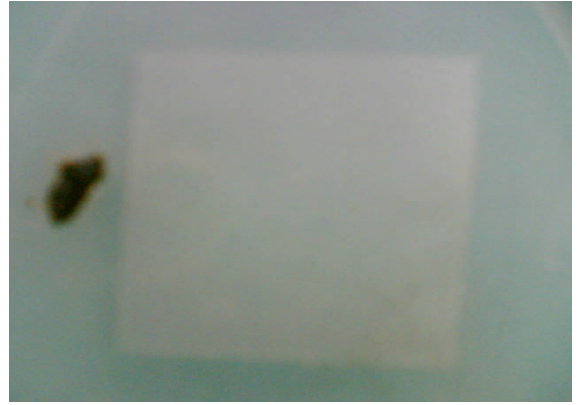
No evidence of
fungi growth

Fungi growth
(Aspergillus Niger)

Figure 4.6: Evidence of fungi growth (Aspergillus Niger) on surface of LDPE films with and without starch under microscope magnification 200X

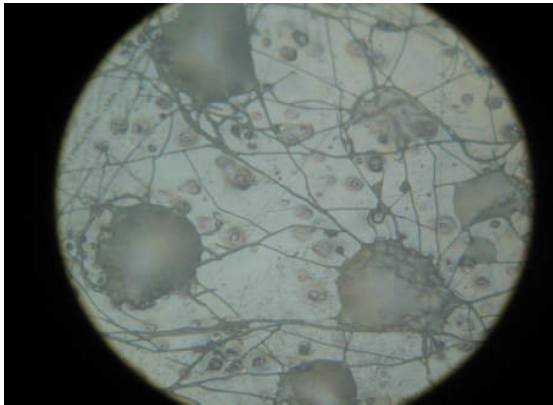


Magnification 200X

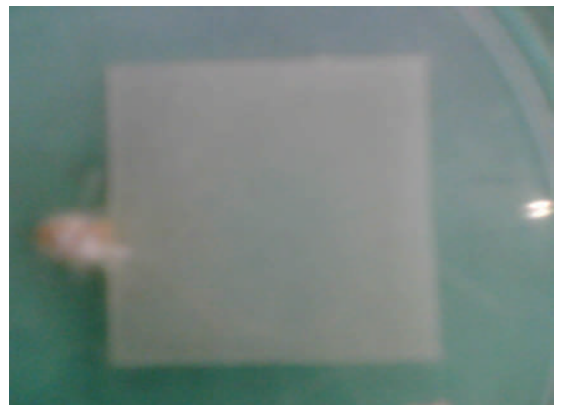


No magnification

(a) LDPE/SS10

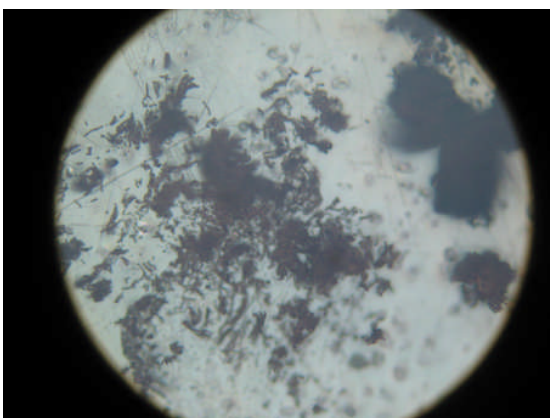


Magnification 200X



No magnification

(b) LDPE/SS20

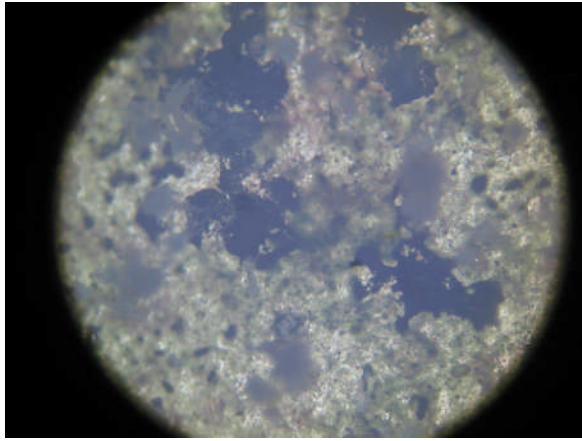


Magnification 200X

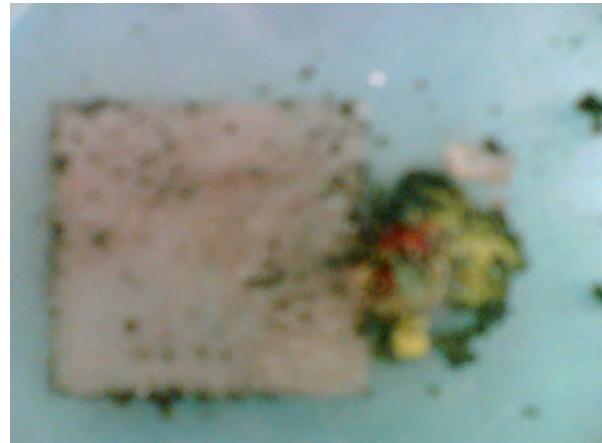


No magnification

(c) LDPE/SS30

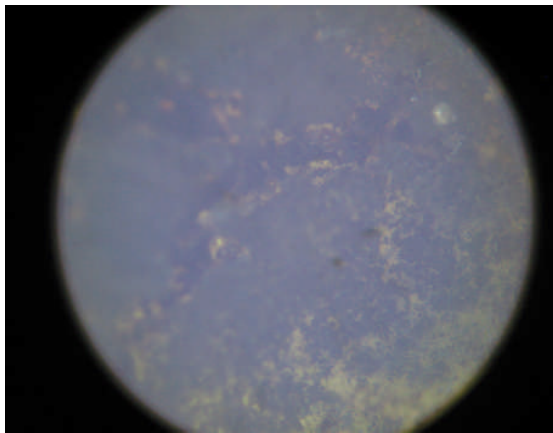


Magnification 100X



No magnification

(d) LDPE/SS40



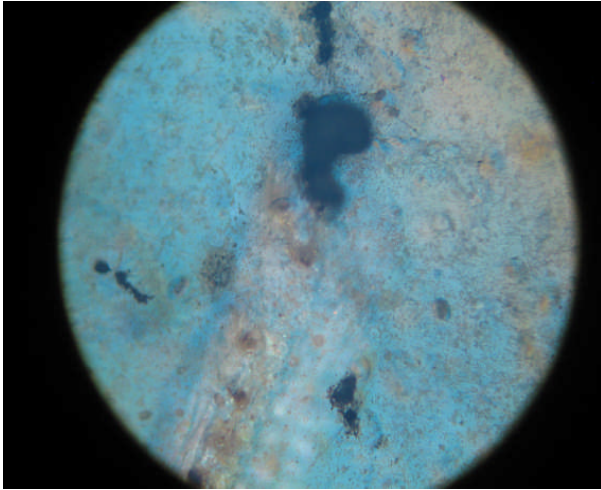
Magnification 50X



No magnification

(e) LDPE/SS50

Figure 4.7: Visual of fungi growth covering surface of LDPE/Gly/SS composite films as the increasing of starch content.

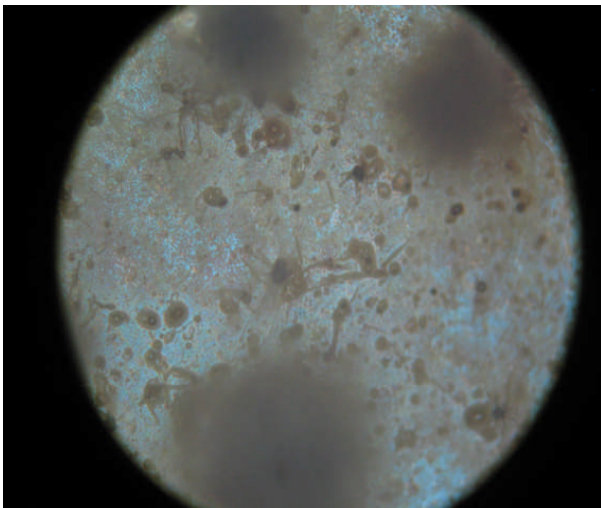


Magnification 200X



No magnification

(c) LDPE/SW10

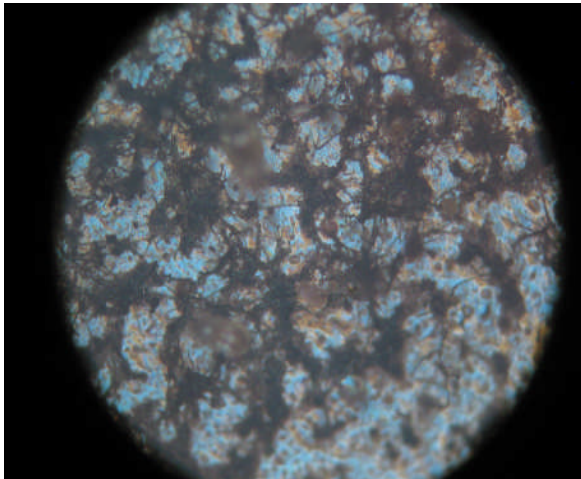


Magnification 100X



No magnification

(d) LDPE/SW20



Magnification 100X



No magnification

(e) LDPE/SW30

Figure 4.8: Visual of fungi growth covering surface of LDPE/SW composite films as the increasing of starch content.

4.6.2 Soil Burial Analysis

All LDPE/starch specimens were exposed to moist compost for a period of 6 months and weight loss was recorded after 6 months. The samples were not discolored indicating that samples were not chemically interacted, but reduction in weight was observed. This is due to bleaching, dissolving or degradation of starch microorganism attack. The rate of biodegradation of LDPE/starch blends are graphically shown in Figure 4.9. From the figure, it was noticed that the rate of biodegradation increases with increase in starch content in LDPE matrix. The percent weight loss increased with increase in starch content in LDPE system. There was about 17% weight loss in 40% starch content LDPE film. The degradation behavior of LDPE/starch follows the second order polynomial equation ($R^2 = 0.9764$), and it can be concluded that the rate of biodegradation depends upon the starch content.

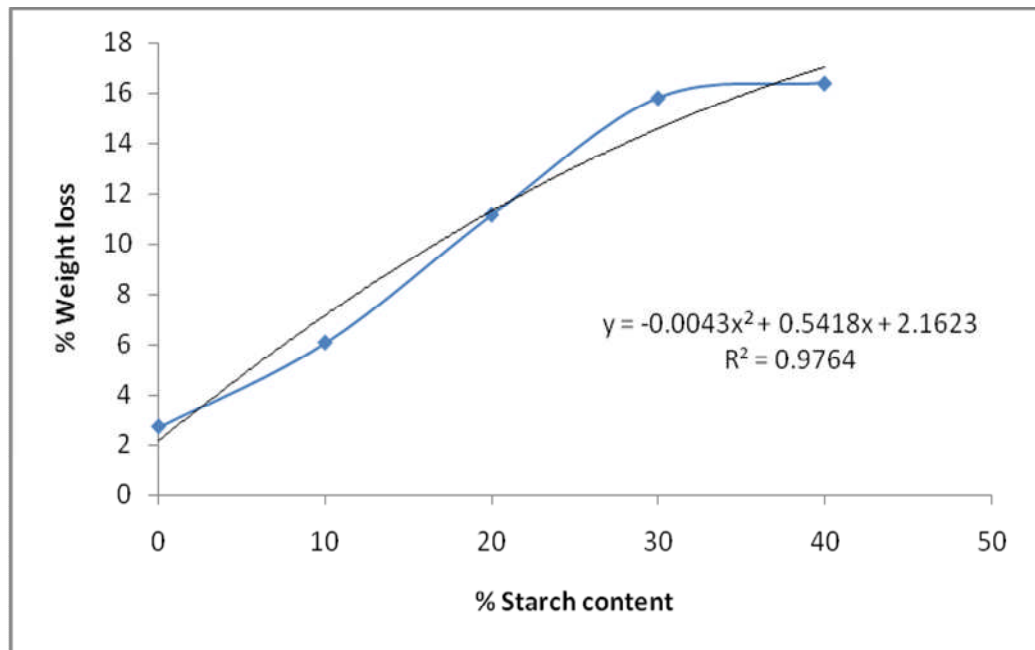


Figure 4.9: Percentage of weight change in LDPE/starch films after decompose in soil for 6 months.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

Based on this study, there is an effective conclusion that starch are strongly affected the physical, chemical, and mechanical properties of LDPE/starch blends. Addition of starch, either sago starch or sago waste has increased the biodegradability characteristics of LDPE wherein microbes assimilate the starch particles and leave the LDPE matrix alone with the weaken bonding of polymer chains. Then extent to break the LDPE chains down into small particles with a large surface area. Thus, high molar mass of LDPE becomes lower and subsequently available to degrade consecutively.

However, the starch content is not effective on the mechanical properties. Starch imparts an adverse effect upon the mechanical properties wherein decreased the tensile strength and elongation at break, while modulus increased. This less effectiveness is due to the hydrophilic nature of starch that is not compatible to hydrophobic nature of synthetic polymers, that result in weakness of interfacial adhesion. In contrast, incorporation of sago waste has increased the tensile strength. This interesting characteristic is because sago waste contains crude fiber and act as reinforcing fillers.

Starch granules retain their spherical shape through processing and act as rigid filler. As starch loading is increased, their cohesive strength becomes stronger than particle-matrix interaction causing of high modulus and lowering of tensile

strength and elongation at break. Apart of mechanical properties, this condition also contributes to reduction of melt flow index (MFI), in such way that rigid particles restrict the flow of matrix.

Starch has aggressive behavior of water absorption due to the existence of hydroxyl group (OH) that is very attractive to form hydrogen bonding with water molecules. In aspect of optical properties, LDPE is semi gloss. Additional of starch in LDPE, retains the semi gloss properties. Nevertheless, with the higher loading of starch, the visual glossiness effect reduces.

Addition of palm based glycerin imparts the plasticizing effect, making the film more elastic and reduces the viscosity there is increased the MFI.

REFERENCES

Abd el- Rahim, H. A., El-Sayid, A. H., Ali, A. M. and Rabie, A. M. 2004. "Synergistic Effect of Combining UV-sunlight-soil Burial Treatment on the Biodegradation Rate of LDPE/starch Blends." *Journal of Photochemistry and Photobiology A: Chemistry*. 163. 547-556.

Akaranta, O. and Oku, G. E. 1999. "Erratum to; Some Properties of Cassava Mesocarp Carbohydrates-Low Density Polyethylene Blends." *Carbohydrate Polymers*. 34. 403-405.

Albertsson, A. C. and Bahidi, Z. G. 1980. "Microbial and Oxidative Effects in Degradation of Polyethylene." *Journal of Applied Polymer Science*. 25. 1655-1671.

Albertsson, A. C and Karlsson, S. (1990). "The Influence of Biotic and Abiotic Environments on the Degradation of Polyethylene." *Progress Polymer Science*. 15. 177-192.

Albertsson, A. C, Andersson, S. O. and Karlsson, S. (1987). "The Mechanism of Biodegradation of Polyethylene." *Polymer Degradation of Stabilization*. 18. 73-87.

Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H. and Kawasaki, N. 1998. "Biodegradable Films Made from Low-density Polyethylene (LDPE), Rice Starch and Potato Starch for Food Packaging Application: Part 1." *Carbohydrate Polymer*. 36. 89-104.

Avella, M., De Vlieger, J. J., Errico, M. E., Fischer, S., Vacca, P. and Volpe, M. G. 2005). "Biodegradable Starch/Clay Nanocomposites Films for Food Packaging Applications. *Food Chemistry*. 93. 467-474.

Bever, M. B. 1986. *Encyclopedia of Material Science and Engineering*. Vol:2. Pergamon Press: New York.

Bhattacharya, M., Reis, R. L., Correló, V and Boesel, L. 2005. "Materials Properties of Biodegradable Polymers." In Smith, R. "Biodegradable Polymers for Industrial Applications." Woodhead Publishing Limited:England.

Bikiaris, D. and Panayiotou, C. 1998. "LDPE/starch Blends Compatibilized with PE-g-MA Copolymers." *Journal of applied Polymer Science*. 70. 1503-1521.

Bikiaris, D., Prinos, J. and Panayiotou, C. 1997. "Effect of EAA and Starch on the Thermooxidative Degradation of LDPE." *Polymer Degradation and Stability*. 56. 1-9.

Brydson, J. A. (1995). "Plastics Materials" 6th Ed. Butterworth-Heinemann Ltd: London.

Chandra, R. and Rutsgi, R. (1997). "Biodegradation of Maleated Linear Low Density Polyethylene and Starch Blends." *Polymer Degradation and Stabilization*. 56. 185-202.

Chandra, R. and Rutsgi, R. (1999). "Biodegradable Polymers." *Progress Polymer Science*. 23. 1273-1335.

Charlesby, A. 1987. "Radiation Chemistry of Polymers." In Farhataziz and Rodgers, M. A. J. "Irradiation of Polymers." USA: VCH Publishers, Inc. 451-474.

Contat-Rodrigo, L. and Greus, A. R. 2002. "Biodegradation Studies of LDPE Filled with Biodegradable Additives: Morphological Changes. I." *Journal of Applied Polymer Science*. 83. 1683-1691.

Cornell, J. H., Kaplan, A. M. and Rogers, M. R. 1984. "Biodegradability of Photooxidized Polyalkylenes." *Journal of Applied Polymer Science*. 29. 2581-2597.

Erlandsson, B., Karlsson, S. and Albertsson, A. C. "The Mode of Action of Corn Starch and a Prooxidant System in LDPE:Influence of Thermooxidation and UV

Irradiation on the Molecular Weight Changes.” *Polymer Degradation and Stabilisation*. 55. 237-245.

Fama, L., Rojas, A. M., Goyanes, S. and Gerschenson, L. 2005. “Mechanical Properties of Tapioca-starch Edible Films Containing Sorbate.” *LWT*. 38. 631-630.

Flores, S., Fama, L., Rofas, A. M., Goyanes, S. and Gerschenson, L. 2007. “Physical Properties of Tapioca-starch Edible Film: Influence of Filmmaking and Potassium Sorbate.” *Food Research International*. 40. 257-265.

Garthe, J. W. and Kowal, P. D. 1994. “The Chemical Composition of Degradable Plastics.” *Agricultural and Biological Engineering*. 6. 17-20.

Gilmore, D. F., Antoun, S., Lenz, R. W. and Fuller, R. C. 1993. “Degradation of Polyhydroxylalkanoates and Polyolefin Blends in a Municipal Wastewater Treatment Facility.” *Journal of Environmental Polymer Degradation* 1. 4. 269-274.

Halley, P. J. 2005. “Thermoplastic Starch Biodegradable Polymers.” In Smith, R. “Biodegradable Polymers for Industrial Applications.” Woodhead Publishing Limited:England.

Hooi, Y. G. 2005. “Mechanical, Water Absorption and Weathering Properties of Polylactic Acid/Rice Starch Composites.” Masters Thesis. Universiti Sains Malaysia. Penang, Malaysia.

Huang, C. Y., Roan, M. L., Kou, M. C. and Lu, W. L. 2005. “Effect of Compatibiliser on the Biodegradation and Mechanical Properties of High Content Starch/low Density Polyethylene Blends.” *Polymer Degradation and Stability*. 90. 95-105.

Khabbaz, F., Albertsson, A. C. and Karlsson, S. 1998. “Trapping of Volatile Low Molecular Weight Photoproducts in Inert and Enhanced Degradable LDPE.” *Polymer Degradation and Stability*. 61. 329-342.

Kim, M. and Lee, S. J. 2002. "Characteristics of Crosslinked Potato Starch and Starch Filled Linear Low Density Polyethylene Films." *Carbohydrate Polymers*. 50. 331-337.

Kim, J., Kim, J. H., Shin, T. K., Choi, H. J. and Jhon, M. S. 2001. "Miscibility and rheological Characteristics of Biodegradable Aliphatic Polyester and Linear Low Density Polyethylene Blends." *European Polymer Journal*. 37. 2131-2139.

Lawton, J. W. 1996. "Effect of Starch Type on the Properties of Starch Containing Films." *Carbohydrate Polymers*. 29. 203-208.

Li, J. Y. and Yeh, A. I. 2001. "Relationship Between Thermal, Rheological Characteristics and Swelling Power for Various Starches." *Journal of Food Engineering*. 50.141-148.

Liu, W., Wang, Y. J. and Sun, Z. 2003. "Effects of Polyethylene-grafted-Maleic Anhydride (PE-g-MA) on Thermal Properties, Morphology and Tensile Properties of Low Density Polyethylene (LDPE) and Corn Starch Blends." *Journal of Applied Polymer Science*. 88. 2904-2911.

Mahara, T. and Singh, B. C. 2006. "Synthesis and Characterization of Biodegradable Polyethylene by Graft Copolymerization of Starch Using Glucose-Ce(IV) Redox System." *Journal of Applied Polymer Science*. 100. 3229-3239.

Mali, S., L. S. Sakanaka, F. Yamashita and M. V. E. Grossman. 2005. Water Sorption and Mechanical Properties of Cassava Starch Films and Their Relation to Plastisizing Effect. *Carbohydrate Polymer*. 60(3): 283-289.

Mani, R. and M. Bhattacharya. 1998. Properties Injection Moulded Starch/Synthetic Polymer Blends-III. Effect of Amylopectin to Amylase Ratio in Starch. *European Polymer Journal*. 34(10): 1467-1475.

Manzur, A., Limon-Gonzalez, M. and Favela-Torres, E. 2004. "Biodegradation of Physicochemically Treated LDPE by a Consortium of Filamentous Fungi." *Journal of Applied Polymer Science*. 92. 265-271.

Matsumura, S. 2005. "Mechanism of Biodegradation." In Smith, R. (Ed). "Biodegradable Polymers for Industrial Applications." Woodhead Publishing Limited:Cambridge, London.

Matzinos, P., Bikiaris, D., Kokkou, S. and Panayiotou, C. 2001. "Processing and Characterization of LDPE/Starch Products." *Journal of Applied Polymer Science*. 79. 2548-2557.

Moore, G. F. and Saunders, S. M. 1995. "Advance in Biodegradable Polymers." *Rapra Review Reports*. 9:2. 3-31.

Nakamura, E. M., Cordi, L., Almeida, G. S. G., Duran, N. and Mei, L. H. I. 2005. "Study and Development of LDPE/starch Partially Biodegradable Compounds." *Journal of Materials Processing Technology*. 162-163. 236-241.

Ohtake, Y., Kobayashi, T., Asabe, H. and Murakami, N. and Nono, K. 1998. "Oxidative Degradation and Molecular Weight Change of LDPE Buried under Bioactive Soil for 32-37 Years." *Journal of Applied Polymer Science*. 70. 1643-1659.

Pongsawatmanit, R., Temsiripong, T. and Suwonsichaon, T. 2007. "Thermal and Rheological Properties of Tapioca Starch and Xyloglucan Mixtures in the Presence of Sucrose." *Food Research International*. 40.239-248.

Psomiadou, E., Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H. and Kawasaki, N. 1997. "Biodegradable Films Made from Low Density Polyethylene (LDPE), Wheat Starch and Soluble Starch for Food Packaging Applications. Part 2." *Carbohydrate Polymers*. 33. 227-242.

Raghavan, D. 1995. Characterization of Biodegradable Plastics. *Polymer-Plastic Technology Engineering*. 34(1): 41-63.

Raj, B., Sankar, U. and Siddaramaiah. 2004. "Low Density Polyethylene/Starch Blend Films for Food Packaging Applications." *Advances in Polymer technology*. 23. 32-45.

Rosa, D. S., Guedes, C. G. F. and Casarin, F. 2005. "Mechanical Behavior and Biodegradation of Poly(ϵ -caprolactone)/starch Blends With and Without Expansor." *Polymer Bulletin*. 54. 321-333.

Sastry, P. K., Satyanayana, D., Rao, D. V. M. 1998. "Accelerated and Environmental Weathering Studies on Polyethylene-Starch Blend Films." *Journal of Applied Polymer Science*. 70. 2251-2257.

Shah, P. B., Bandopadhyay, S. & Bellare, J. R. 1995. "Environmentally Degradable Starch Filled Low Density Polyethylene." *Polymer Degradation Stabilization*. 47. 165-173.

Steven, E. S. 2002. "Green Plastics, An Introduction to the New Science of Biodegradable Plastics." Princeton University Press: USA.

Thakore, I. M., Iyer, S., Desai, A. and Lee, A. 1999. "Morphology, Thermochemical Properties and Biodegradability of Low density Polyethylene/Starch Blends. *Journal of applied Polymer Science*. 74. 2701-2802.

Tharanathan, R.N. 2003. Biodegradable Films and Composite Coatings: Past, Present and Future. *Trends in Food Science & Technology*. 14: 71-78.

Thiebaud, S., Aburto, J., Alric, I., Borredon, E., Bikiaris, D., Prinos, J. and Panayiotou, C. 1997. "Properties of Fatty Acid Esters of Starch and their Blends with LDPE." *Journal of Applied Polymer Science*. 17. 705-721.

Volke-Sepulveda, T., Favela-Torres, E., Manzur-Guzman, Limor-Gonzalez, M. and Trejo-Quitero, G. 1999. "Microbial Degradation of Thermo-oxidized Low Density Polyethylene. *Journal of Applied Polymer Science*. 73. 1435-1440.

Wu, C. S. 2003. "Physical properties and Biodegradability of Maleated-polycaprolactone/starch Composite." *Polymer Degradation and Stability*. 80. 127-134.

Zheng, Y. and Yanful, E. K. 2005. "A Review of Plastic Waste Biodegradation." *Critical Review in Biotechnology*. 25. 243-250.