EFFECT OF ADDITIVES, POLYVINYL ALCOHOL AND SILICA ON PROPERTIES OF SAGO STARCH PLASTIC FILMS

By

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LIST OF SYMBOLS

Symbol	Description
%	Percentage
°C	Degree Celcius
Wt%	Weight percent
EB	Elongation at Break
TS	Tensile Strength
MPa	Mega Pascal
ml	Mililiter
mm	Milimeter
cm	Centimeter
μm	Micrometer
g	Gram
h	Hours
Wa	Water Absorption
We	Weight of plastic film at the adsorbing equilibrium
Wo	The first dry weight of plastic film
G	Weight gain
t	Time tested
А	Area

LIST OF ABBREVIATIONS

Abbreviation Description

ASTM	American Society for Testing and Materials
MSW	Municipal Solid Waste
PVA	Polyvinyl alcohol
PLA	Polylactic acid
GLU	Glutaraldehyde
GLY	Glycerol
PEG	Polyethylene glycol
SEM	Scanning Electron Microscopy
WVT	Water Vapor Transmission
STMP	Sodium Trimetaphosphate

KESAN BAHAN - BAHAN PENAMBAH, POLIVINIL ALKOHOL DAN SILIKA KE ATAS SIFAT FILEM PLASTIK KANJI SAGU

ABSTRAK

Dalam penyelidikan ini, kajian mengenai sifat-sifat filem plastik kanji sagu dengan penambahan pelbagai bahan penambah, polivinil alkohol dan silika telah dijalankan. Bahan penambah yang digunakan dalam penyelidikan ini adalah gliserol (GLY), polietilena glikol (PEG) dan glutaraldehid (GLU). Gliserol dan polietilena glikol digunakan sebagai pemplastik untuk mengatasi kerapuhan filem, disebabkan oleh daya antara molekul yang tinggi. Sementara itu, glutaraldehid telah digunakan sebagai agen sambung silang untuk meningkatkan kekuatan tensil filem dengan meningkatkan struktur rentas yang dihubungkan. Filem plastik kanji sagu disediakan melalui proses campuran diikuti oleh kaedah tuangan. Daripada keputusan yang diperolehi, filem dengan tambahan 2 % berat glutaraldehid menunjukkan kekuatan tensil tertinggi. Selain itu, filem menggunakan pemplastik gliserol mempamerkan pemanjangan pada takat putus dan kekuatan tensil yang lebih tinggi daripada filem menggunakan pemplastik polietilena glikol disebabkan gliserol mempunyai kesan pemplastik yang lebih baik. Ujian penguraian menunjukkan bahawa kehilangan berat filem plastik kanji sagu tanpa agen pemplastik lebih rendah daripada filem menggunakan pemplastik gliserol dan polietilena glikol. Keberkesanan polivinil alkohol (PVA) pada filem plastic kanji sagu telah dikaji dan dibandingkan dengan kehadiran gliserol sebagai agen pemplastik dan glutaraldehid sebagai agen sambung silang. Keputusan ujian tensil menunjukkan bahawa filem plastic kanji sagu dengan 3 % berat PVA mempamer peningkatan yang besar dalam kekuatan tensil,

pemanjangan pada takat putus dan rintangan air tetapi merendahkan sifat-sifat penguraian filem plastik kanji sagu. Ketiga, silika ditambah ke dalam campuran filem plastik kanji sagu sebagai pengisi. Keputusan menunjukkan peningkatan kekuatan tensil pada 2 % berat silika tetapi menurunkan pemanjangan pada takat putus dan rintangan air filem plastik kanji sagu. Dengan peningkatan kuantiti silika, kehilangan berat sampel kesemua campuran filem semakin berkurang. Akhir sekali, pengubahsuaian kanji sagu digunakan untuk menghasilkan filem plastic kanji sagu. Daripada keputusan yang diperoleh, kanji sagu yang diubahsuai mempunyai keserasian dan interaksi dengan PVA yang lebih baik berbanding kanji sagu yang tidak diubahsuai. Oleh sebab itu, kekuatan tensil filem lebih tinggi tetapi mempunyai pemanjangan pada takat putus yang lebih rendah. Selain dari itu, rintangan air filem juga lebih rendah dan seterusnya menyumbang kepada penurunan penguraian filem plastik kanji sagu.

EFFECT OF ADDITIVES, POLYVINYL ALCOHOL AND SILICA ON PROPERTIES OF SAGO STARCH PLASTIC FILMS

ABSTRACT

In this research, studies on properties of sago starch plastic films with the additional of various additives, polyvinyl alcohol and silica were carried out. The additives used in this research were glycerol (GLY), polyethylene glycol (PEG) and glutaraldehyde (GLU). Glycerol and polyethylene glycol were used as plasticizer to overcome film brittleness, caused by high intermolecular forces. While, glutaraldehyde was used as crosslinking agent to increase the tensile strength of films by increasing the cross linking structure. Sago starch plastic films were prepared through blending process followed by casting method. From the results obtained, film with the addition of 2 wt% glutaraldehyde shows the highest tensile strength. Besides that, results showed that the glycerol-plasticized films exhibited higher elongation at break and tensile strength than that of polyethylene glycolplasticized films, which mainly due to the better plasticizing effect of glycerol. Degradability test revealed that the weight loss of unplasticized sago starch plastic films was lower than of glycerol- and polyethylene glycol-plasticized sago starch plastic films. The effectiveness of polyvinyl alcohol (PVA) on sago starch plastic films was studied and compared in the presence of glycerol as plasticizing agent and glutaraldehyde as crosslinking agent. The tensile test results showed that the sago starch plastic films with 3 wt % of PVA exhibit significant improvement in tensile strength, elongation at break and water resistance but reduced the degradation behaviour of the sago starch plastic films. Thirdly, silica was added as filler into the blend of sago starch plastic films. The result showed that, an improvement in tensile strength at optimum silica amount (2 wt %) but reduced the elongation at break and water resistance of the sago starch plastic films. The weight loss of all blended films were decreased with an increase of silica amount. Last but not least, modified sago starch is used to form sago starch plastic films. From the result obtained, the modified sago starch had better compatibility and interaction with PVA than unmodified sago starch. Thus, the tensile strength of film was higher but lower in elongation at break. Besides that, the lower water absorption and water vapor transmission of modified sago starch plastic films.

CHAPTER ONE

INTRODUCTION

1.1 Overview

Ahead of the 1930's most house-hold items, durable materials, and industrial products were produced from metals, wood, leather, glass, paper, and vulcanized natural rubber (Grulke, 1994). Since that time, plastics have replaced many of those materials because of their ease of forming and low cost.

Since the 1976, plastics materials have been used as an important stuff in the United States. Plastics have crept more and more and seldom unnoticeably into our homes, offices, cars, even our bodies so much so that, it was chosen as one of the greatest innovations of the millennium. Petrochemical based plastics (e.g. polyamides, polyesters, polyolefins, and etc.) have been broadly used for wrapping and packaging application, because of their matchless characteristics such as they are offered at low-priced and in big quantity. Besides that, they also exhibit favourable properties such as good mechanical strength and applicability in industrial processing (Davis and Song, 2006, Tharanathan, 2003).

Generally, these plastics show very low water vapour transmission rate, hydrophobic and, most crucially, they are absolutely non-degradable, posing a serious environmental hazard, taking into unease that over 67 million tons of wrapping wastes are produced yearly only in the Europe (Klingbeil, 2000).

The developments of plastic from natural sources have been increased day by day. This is for the purpose of protecting the environment from pollution, damage

and toxic cause by petroleum based plastic. Starch has been considered as one of the most suitable material among all natural biopolymer. This is because, starch are biodegradable, usually obtainable and lower price. There is a main form of accumulated carbohydrate in plants for example sago, corn, rice, potatoes, and wheat. Several researches have been reported on starch based films made from various starches such as high amylose corn, potato and cassava, but very little work has been reported on sago starch film. Starch from sago palm (*Metroxylon sagu Rottb.*) is a gradually become main socioeconomic crop in Southeast Asia. Sago starch is the only example of manufacturing (food and non-food) starch imitative from diverse sources than ordinary starches for instance cereals (rice and corn), roots (tapioca), tubers (potato), and legumes (pea and mung bean). Sago starch has own special properties but a few of its physicochemical properties quite similar to common starch such as cassava and potato (Karim et al., 2008a, Karim et al., 2008b).

The additional of plasticizer is required to decrease film brittleness, caused by high intermolecular forces. Plasticizer reduces these forces by raise the mobility of polymer chains, thus improving extensibility and flexibility of the film. Glycerol and polyethylene glycol are the most popular plasticizers utilized in film-making methods, due to compatibility and stability with hydrophilic bio-polymeric packaging chain (Cervera et al., 2004). Glutaraldehyde is used to determine the effect of crosslinking agent on tensile properties and degradation behavior of sago starch plastic films.

Nowadays, degradable plastic materials have been widely produced. Unfortunately, the price is higher compared to the common hydrocarbon plastic materials. For commodity uses, the price of the degradable plastic materials in the market cannot compete with hydrocarbon plastic materials. This situation created big problems because the production cost per product was increased. While for higher mechanical properties, the use of common fiber and reinforcement will also create problems to the environments. Other than that, introduction of natural fiber as the reinforcing materials is one of the options to diminish the price and at the same time is environmental friendly.

Further research of biodegradable plastic from natural polymer such as starch or polysaccharides has increase due to consumer attention in expediency and food quality. Eco-efficient manufactured goods are the new production of bio based creations produced by sustainable substances that concur with ecological and economical requirements including acceptable of environmentally disposal of postuser waste.

Sago palm is one of the main starch manufacture harvests and it is available in Sarawak. *M. sylvestre, M. longispinum, M. sagu, M. microcanthum,* and *M. rumphii* are the important species widely used. Traditionally, sago starch can be cooked in various ways like the simple *sago upma* or as a pancake. Apart from its uses for the food industry, sago starch can also be used as a key material input in various industries such as plywood, paper, and textile industry. Due to the raised concern over environmental contamination and pollution effected by non-degradable substances, the development of biodegradable products for various applications is on demand. Starch-based materials have been proven to be an excellent biodegradable source. Therefore, sago starch was selected to be used as the main material in manufacturing biodegradable plastic.

Sago starch contains moisture contents ranging between 10.6% and 20.0%, and oval granules with diameters in the range of 20 to 40 μ m. The total amylose contents which are the lipid free starch in sago starch ranged between 24% and 31%, whereas the apparent amylose content which is starch with lipid was slightly lower, especially in the range of 24% to 30%. The gelatinization temperature for sago starch is high as compared to corn, peas and potatoes, but low than sweet potatoes and yam. These led to important properties of sago starch such as high viscosity with proper extraction, easily moulded and ease to gelatinize. Consequently, it illustrates that starch has a large potential to be produced into biodegradable polymer especially as edible plastic for food packaging application. Preparations of sago starch plastic films in this research work through the simplest and affordable processing method with low cost technology. (Tian et al., 1991, Veletudie et al., 1995).

1.2 Problem Statement

Usages of plastic materials keep increasing years ahead. It was started in 1930 when major thermoplastic such as polystyrene, poly (vinyl chloride), polyolefins and poly (methyl methacrylate) were developed (Sangeeta and Asim, 2007). Since then, plastic have been found useful in applications ranging from transportation, packaging, medical appliances and communications. The global consumption of these plastics is in the region of 22-23 million tonnes yearly (Tan, 1997). Unfortunately, plastic obtained from petrochemical processes are tricky targets for naturally occurring decomposers such as bacteria and fungi, mainly due to their macromolecular structure. Plastic materials usually generate difficulties and pollution to the environment because of the non-degradable substances and long lasting life of these materials (Wang et al., 2004). As a result, the waste will gather in ecosystems causing an environmental risk such as shortage of landfill, air pollution due to open burning of the plastic materials and also higher cost for recycling. Because of that, blends of starch with other biodegradable synthetic polymeric materials or natural polymer have been explored for wide packaging applications.

1.3 Research Objectives

The aim of this research is concerned with biodegradability of sago starch blend films. The primarily objectives for this research work are:

- I. To determine the optimum plasticizer (glycerol and polyethylene glycol) and crosslink agent (glutaraldehyde) on the tensile properties, FTIR analysis, water vapor transmission, water absorption, SEM morphological and soil burial degradation behaviour of sago starch plastic films.
- II. To study the effect of polyvinyl alcohol (PVA) amount on the tensile properties, water vapor transmission, water absorption, SEM morphological and soil burial degradation behaviour of sago starch plastic films.
- III. To investigate the effect on silica on properties of PVA/sago starch plastic films in term of tensile properties, water vapor transmission, water absorption, SEM morphological and soil burial degradation behaviour.
- IV. To evaluate the effect of modified sago starch that enhances the strength and other important properties on PVA/sago starch plastic films.

1.4 Organization of the Thesis

There are five chapters in this thesis and each chapter gives information related to the research interest as following:

- Chapter 1 starts with an introduction of the research; the usage of the common commodity hydrocarbon materials and problems created by the materials, its impact on the environment and the advantages the motivation and the objectives.
- Chapter 2 presents an overview of biodegradable polymer-based film packaging, including a brief outline of polyvinyl alcohol, starch, and past related research that investigate the methods to improve the properties of sago starch blend.
- **Chapter 3** includes the procedure for film preparation, materials selection, type of testing required to investigate the properties and structure of samples and state the standard and testing parameter involved thru this research.
- Chapter 4 contains the result of the standard test. This includes a detailed explanation of each figure and graph. The effect of additives, PVA, silica and modified starch addition were broadly explained in term of its tensile properties, biodegradability, water vapour transmission and water absorption. The deviation in this test will further understood with results from FTIR and SEM.

• Chapter 5 includes the conclusion and summary of the entire research work and findings. This chapter also includes the improvements to be done on this project in future.

CHAPTER TWO

LITERATURE REVIEW

2.1 Plastic Waste

The huge use of plastics and production in every part of our daily life has boosted the plastic waste in enormous amounts. Waste plastics disposal has created serious environmental problem because of this polymeric materials is not degradable and not decompose easily. Plastic waste is now considered as a worldwide environmental problem (Nawang et al., 2001). Plastic packaging waste is a particularly visible problem and represent 20 to 30% of the waste stream (Albertsson and Huang, 1995). Polyethylene for example, is non-degradable and has been found to last in the soil over 100 years (Aminabhavi et al., 1990). Non-degradable plastics pose a serious problem to the marine environment, resulting in entrapment and ingestion hazards to marine life (Kaplan and Mayer, 1993). The environmental impact of persistent plastic wastes is increased general global concern, and disposal methods are limited. Although in Malaysia, there are laws prohibiting the indiscriminate disposal of plastics, these laws have not been executed to the letter. This has resulted in blocked drains leading to litter heaps of plastics and flooded streets; many beaches are eye-sores with various type of plastics seen floating on the sea. Over the years, public concern over waste management has increased due to the decreasing availability of landfills, environmental concern and public perception.

There are various options being considered in order to overcome some of the plastic waste disposal problems such as reuse of traditional non-degradable synthesis plastics, recycling, and processing procedures modification for non-degradable synthetic polymers. So that, fewer resources are needed, reduce incineration, and chemical destruction, and the development of biodegradable plastics (Kaplan and Mayer, 1993). Recycling methods for plastics waste are expensive and often energy-intensive. Satisfactory landfill sites are limited while incineration may generate toxic air pollution. It is important to find durable plastic replacements, especially in disposable and short-term packaging applications. Additionally, petroleum sources are becoming limited. The continuously growing public concern in the problem has encouraged research interest in biodegradable polymers as alternatives to conventional non-degradable polymers such as polyethylene and polystyrene and etc. (Janssen and Moscicki, 2009).

2.1.1 Types of Waste

According to (Taylor and Allen, 2006), plastic wastes created by the high consumption of human activities range from relatively harmless substances such as food and paper waste to toxic substances such as batteries, paint, healthcare waste, sewage sludge derived from wastewater treatment. For instance, high-level (radioactive) waste in form of spent nuclear fuel rods. A simple classification of waste into broad categories according to its origin and risk to human and environmental health:

• Household waste

- Municipal
- Industrial wastes
- Construction and demolition wastes
- Medical wastes
- Agricultural waste
- Radioactive wastes
- Mining wastes
- Universal wastes

Among the 9 major classes of wastes; the municipal solid waste (MSW) is the most complex solid waste stream compared to the other homogeneous waste streams resulting from industrial or agricultural activities (Kaosol, 2009). Examples of solid waste are garbage, plastics, bottles, paper, metals, fabric and abandoned automobiles. MSW is generated by residential, offices, shops, institutions, commercial activities, school and supermarket. A projection of post-consumer plastic waste is shown for different sectors in the year 2000 in Figure 2.1. Based on the total waste generated, the packaging sector shows the highest post-consumer plastic waste compare to the other sectors. PE, PP, PS, PVC, PET and PVC are employed for packaging and other short-life plastic goods, furnishings and long-life goods, mostly construction material such as window frames and pipes. Short-life products, disposed of within a few years, have caused serious plastic waste problems, particularly when incinerated. The average life duration of the long life products is around 34 years. Long-life plastic goods produced and sold since the 1960s are now just starting to enter the waste stream.



Figure 2.1: A projection of post-consumer plastic waste is shown for different sectors in the year 2000. (http://www.lotfi.net/recycle/plastic.html)

2.1.2 Plastic Waste Management

In today's society, the handling of garbage or plastic waste has become an increasing concern. It is a big challenge for communities and governments for the effective plastic waste management. Communities are seeing annoyance problems from poorly or improperly maintained landfill sites and concerns have been expressed that the many, unsightly dumps are not in keeping with the expectations of the province's growing tourism industry. The uncontrolled burning at the sites, smoke, odours, vermin, and excessive wind borne litter are the problems and challenge of the many of the landfill sites.

Different strategies have been proposed to deal with household waste management. These are recycling, energy recovery and incineration, and chemical utilization.

2.1.2.1 Recycling

Recycling is an alternative way to reduce trash out of landfills. Most plastics can be recycled. The definition of plastic recycling is a process of recovering waste plastic or scrap by reprocessing the material into functional products, sometimes totally dissimilar in shape from their original figure. For instance, this could mean melting down soft drink bottles and then casting them as plastic chairs and tables. Generally, a plastic is not recycled into the same type of plastic, and products made from recycled plastics are often not recyclable. Besides that, plastic poses unique challenges compared to glass or metallic materials. For example, due to the huge number of types of plastic, they each have a resin identification code, and must be sorted before they can be recycled. The sorting process is costly compare to metals which can be sorted using electromagnets, no such 'easy sorting' capability exists for plastics. In addition to this, while labels do not need to be removed from bottles for recycling, lids are often made from a different kind of non-recyclable plastics. To help in identifying the materials in various plastic items, resin identification code numbers 1-6 have been assigned to six common kinds of recyclable plastic resins. with the number 7 indicating any other kind of plastic, whether recyclable or not. Standardized symbols are available incorporating each of these resin codes (Schiller, 2010).

Recycling involves the collection, separation, selection, cleaning and reprocessing of plastic materials from garbage. For effective recycling, there must be public awareness, community support, government incentive and regulation, and integrated waste management. However, recycling is tedious and expensive due to difficulty in separation of polymer mixtures and producing pure polymers. Because of the highly dispersed nature of plastics waste, recycling is only suited for high-cost, low-volume specialty polymers. Polymer mixtures can be used in less critical applications, like in the production of benches, pots and flower pots. For that reason, there must be a capable infrastructure for the ease of separation, collection of used articles, less contamination and an established market for reprocessing or reusing recycled materials for recycling to be successful (Tan, 1997).

Figure 2.2 shows the result of the model projections for the future. The total virgin plastics consumption is expected to reach 20 222 kt by the year 2030 and over 18 800 kt waste will be generated. This is 69 % of the total plastic consumption (including plastic recycling). If the recycling rate remains constant, 6600 kt waste will be recycled (35% of total waste generated, including primary, secondary and tertiary recycling) and the rest will be disposed. The total plastic comsumption (including recycling) is expected to increase at an annual growth rate of about 5 % between 2001 and 2030 (Nitin et al., 2006).



Figure 2.2: Projection of total plastic consumption (including recycling and additives), waste generated, waste available for disposal, waste recycled and additives consumption (Nitin et al, 2006).

2.1.2.2 Energy recovery and Incineration

Energy recovery is defined as the recovery of energy in a useable form from mass burning or refuse-derived fuel incineration, pyrolysis or any other means of using the heat of combustion of solid waste that involves high temperature (above twelve hundred degrees Fahrenheit) processing. Incineration is defined as reducing the volume of solid wastes by use of an enclosed device, using controlled-flame combustion. Pyrolysis is described as the process in which solid wastes are heated in an enclosed device in the absence of oxygen to vaporization, producing a hydrocarbon-rich gas capable of being burned for recovery of energy. The objective is to make sure the maximum energy recovery by disposing as much waste as possible in combined heat and power plants. The energy content of waste is exchanged into both heat and electricity. From of the full amount volume of waste for incineration, 84% was burned at combined heat and power plants and 16% at plants only generating heat (Clark County Solid Waste Management Plan, 2000).

Although under controlled conditions, a large amount of energy can be liberated by the incineration of plastic materials, other environmental factors have to be taken into consideration. The large amount of carbon dioxide produced, raising global temperature and greenhouse effect. The liberation of acidic oxides of nitrogen and sulphur are also added problem to the environment. At last, installation of incineration plants involves high cost and not profitable (Clark County Solid Waste Management Plan, 2000).

2.1.2.3 Chemical Utilization

This involves the chemical transformation of polymeric materials into low molecular weight chemicals. At high temperature and pressure, polyethylene, polypropylene and polystyrene, react with hydrogen through a process known as cracking, to give a plastic derived fuel (hydrocarbon mixture in high yield). Due to recent advances in cycling, such as pyrolysis, etc., plastics derived fuel of better quality can now be obtained in high yields.

2.2 Plastic

Previous to 1930, the majority of industrial parts and household products were prepared of wood, paper, metals, glass, leather, and vulcanized natural rubber. Plastics have since invaded markets for all of these materials and in addition, because they are readily moulded into complex shapes with lowest cost compared to the above mentioned materials. Plastic is a long chain molecule that composed of several thousand repeating units (called mers) that are linked together in a chain-like form. The number of particular segments repeat is referred to as *n*, the degree of polymerization. As *n* becomes larger, the polymer molecule becomes longer and the molecular weight of polymer increases. There are different types of plastics just as there are different types of metals and ceramics. There are thousands of plastics and understanding the properties of plastic will help the plastic product designer to make a more useful decision when selecting a plastic material for particular application. Plastics are more accurately defined as polymer (Muccio, 1991). (Strong, 2000)

According to Strong (2000), plastics are materials composed principally of large molecules that are synthetically made or, if naturally occurring, are highly modified. Plastics play a key role in packaging. In the general public, packaging is necessary where it encloses, improves and keeps the goods from processing and manufacturing, material handling would be a chaotic, incompetent and costly exercise (Robertson, 1993). Plastic such as polyethylene (PE), polypropylene (PP), etc., are fast replacing traditional packaging materials for instance wood, paper, and metal in packaging application. This is due to the good mechanical integrity, moisture and gas barrier properties, transparency, inertness to environmental exposure, thermal process ability, light-weight, durability and shatter resistance

properties. In addition, they are low in cost. These attractive properties attributes to their large consumption (Kennethmarsh and Betty Bugusu, 2007).

2.2.1 Development of New Degradable Packaging Materials

Development of new degradable packaging materials has been strongly advocated due to environmental friendly of degradable plastics. Environmental pollution by petroleum based polymers has assumed dangerous proportions in developing countries. Consequently, efforts to solve these problems have been made such as by introducing the polymer biodegradable in daily use throughout minor modifications of their structures. Lately, a huge number of biodegradable polymers have been synthesized and some enzymes and microorganisms for degrading them have been identified. Across the globe, a number of governments and regional economic integration organizations have been established programs for identifying and assessing substances that could cause long-term harm. Harm is defined as the undesirable effects resulting from the accumulation in living organisms of degradation-resistant substances above certain concentrations.

Biodegradation can only occur within the microorganisms take part in a middle role in the biodegradation process. Biodegradation can be defined as the natural process by which organic substances are degraded by microorganisms (mainly aerobic bacteria) into simpler compounds, such as water, ammonia and carbon dioxide. A number of standards authorities have required to produce definitions for biodegradable plastics and some of these are provided below:

ISO 472: 1988 — A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastics and application in a period of time that determines its classification. The change in chemical structure results from the action of naturally occurring microorganisms.

ASTM sub-committee D20.96 proposal — Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics.

Japanese Biodegradable Plastic Society1 draft proposal — Biodegradable plastics are polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms.

DIN 103.2 working group on biodegradable polymers — Biodegradation of a plastic material is a process leading to naturally occurring metabolic end products.

Common definition of biodegradation — It is a process where the original form of a substance disappears because of fungi, bacteria, yeasts and their enzymes consume it as a food source. Biodegradation is a relatively rapid process in suitable states of temperature, moisture, and oxygen availability. Biodegradation for limited periods is a reasonable target for the complete assimilation and disappearance of an article

leaving no toxic or environmentally risky residue. Biodegradable polymers are useful for a variety of applications in agriculture, medical, drug release and packaging fields (Chandra and Rustgi, 1998).

Defining the degree of biodegradation is a consideration — complete degradation into these final simple components should be distinguished from partial degradation into a different related compound. Moving forward, industry will likely need an increasingly comprehensive body of knowledge about the biodegradation products resulting from a substance, its ability to bio-accumulate and its toxicity.

2.2.2 Degradable Plastics

A degradable plastic is a plastic created to endure a large transform in chemical structure under specific environmental conditions, resulting in loss of some mechanical and physical properties as measured by standard tests method appropriate to the plastic and the application in a period of time that determines its classification (Otey et al., 1987). Degradation of plastic materials can occur via the effect of sunlight and catalysts (photo-degradation), microorganisms (biodegradation), moisture and air (chemo-degradation), and wind and abrasion (mechanical degradation). The degradation of plastics involves a combination of two or more processes. The causes of biodegradation of plastics include;

- i) mechanical processes resulting from the activities of termites, insects and rodents;
- ii) fouling processes in which organisms use the plastic as a support;

iii) chemical activities in which constituents of plastics serve as sources of nutrients for organisms, and dissimilarity process in which the plastic is chemically damaged by corrosive substances, as produced and secreted by an organism (Ibrahim, 2000).

2.2.3 Factors Affecting the Polymer Degradation

The durability of polymers is generally affected by purity, initial molecular weight or melt flow index (MFI), degree of crystallinity, orientation (Stivala et al., 1983), type, level and dispersion of any added pigment, thickness of sample (Winslow et al., 1966) and type of anti-oxidant and UV-stabilizer (Pagga and Beimborn, 1993, Garcia et al., 1991).

The crystalline and amorphous structure of polymer, really affect the polymer degradability. A semicrystalline nature tends to limit the accessibility, effectively confining the degradation to the amorphous regions of the polymer. However, contradictory results have been reported. For example, highly crystalline starch materials and bacterial polyesters are rapidly hydrolyzed. The chemical properties that is important as well as the chemical linkages in the polymer backbone, their position, the pendant groups, and their chemical activity, end groups and their chemical activity (Bastioli, 2005, Lim, 2007).

Besides that, rates of degradation have dramatically affected by molecular weight distribution of the polymers. This effect has been demonstrated for a number of polymers, where a crucial lower limit must be present earlier than the process will begin. The molecular origin for this outcome is still subject to speculation, and has been attributed to a range of reasons such as changes in chain flexibility, enzyme accessibility, crystallinity, fits with active sites, or other aspects of morphology (Bastioli, 2005, Lim, 2007).

Furthermore, the polymer degradation properties also affected by the interaction of other polymers (blends). These additional materials may operate as barriers to avoid movement of enzymes, moisture, microorganisms, or oxygen into the polymer domains of interest. The susceptibility of a degradable polymer to microbial attack is sometimes decreased by grafting it onto a non-degradable polymer or by cross linking (Bastioli, 2005, Lim, 2007).

The degradation of plastics can be said to start as soon as the polymer is synthesized, and is increased by residual stresses left by moulding process. This can be followed by exposure to light (e.g. UV), humidity, oxygen, heat, bacteria and stress (El-Awady, 2003, Ismail and Awang, 2008, Abd El-Rehim et al., 2004, Krishna Sastry et al., 1998, Rui et al., 2007). Plastics can be contaminated by other materials, including other plastics.

2.3 Starch

Starch is found in all plant seeds and tubers. Starch is used for energy storage in plants. It is the structure in which glucose is accumulated for afterwards use. Starch is consist of individual unit of glucose, linked together in chains by alpha 1-4 and occasional alpha 1-6, linkages. The linkage give in linear chains that primarily compacted molecules called amylose, where as the alpha 1-6 linkages serve as

branching points to produce branched-chain molecules called amylopectin (Thierry et al., 2007).

Starch can be divided into two principal polysaccharides: amylose and amylopectin. Although the starch from each plant is unique, most starches consist of two types of molecules: 20-25 % amylose and 75-80 % amylopectin. Chemical structure of glucose, amylose and amylopectin can be seen in Figure 2.3, Figure 2.4 and Figure 2.5 respectively. The relative proportions of amylose to amylopectin both depend on the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none (~3%) (Fringant et al., 1996, Thirathumthavorn and Charoenrein, 2007, Gena et al., 2003, Gloria et al., 2007, Van Soest et al., 1996).



Figure 2.3: Structure of glucose (Li, 2010)



Figure 2.4: Structure of amylose (Li, 2010)



Figure 2.5: Structure of amylopectin (Li, 2010)

Amylose and amylopectin are inherently incompatible molecules; amylose having lower molecular weight with a relatively extended shape whereas amylopectin has huge but compact molecules (Abdul Majid, 2010).

2.3.1 Starch based plastic

Starch can be utilized to form biodegradable or edible films. Different sources of starch, high amylose starch and modified starch (Mali and Grossmann, 2003, Roth and Mehltretter, 1967, Mali et al., 2006, Wolff et al., 1951) have been used to form plastic films by casting from aqueous solution. These films show to have moderate oxygen barrier properties but poor mechanical properties and moisture barrier, thus limit their broad applications.

Starch has been considered as one of the most promising one along with all natural biopolymer. This is because of its biodegradability, easy availability, and lower cost. Starch is the major form of stored carbohydrate in plants such as rice, wheat, corn, and potatoes. Starch is composed of a mixture of two molecules - linear amylose and highly branched amylopectin. Amylose molecules consist of 200 -20,000 glucose units which form a helix as is a result of the bond angles between the glucose units. Amylopectin is a highly branched polymer including short side chains of glucose units attached to every 20-30 glucose units along the chain. Amylopectin molecules may contain up to two million glucose units (Ray and Bousmina, 2005).

Starch can also be used as filler to produced reinforced plastics (Bagheri, 1999, Evangelista et al., 1991). Normally, a small amount of starch (6-30%) was compounded with synthetic polymer (i.e. polyethylene and nylon), increasing the product biodegradability.

Once biodegradability is needed, thermoplastic starch (TPS) can be an option material for replacement of many petroleum-based products and has achieved greatly interest. The preparation of TPS involves the interaction of native starch and plasticizer. During process, plasticizer molecules go through starch particles substituted intramolecular and intermolecular hydrogen bonds. Glycerol is one of the most popular polyol that have been used as thermoplastic starch plasticizer. By using glycerol, better film formation and tensile properties is produced (Jin-Hui et al., 2006). However, because of the –OH group in the glycerol make the structure has poor water resistance (Xiaofei and Jiugao, 2004).