

**PREPARATION AND PROPERTIES OF
BIODEGRADABLE POLYMER BLENDED FILM
BASED ON POLYVINYL ALCOHOL AND
TROPICAL FRUIT WASTE FLOUR**

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**UNIVERSITI SAINS MALAYSIA
2011**

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TROPICAL FRUIT WASTE FLOUR**

by

OOI ZHONG XIAN

**Thesis submitted in fulfillment of the requirements for
the degree of Master of Science**

OCTOBER 2011

DECLARATION

I declare that the content presented in this dissertation is my own work which was done at Universiti Sains Malaysia unless informed otherwise. The dissertation has not been previously submitted for any other degree.

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam disertasi ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Disertasi ini juga tidak pernah disertakan untuk ijazah yang lain sebelum ini.

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ACKNOWLEDGEMENT

First of all, I would like to express my deepest gratitude to my beloved mother, Chen Yean Phin for her endless love, and tolerance. Not to forget my sister, brother, and loved one, Yi Peng for their persevering support, encouragement and unconditional support all this while.

I am greatly indebted to my dedicated supervisor, Prof. Dr. Hanafi Ismail for his support, guidance, encouragement, advice, and also generosity in sharing knowledge during period of my studies. I am grateful and thank you very much for driving me towards the correct pathway throughout the course of my master research. Sincere thanks to my co-supervisor, Assoc. Prof. Dr. Azhar Abu Bakar and Assoc. Prof. Dr. Noor Aziah Abdul Aziz for spending their effort and valuable time to carry out my master research and examine my research paper and thesis prior to submission.

Not forgetting to thank the dean of School of Materials and Mineral Resources Engineering (USM), Prof. Dr. Fauzi Mohd Noor and technical staff especially to Mr. Rashid, Mr. Khairi, Mr. Faizal, Madam Fong, and Mr. Sharil. This project would have never been completed without their valuable support and advice during period of my studies.

Last but not least, I would like to thank my dear friends Sam, Razif, Hamid, Ragu, Chia Ching, and Khoo that support behind me and give me advices and suggestions to conduct a proper experiment throughout the studies.

To all the people, who have helped me throughout my master research, directly or indirectly; your contribution shall not be forgotten. Thank you very much!!!

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LIST OF SYMBOLS

Symbol		Description
W_a	--	Percentage of water absorption (g)
W_e	--	Weight of the wet film at the adsorbing equilibrium (g)
W_i	--	Initial weight of the dried film (g)
ΔW	--	Weight change (g)
Δt	--	Time of transfer (h)
L	--	Film thickness (mm)
A	--	Area (m ²)
W_d	--	Dry weight of the specimen after degradability test (g)

LIST OF ABBREVIATIONS

Abbreviation		Description
ASTM	--	American Society for Testing and Materials
BWF	--	Banana skin waste flour
FESEM	--	Field Emission Scanning Electron Microscope
FT-IR	--	Fourier transform infra-red
GLU	--	Glutaraldehyde
HMTA	--	Hexamethylenetetramine
JWF	--	Jackfruit waste flour
KBr	--	Kalium bromide
MPa	--	Mega Pascal
MSW	--	Municipal solid waste
PVOH	--	Polyvinyl alcohol
RH	--	Relative humidity
RWF	--	Rambutan skin waste flour
TFWF	--	Tropical fruit waste flour
US	--	United state
WVT	--	Water vapor transmission
WVTR	--	Water vapor transmission rate

**PENYEDIAAN DAN SIFAT ADUNAN FILEM POLIMER BIO-URAI
BERASASKAN POLIVINIL ALKOHOL DAN TEPUNG SISA BUAH TROPIKA
ABSTRAK**

Dalam kajian ini, adunan polimer baru dengan mencampurkan tepung sisa buah tropika dan polivinil alkohol (PVOH) melalui kaedah penuangan larutan telah disediakan dan diuji. Pertama sekali, tepung sisa rambutan (RWF) dipilih untuk adunan dengan PVOH. Filem PVOH/RWF polimer bio-urair pada nisbah berat yang berbeza antara PVOH dan RWF disediakan dan kesan agen pemplastik pada sifat-sifat filem yang dihasilkan telah ditentukan. Keputusan kajian menunjukkan bahawa filem menggunakan pemplastik gliserol mempamerkan pemanjangan pada takat putus yang lebih tinggi, tetapi kekuatan tegangan dan modulus Young lebih rendah daripada filem menggunakan pemplastik sorbitol disebabkan gliserol mempunyai kesan pemplastik yang lebih baik. Ujian penguraian menunjukkan bahawa kehilangan berat filem PVOH/RWF tanpa agen pemplastik lebih rendah daripada filem menggunakan pemplastik gliserol dan sorbitol. Kedua, keberkesanan glutaraldehid (GLU) dan heksametilenatetramina (HMTA) sebagai agen sambung silang pada filem PVOH/RWF telah dikaji dan dibandingkan dengan kehadiran gliserol sebagai agen pemplastik. Keputusan ujian tensil menunjukkan bahawa filem PVOH/RWF disambung silang dengan HMTA mempamer sedikit peningkatan dalam kekuatan tensil dan modulus Young, tetapi pemanjangan pada takat putus yang lebih rendah daripada filem yang disambung silang dengan GLU disebabkan ikatan sambung silang yang lebih baik oleh HMTA seperti ditunjukkan oleh keputusan Fourier transform infrared (FT-IR). Filem disambung silang dengan HMTA menunjukkan sifat halangan air yang lebih baik berbanding dengan filem disambung silang dengan GLU dan filem tanpa agen sambung

silang. Ujian pencuciaan semula jadi menunjukkan bahawa penambahan 1.5 % berat glutaraldehid dan heksametilenetetramina tidak memberi kesan kepada ketahanan cuaca filem PVOH/RWF tetapi ujian penanaman dalam tanah menunjukkan bahawa penurunan berat sampel yang lebih tinggi oleh filem tanpa agen sambung silang berbanding dengan filem yang disambung silang oleh GLU dan HMTA. Akhir sekali, dua jenis tepung sisa buah tropika yang berlainan iaitu tepung sisa kulit pisang (BWF) dan tepung sisa kulit nangka (JWF) telah diadun dengan polivinil alkohol (PVOH) dan dibandingkan dengan adunan PVOH/RWF. Filem polivinil alkohol terisi tepung sisa buah tropika mempunyai kekuatan tensil dan pemanjangan pada takat putus yang lebih rendah tetapi modulus Young yang lebih tinggi daripada filem PVOH sahaja. Filem PVOH/RWF menunjukkan kekuatan tensil dan modulus Young tertinggi tetapi penyerapan air dan kadar transmisi wap air terendah berbanding dengan filem PVOH/BWF dan PVOH/JWF pada nisbah berat yang sepadan. Sementara itu, filem PVOH/JWF menunjukkan pemanjangan pada takat putus yang tertinggi, diikuti oleh filem PVOH/RWF dan PVOH/BWF. Ujian penguraian menunjukkan bahawa penurunan berat oleh filem PVOH/BWF adalah tertinggi berbanding dengan filem PVOH/RWF dan PVOH/JWF pada nisbah berat yang sepadan.

Keywords: Bio-urai; Polivinil alkohol (PVOH); tepung sisa buah tropika; agen pemplastik; agen sambung silang

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FRUIT WASTE FLOUR**

ABSTRACT

In this study, a new polymer blends by blending tropical fruit waste flour with polyvinyl alcohol (PVOH) using solution casting method was prepared and examined. Firstly, the rambutan waste flour (RWF) was selected to blend with PVOH. Plasticized biodegradable PVOH/RWF films at different weight ratio of PVOH and RWF content were developed and thus effect of plasticizing agents on the properties of resulting films was evaluated. Results showed that the glycerol-plasticized films exhibited higher elongation at break, but lower tensile strength and Young's modulus than that of sorbitol-plasticized films, which mainly due to the better plasticizing effect of glycerol. Degradability test revealed that the weight loss of unplasticized PVOH/RWF films was lower than of glycerol- and sorbitol-plasticized PVOH/RWF films. Secondly, the effectiveness of glutaraldehyde (GLU) and hexamethylenetetramine (HMTA) as crosslinking agents on PVOH/RWF films was studied and compared in the presence of glycerol as plasticizing agent. The tensile test results showed that the PVOH/RWF films crosslinked with HMTA exhibit slightly improvement in tensile strength and Young's modulus, but lower elongation at break than that of GLU-crosslinked films, which attributed to the better crosslinking effect of HMTA as shown by the Fourier Transform Infrared (FT-IR) results. HMTA-crosslinked film showed better water barrier properties as compared to GLU-crosslinked and non-crosslinked films. Natural weathering test revealed that the addition of 1.5 wt% glutaraldehyde and hexamethylenetetramine did not significantly affect the weatherability of the PVOH/RWF films, but the soil burial

test showed that the weight loss of non-crosslinked films was higher than GLU- and HMTA-crosslinked films. Last but not least, two other different types of tropical fruit waste flour, banana waste flour (BWF) and jackfruit waste flour (JWF), were blended with polyvinyl alcohol (PVOH) and compared with the PVOH/RWF blends. The tensile strength and elongation at break of tropical fruit waste flour filled polyvinyl alcohol were lower, but the Young's modulus was higher, than that of unfilled PVOH film. PVOH/RWF film exhibited highest tensile strength and Young's modulus, but lowest water absorption and water vapour transmission rate than those of the corresponding PVOH/JWF films and PVOH/BWF films. Meanwhile, the elongation at break of the PVOH/JWF films was the highest, followed by PVOH/RWF and PVOH/BWF. Degradability test revealed that the weight loss of PVOH/BWF films was the highest as compared to the corresponding PVOH/RWF films and PVOH/JWF films.

Keywords: Biodegradable; Polyvinyl alcohol (PVOH); tropical fruit waste flour; plasticizing agents; crosslinking agents

CHAPTER 1

INTRODUCTION

1.1 Overview

Plastic industry plays a crucial role in the economic development and to increase the economic welfare of the population. As plastic are readily molded into complex shapes with lowest cost, sturdy, plentiful, easy to carry and store, thus they were introduced a quarter century ago and most of industrial designers prefer to choose plastic as material for their ergonomic and aesthetic (Roach, 2003). In spite of the obvious benefits, plastic industry also significantly contributes to environmental degradation. According to Baker (2010), an estimated 500 billion to 1 trillion plastic bags are produced and consumed worldwide every year, then ending up as litter with uncontrolled consumption and quick disposal of plastic bags. The discarded plastic bags not only causing the landfill problem, and also tend to damage the marine environment. As reported by Rutkowska et al. (2002), several hundred thousand tons of plastics have been discarded into marine environment every year. Owing to the fact that petroleum based plastic bags are non-degradable, thus the discarded plastic bags in sea often mistaken as food by marine animals causing marine animals deaths every year. Consequently, these non-degradable polymers become a significant source of environmental problem and damaging the ecosystem.

In order to solve this problem, environmental friendly degradable plastics are currently increasing in popularity. The development of biodegradable plastic can be categorized into the following (Sedlarik et al., 2007):-

- i. Biopolymers or polymers of natural origins that use polysaccharides such as starch.
- ii. Synthetic biodegradable polymers, for example oil based polymers with a hydrolysable backbone chain such as polyvinyl alcohol.
- iii. Synthetic polymers that undergo chemical or physical modification (blends with degradation accelerator additives) to achieve biodegradability.

Among the several kinds of biodegradable polymers, polyvinyl alcohol (PVOH) is the most promising polymer due to technological potential as a water-processable polymer (Siddaramaiah et al., 2004), thus allowing PVOH to form a varied thickness of biodegradable film by a conventional solution casting method. From the previous study done by Sin et al. (2010), the PVOH is readily attacked and consumed by microorganism and enzymes. Besides, PVOH is growing interest by most researchers due to its desirable characteristics like excellent chemical resistance, good mechanical properties and physical properties that have been employed in various applications, not only pharmaceutical and biomedical applications, but also dip coating, adhesives and solution casting film (Ramaraj, 2007; Sedlarik et al., 2007). However, PVOH is a vinyl polymer in which the backbones are joined by the carbon-carbon linkage causing the biodegradability is low compared to other biodegradable plastic such as poly(lactic acid) and poly(caprolactone) (Ishigaki et al., 1999) and the cost of PVOH is quite expensive and not economical to manufacture (Ramaraj, 2006). In order to enhance the

biodegradability and cost reduction, the mixture of two polymers so called polymer blending is the effective ways to develop the new blended products (Utracki, 1990). Highly polar and water soluble characteristic of PVOH is typically used to blend with the natural polymers. For instance, the PVOH/starch blend is one of the most popular biodegradable plastic (Tang et al., 2008). Several researchers have reported the properties and characterization of PVOH-starch blended films (Tudorachi et al., 2000; Jayasekara et al., 2004; Park et al., 2005; Shi et al., 2009; Yun and Yoon, 2009).

The incorporation of a natural polymer like starch is expected to provide cost reduction to biodegradable plastic. However, the expanding usage of agricultural material will lead to higher demand of agro based resources, which inherently increase the cost of this material. Therefore, the possible strategy is to utilize the discarded portion from the agricultural material. Ideally, the waste utilization would be particularly beneficial, in terms of the economic and environmental sense. As a result, there is gaining a great interest for the researcher in adopting the waste material for combination with the biodegradable polymeric material. A number of studies have been reported on the uses of waste from organic industry (Ozaki et al., 2005; Ramaraj and Poomalai, 2006; Sedlarik et al., 2007), and also inorganic industry (Saha et al., 2005) for the preparation of low cost biodegradable polymer.

To the best of our knowledge, there is no research work involving the tropical fruit waste flour blended with the PVOH for the production of biodegradable polymeric materials. Tropical fruit is originated in the equatorial country like Malaysia, which subjected to tropical climate. Wide variety of tropical fruit can be found in Malaysia

such as durian, mangosteen, jackfruit, rambutan, banana, guava, and etc. After eating or industrially processed, peeling of the fruit causing waste disposal and resulting in large quantities of waste. Among the tropical fruit that very popular in South East Asia, the rambutan skin, banana skin, and jackfruit skin were selected and utilized in this study in order to fabricate the biodegradable polymer films with the PVOH matrix. On a fresh weight basis, the rambutan skin account for 47.5 % (Tindall, 1994), banana composed of 40 % skin (Lee et al., 2010), whereas non-edible jackfruit part are composed of 70 % (Hasan et al., 2008). Normally, those tropical fruit waste will be sent to landfill and cause waste disposal problem with rats and flies that lead to adverse environmental effects consequently, if not correctly handled and managed. Thus, the utilizing of such wastes would certainly solve the disposal problem.

However, the blend of the PVOH and tropical fruit waste flour (TFWF) has lower value in elongation at break because tropical fruit waste flour and PVOH itself is brittle as similar as polyvinyl alcohol and starch blends as reported by Ke and Sun (2003). Therefore, plasticizing agent is needed to impart the flexibility to the PVOH and tropical fruit waste flour blended films. Plasticizing agent is defined as an additive that is used to soften the cast blended films. The plasticizing agent that commonly used for the PVOH/starch blends is glycerol (Follain et al., 2005; Sreedhar et al., 2005; Xiong et al., 2008; Moraes et al., 2009; Zhou et al., 2009). However, there are other types of plasticizing agents that are used by researcher such as sorbitol (Yun et al., 2006; Russo et al., 2009), urea (Tudorachi et al., 2000), polyethylene glycol (Sreedhar et al., 2005), and amino acid (Orts et al., 2007). According to McHught and Krochta (1994), the sorbitol and glycerol plasticized effectively the whey protein edible films because of the

polyols that able to increase the intermolecular spacing while decrease the internal hydrogen bonding. Therefore, the sorbitol and glycerol were selected and studied for plasticizing the PVOH/tropical fruit waste flour blends. The adding of the plasticizing agents results in plasticizing action to increase the film elongation, but plasticizing effect causing reduction in tensile strength (Lin et al., 1991), and poor water resistance of the blended films are still an unresolved problem.

Cajlakovic et al. (2002) reported that PVOH must be crosslinked in order to be useful for wide variety of application, and the crosslinking agents for PVOH hydrogel including glutaraldehyde, formaldehyde, and acetaldehyde. Besides, crosslinking agents such as boric acid (Yin et al., 2005), epichlorohydrin (Sreedhar et al., 2006), and glutaraldehyde (Mansur et al., 2008) were used to react with the starch and PVOH to form the macromolecular network. In addition, Zhou et al. (2008) mentioned that the crosslinking agents were usually added into aqueous solution of PVOH/starch mixture followed by casting method in order to improve their physical and mechanical properties. Therefore, by preparing the plasticized biodegradable PVOH/tropical fruit waste flour blends, the weak tensile properties will be improved through the crosslinking reaction. In this study, two types of crosslinking agent, i.e. glutaraldehyde and hexamethylenetetramine were used to create linkages between the hydroxyl group of the PVOH and tropical fruit waste flour and compare the effectiveness of each crosslinking agent on the improvement of tensile properties and water barrier properties.

1.2 Problem Statement

The petroleum based plastic materials such as polyolefin, polystyrene, polyethylene terephthalate and etc, have been considered as essential part in our daily life. In spite of the obvious benefit of the synthetic plastic, the high degree of chemical stability of petroleum based plastic materials have resulted in a low degradation rate in the environment (Sreedhar et al., 2006). Therefore, these plastic in the end of their service were discarded and contribute significantly to the shortage of landfill availability. Moreover, there is some problems existence for plastic waste recycling. As reported by Averous and Halley (2009), the material recycling implied to the difficulties of the collection, separation, cleaning and possible contamination on the plastic and hard to find economical viable outlet, whereas energetic recycling (incineration) may emit some toxic gas. Polyethylene/starch blends is the popular research material done by most researcher (Bikiaris and Panayiotou, 1998; Rutkowska et al., 2002; Huang et al., 2005; Walker et al., 2007), however, Yabannavar and Bartha (1994) demonstrated the ability of polyethylene blends to biodegrade was mainly affected by the additives and confined to the types of additives, but polyethylene itself were not degraded. Additionally, the expanding usage of agricultural material will lead to higher demand of agro based resources, which inherently increase the cost of this material. Thus, the combination of economical and ecological demands has led to the utilization of waste to incorporate into biodegradable polymers. It is believed that the incorporation of biodegradable additives such as tropical fruit waste could enhance the biodegradability of biodegradable polymer. And, this is an alternative way to solve the waste disposal problem.

1.3 Research Objectives

The aim of this research is concerned with biodegradability of tropical fruit waste flour blended films. The primarily objectives for this research work are:

- i. To fabricate the environmentally friendly biodegradable film based on PVOH and tropical fruit waste flour using solution casting method.
- ii. To study the effect of two different types of plasticizing agents on the tensile properties, water absorption, water vapor transmission rate, and degradability by natural weathering and soil burial of rambutan waste flour filled PVOH blends.
- iii. To evaluate the effect of two different types of crosslinking agents that enhances the strength and other important properties on PVOH/RWF films.
- iv. To investigate the effect of three different types of tropical fruit waste flour (rambutan skin waste flour, banana skin waste flour, and jackfruit skin waste flour) on the properties of PVOH/TFWF films in term of tensile properties, water absorption and water vapor transmission rate, degradability by natural weathering and soil burial, and morphological properties after degradation.

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** describes the introduction of the project. It covers brief introduction about research background, problem statement, and research objectives.
- **Chapter 2** shows current problem and generation of plastic waste, introduction of environmental degradable polymer and benefit of polymer blends. It also covers the brief explanation regarding to the polyvinyl alcohol, tropical fruit waste flour, and other materials used in this project.
- **Chapter 3** contains the information about the materials and equipments specification, and experimental procedure used in this study.
- **Chapter 4** presents the results and discussion of this research. The effect of various types of plasticizing agents, crosslinking agents, and tropical fruit waste flour will be discussed in term of its tensile properties, water absorption, water vapor transmission rate, Fourier transform infra-red, and biodegradability under different environmental conditions.
- **Chapter 5** concludes the findings of the research based on results and discussion in **Chapter 4** with suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Solid Waste

Under US legal regime, solid waste is defined as “any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities” (Getu, 2009). However, the solid wastes also can be classified as hazardous waste or non-hazardous waste depending on their effect to the environment and human health (Bassis, 2004).

2.1.1 Categories of Waste

According to Pichtel (2005), the wide spectrum of wastes generated by manufacturers, industries, or consumers possessing different chemical and physical properties, thus it is practical to classify wastes in order to implement cost-effective management strategies that are beneficial to public health and environment. The major classes of waste were classified as:-

- Municipal
- Industrial
- Hazardous
- Medical

- Universal
- Construction and demolition
- Radioactive
- Mining
- Agricultural

Among the 9 major classes of solid waste, 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). MSW is generated by residential, offices, commercial activities, shops, institutions, supermarket, and schools. Examples of the solid waste are garbage, plastics, bottles, paper, metals, fabric, and abandoned automobiles. The composition weight percent of component in MSW generated in Kuala Lumpur are shown in Figure 2.1. Based on the total MSW generated, the food (waste from cooking and serving of food), mixed paper, and plastic are the main components by weight. However, the food waste and paper are considered as biodegradable waste whereas plastic is non-biodegradable waste. Thus, the amount of plastic waste generated has a direct impact on the environmental problem, and burden to the landfill.

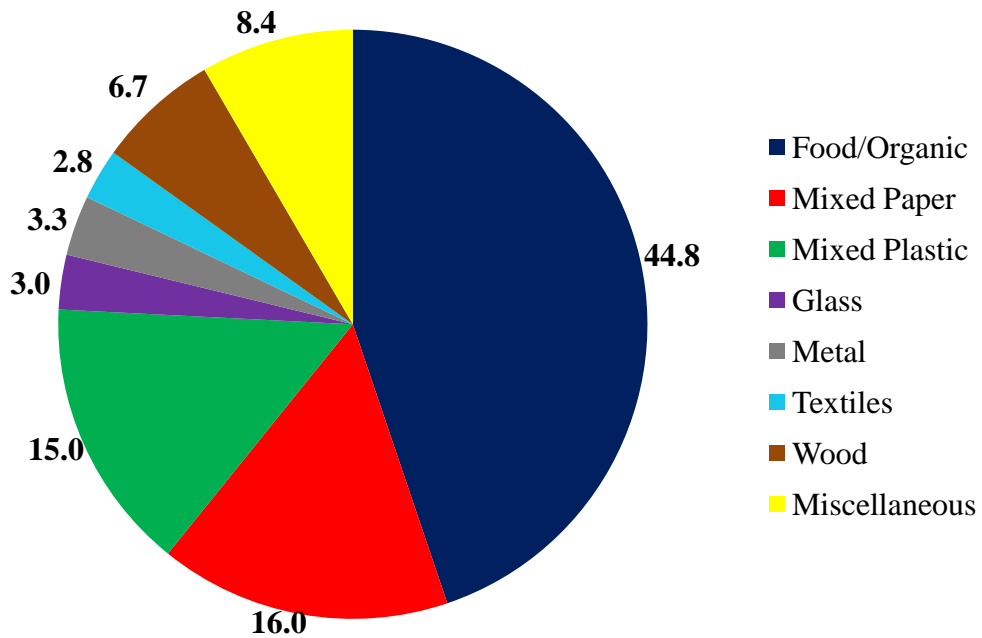


Figure 2.1: Composition weight percent of component in MSW generated in Kuala Lumpur, Malaysia. (Periathamby et al., 2009)

2.1.2 Generation of Plastic Waste and Its current Problem

MIDA (2011) reported the plastics industry in Malaysia has been rated the most competitive among the countries in Asia. The petrochemical industry is an important sector with investments totaling RM 57.2 million as at the end of 2008. From being an importer of petrochemical, the Malaysia currently is an exporter of major petrochemical product and wide variety of petrochemical that produced in Malaysia are polyolefin, polystyrene, polyvinyl chloride, polybutylene terephthalate, and etc. Due to these large scale plants as strong base of supporting services have contributed significantly to the processing of plastic product by supplying steady feedstock material. As a result, the plastic industry in Malaysia is growth rapidly.

Nowadays, Malaysia has tremendous growth in its economy, brought to the population growth at the same time. However, increasing of population, the rise in community standards and rapid urbanization will accelerate the MSW generation especially in developing countries (Minghua et al., 2009) such as Malaysia. In Malaysia, Kuala Lumpur's population is estimated about 1.604 million but the quantity of waste generated in Kuala Lumpur was increased from 2,620 tons in 1995 up to 4000 tons per day in the year 2007 (Saeed et al., 2008). Economic growth in addition to population and urbanization seriously impose the industrial pollution and degradation of urban environment with a booming amount of wastes (Medina, 2000; Saeed et al., 2008).

With more plastics being produced, the more plastics waste is generated. As mentioned, plastic waste contributed significant portion of the total municipal solid waste. Most of the plastic waste such as polyolefin, polyethylene terephthalate, and polystyrene are basically non-degradable. Typically, the non-degradable plastics do not contain hazardous material that will cause any significant impact on the human health. But, it will be inert in the landfill environment, and will not degrade to any significant degree. They will remain in the landfill environment and may well intact if they are dug up a century later. There are some common methods that used to manage the plastic waste are recycling and incineration. However, these methods are inefficient and may harm the environment. For example, the mixed plastic wastes with different classes of properties are greatly limiting the recycling process whereas the incineration or burning of the plastic waste will cause the air pollution by emitting the toxic gases.

2.2 Plastic

Plastics are materials composed principally of large molecules that are synthetically made or, if naturally occurring, are highly modified (Strong, 2006). According to Muccio (1991), plastics are more accurately defined as polymer with a long chain molecules (macromolecules) that composed of more than thousand repeating units (called monomers) that are linked together in a chain like form and the number of particular segments repeat is referred as n , the degree of polymerization. A polymerization is a chemical reaction in which monomer molecules react to form polymer. Polymer resulting from polymerization involving a single type of monomer called homopolymer, whereas more than one type of monomer is copolymer (Stevens, 2002).

2.2.1 General Perspective

Before 1930, most of the household goods and industrial components were made of conventional materials, i.e. metals, wood, glass, leather, and vulcanized rubber. Thereafter, the plastics have creating their own markets. There is widespread use of plastic owing to their unique combination of properties such as lightweight, low cost, low modulus, desirable strength and readily molded into complex shapes compared to the conventional materials (Schoch, 2005). Additionally, the plastic materials possess intrinsic advantages over conventional material by being self coloring when suitably compounded. By incorporating some colorant into the plastic compound, the surface is

finished permanently as the part is made (Lewis, 1993). Some types of plastic materials are also highly resistance to chemical attack and ideal for a wide variety of solution tank and packaging. Thus, most of the industrial designers prefer to choose plastics as components' material or consumer products. Plastics currently become an essential part in our daily life.

There are various types of manufacturing process used to fabricate plastic products, as following (Stevens, 2002):-

- i. Extrusion – a process in which forced the heated plastic through a shaping orifice in continuous formed shape, i.e. film, sheet, rod, or tube.
- ii. Injection molding – a process in which forcing the molten material into the cavities of a tightly closed mold under pressure.
- iii. Blow molding – a method in which heated plastic is forced into the shape of die ring by internal gas pressure.
- iv. Solution Casting – a process in which a cast film was made by depositing a layer of plastic in solution form onto a mold (glass plate), solidifying, and peeling the film from the surface.

In spite of the obvious benefit, the product molded or fabricated with plastic materials are more resistance to weather and rusting than metal products. This factor significantly contributes to environmental degradation when plastic wastes are growing worldwide.

2.2.2 Non-Degradable Plastic

Until now, most of the commodity plastics are non-degradable such as polyolefin which were used in various application including packaging, agricultural mulch films, and etc, to provide the durability and resistance to various form of degradation effect when exposure to sunlight as well as the microorganism attacked. Those plastic are widely used because of their highly resistance to chemical and physical degradation. On the other hand, this characteristics causing those non-degradable plastic are persist in the environment long after their useful life is over, revealed that the long lasting plastic are not suitable to be used in the short lived application.

With the growing awareness on the landfill crisis from the plastic waste, the accumulation of the plastic waste needs immediate resolution. Therefore, many places in the world have banned the non-degradable plastics and the invention of the environmental friendly plastics (degradable plastic and biodegradable plastic) have been intensively studied and developed underway in recent years, and continues to be an interest area for many scientist (Ramaraj, 2007).

2.2.3 Environmental Degradable Plastic

Degradable plastic is a polymer designed to undergo a significant change in its chemical structure under specific environmental conditions and resulting in a loss of some properties (Swift, 1995; Marechal, 2003). In order to solve the waste disposal

problem, there are two classes of environmental degradable plastics are produced. The first class is the plastics typically include the utilization of natural additives (e.g. starch, cellulose and etc) with a conventional petroleum based matrix. This class of plastic materials is partially degradable under consideration because the microbes are able to consume the natural macromolecules within the plastic matrix and left the weakened plastic materials with rough and open edges. Another class of plastic materials is completely biodegradable after a period of useful life, this kind of plastic material is derived from the renewable resources and the fiber reinforcements produced from common crops, so that these plastic materials can be consumed entirely by microbes resulting carbon dioxide and water as environmental friendly by-products (Kolybaba et al., 2003). When the environmental degradable plastics are disposed in landfill or soil, the degradation of plastic materials may occur in various routes. According to Swift (1995), environmentally degradable plastics can be divided into four different categories by referring to a process of degradation as following:-

- i. Biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as fungi, algae, fungi and etc.
- ii. Hydrolytic degradable plastic is a degradable plastic in which the degradation results from hydrolysis.
- iii. Oxidative degradable plastic is a degradable plastic in which the degradation results from oxidation.
- iv. Photodegradable plastic is a degradable plastic in which the degradation results from the action of sunlight.

Figure 2.2 shows all the degradation mechanisms will undergo disintegration which may remain in the environment as small pieces or they may be completely biodegraded (no residue remain) and ultimately mineralized.

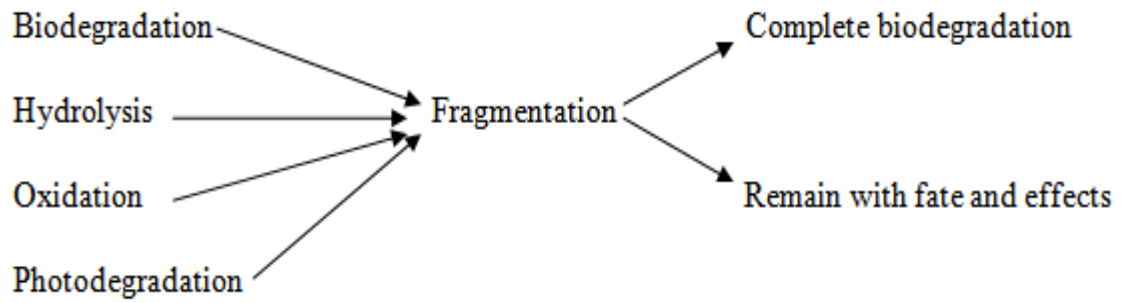


Figure 2.2: Degradation pathways for environmentally degradable polymers (Swift, 1995).

2.2.4 Factors Affecting Biodegradation

According to Kyrikou and Briassoulis (2007), biodegradation is basically an electron transfer process; the biological energy is obtained through the oxidation of reduced materials. The microbes will release the enzymes and to catalyze the electron transfer by removing the electron from the organic substrates to capture the energy through the oxidation process. Oxidation process is considered an essential chemical reaction to initiate subsequent biodegradation (Matsunaga and Whitney, 2000). Many organic materials are easily degraded under aerobic conditions, because oxygen is the terminal electron acceptor. When the biodegradation follows this pattern, the population of microbes will grow quickly and reach high densities. Consequently, the initial rate of

biodegradation is rapid but becomes limited by the supply rate of oxygen (Kyrikou and Briassoulis, 2007).

There are numerous factors that affecting the biodegradation rate such as moisture content, temperature, pH, oxygen availability, other chemicals, presence of suitable microbes, and availability of nutrients (Vidali, 2001; Stevens, 2002). For instance, the biodegradable plastic will not environmentally biodegrade in a landfill if inadequate moisture (Stevens, 2002). Since microbes require a moist environment to survive (Zabel and Morrell, 1992) and be able to export hydrolytic enzymes that break down the biopolymers (*Khachatourians and Qazi, 2008*). Thus, the organic substrate must be water-wettable in order to initiate the biodegradation process. For example, the synthetic plastics are bioinert (cannot hydrobiodegrade) because they are hydrophobic and resistant to hydrolysis (Kyrikou and Briassoulis, 2007). Other than that, the biodegradable plastic experiences the rapid dissolution when exposed to particular aqueous solution (e.g. soluble in hot water). Also, the exposure to a chemical solution with high pH (e.g. Nodax–alkaline digestible) causes a rapid structural breakdown of the plastic materials (Kolybaba et al., 2003).

Regardless of environmental, the biodegradation rate also depends on the chemical structures and constituents of the biodegradable plastic itself. Some plastics degrade at a faster rate than others because the chemical structures of each plastic are different. As mentioned by Stevens (2002), the chemical structures of the common commodity plastics like polyolefin which contain the carbon-carbon single bonds in their backbones making them particularly resistance to degradation. Nevertheless, the

polyvinyl alcohol (PVOH) also having the carbon-carbon single bonds in their backbones, but occurrence of hydroxyl groups on alternate carbon atoms makes it hydrophilic and this characteristic helps to promote degradation through hydrolysis mechanisms.

2.3 Polymer Blends

2.3.1 Historical Outline

The earliest polymer blends occurred long before the synthetic polymers. In the mid of 1800's, the first commercialization of modified natural product in which natural resinous product, shellac was added to nitrocellulose to improve the coating toughness. Thereafter, in the early of 1900's, phenolic thermosetting polymers were introduced by blending phenolic with vulcanized natural rubber for improved the phonograph records over the brittle phenolic system (Robeson, 2007).

In terms of synthetic polymer, the first commercial thermoplastic is polystyrene in 1915, followed by polymethacrylate in 1927, polyvinyl acetate in 1928, polyvinyl chloride in 1931. The initial reason for blending was to toughen the rigid resin or vice versa (Utracki, 2000). During the early of 1940's, polyvinyl chloride and butadiene acrylonitrile copolymer elastomers (NBR) was one of the early commercial synthetic polymer blends until today still available in the market (Seymour, 1989; Robeson, 2007). Another polymer blend was acrylonitrile-butadiene-styrene (ABS) by melt-blending copolymers of styrene and acrylonitrile with NBR (Seymour, 1989).

The commercial development of polymer blends was rapid growth in the late 1960's by gaining major interest for many researchers, especially polymer industry since the polymer blends could potentially offer a large number of different commercial products with the desirable properties (Robeson, 2007).

2.3.2 The Reason for Blending

There is no doubt that the main reason for blending, compounding, or reinforcing is to meet the desirable properties as well as to adjust the cost-performance balance and tailor the technology to fabricate product for specific end use application. Generally, the important factors that contribute to the interest in polymer blends can be listed as (Utracki, 2002):-

- i. Polymer blends offer useful and economic means of upgrading recycled and off-specification polymers.
- ii. To develop a new product by blending of two or more commercially available polymers is more cost-effective way than developing the totally new polymer involving high research, and capital cost to meet the customer or market requirements.
- iii. Several properties can be uniquely combined by forming a high performance blend from synergistically interacting polymers.
- iv. Polymer blending allows custom production of different blends (e.g. different blend ratio) in a wide range of production volumes. In contrast, the

polymerization plant for a new polymer is not as flexible and not economical for small volumes production.

- v. Polymer blending can be done at relatively low cost conventional equipment. But, new polymer requires high investment risk to develop intensive plant and reactor for the production and research purpose.
- vi. The polymer blends can be generated, formulated, optimized, and even commercialized at a faster rate than new polymer.

2.4 Polyvinyl Alcohol (PVOH)

Since 1930s, polyvinyl alcohol (PVOH) is synthetic polymer that used in wide range of industrial (DeMerlis and Schoneker, 2003). The name of polyvinyl alcohol is based on the repeating structural unit, and it is not monomer based (Stevens, 2002) because Polyvinyl alcohol (PVOH) is not produced direct from the polymerization of the corresponding monomer, but produced from the free radical polymerization of vinyl acetate, followed by alkaline alcoholysis of the functional acetate groups (Chiellini et al., 2003; Moraes, 2009), as shown in Figure 2.3. The general properties of PVOH are listed in Table 2.1.

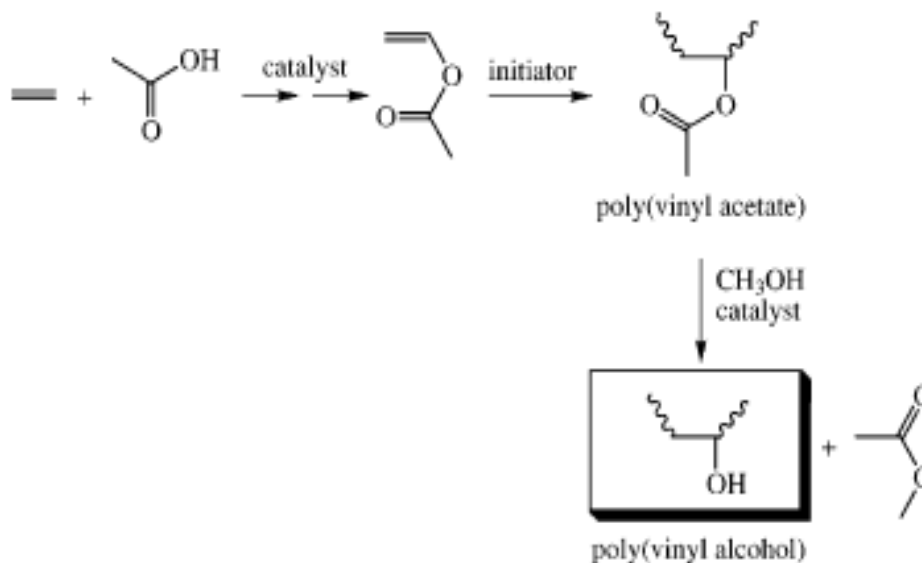


Figure 2.3: Reaction sequence used in production of PVOH (Chiellini et al., 2003)

Table 2.1: General chemical identity and physical properties of polyvinyl alcohol (DeMerlis and Schoneker, 2003)

CAS no.	9002-89-5
Molecular weight	30,000 -200,000
Structural formula	$(-\text{CH}_2\text{CHOH}-)_n(-\text{CH}_2\text{CHOCOCH}_3-)_m$
Empirical formula	$(\text{C}_2\text{H}_4\text{O})_n(\text{C}_4\text{H}_6\text{O}_2)_m$
Physical appearance	Odorless, white granular powder
Specific gravity	1.19-1.31
Solubility	Insoluble in aliphatic and aromatic hydrocarbon but soluble in water

With the different degree of hydrolysis, different grade of PVOH can be obtained. PVOH thus can be generally classified into two groups, which is partially hydrolyzed, and fully hydrolyzed (DeMerlis and Schoneker, 2003). The higher degree of hydrolysis will give rise to the fully hydrolysed PVOH and vice versa. The structural formulas of the partially hydrolyzed and fully hydrolyzed PVOH are shown in Figure 2.4.

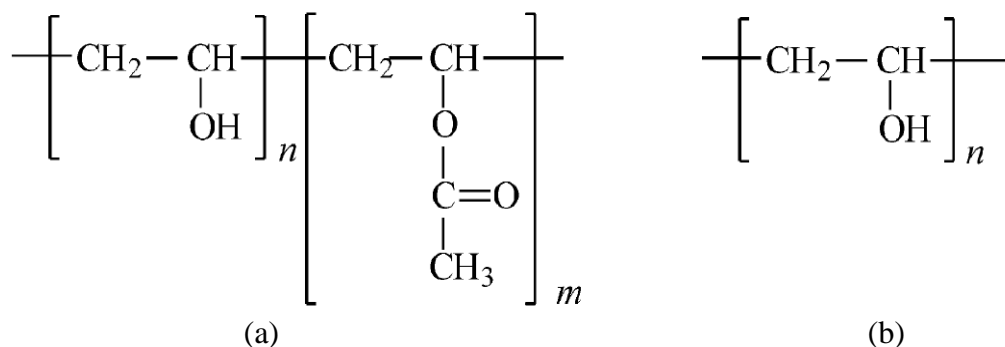


Figure 2.4: Structural formula for (a) Partially hydrolyzed PVOH, (b) Fully hydrolyzed PVOH (DeMerlis and Schoneker, 2003).

Additionally, by varying the different degree of polymerization, the hydrolysis degree, initial length of vinyl acetate polymer, distribution of hydroxyl group, and crystallinity will result in different molecular weights, solubility, strength, and adhesiveness to the PVOH obtained (Chiellini et al., 1999). For examples, the partially hydrolyzed PVOH can be soluble in cold water, whereas the fully hydrolyzed PVOH can be soluble in hot water (> 60 °C) only. Besides, the degree of swelling of PVOH is governed by the average chain length in the amorphous region, so the PVOH swelling by water when increasing of amorphous region (Patachia-Bodonea, 2003). In other way of saying, the presence of residual acetate groups will decrease the crystallinity of PVOH (By referring Figure 2.4).

The PVOH is well known synthetic polymer with its exceptional properties such as water solubility, good optical and tensile properties, low gas permeability, good thermal properties, resistance to organic solvents and oils, non toxicity and valued for its biodegradability (DeMerlis and Schoneker, 2003; Patachia-Bodonea, 2003; Siddaramaiah et al., 2004; Ramaraj, 2007). Lin and Tung (2010) also reported PVOH is synthetic biodegradable polymer with the technological potential as a water processable

polymer (Siddaramaiah et al., 2004), thus allowing the PVOH for film production using solution casting method. Briston (1988) also reported that PVOH is an unusual polymer in one other respect, being soluble in water.

In terms of biodegradability, polyvinyl alcohol is one of the rare polymers that having a backbone of carbon-carbon single bonds, but it tends to degrade due to occurrence of hydroxyl groups on alternate carbon atoms causing enzymatic oxidation of hydroxyl groups form carbonyl groups in the polymer backbone, and followed by hydrolysis of two carbonyl groups (-CO-CH₂-CO-) causes polymer chain cleavage which resulting to a decrease in molecular weight of PVOH (Kale et al., 2007). Thus, polyvinyl alcohol is an exception to the rule that polymers with carbon-carbon single bonds are resistance to degradation (Stevens, 2002). Matsumura et al. (1993) also reported PVOH has been confirmed to be biodegradable under aerobic conditions. Additionally, the PVOH can be biodegraded by releasing non-toxic substances (Davis, 2003). However, the biodegradability of PVOH is low compared to other biodegradable plastic due to PVOH is a vinyl polymer in which the backbones are joined by the carbon-carbon linkages (Ishigaki et al., 1999).

Owing to its solubility, technology that mainly used for PVOH production is casting technique from viscous water solution. Since PVOH films are increasing used as packaging material, thus most of the researchers (Mao et al., 2000; Li et al., 2005; Dean et al., 2008; Yang et al., 2008; Zou et al., 2008) applied the extrusion technique for PVOH films production. However, processing at high temperatures is very sensitive to