PREPARATION AND PROPERTIES OF POLYVINYL ALCOHOL/SOYA BEAN FLOUR BIODEGRADABLE FILM

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LIST OF SYMBOLS

Symbol	**Description**
%	percentage
ºC	degree Celsius
A	area of test area
G	weight gain
g	gram
kg	kilogram
mL	mililiter
mm	millimeter
µm	micrometer
nm	nanometer
h	hours
MPa	Mega Pascal
Mtonne	Mega tonne
phr	part per hundred rubber
t	time

W_0	Initial weight of dry samples
Wa	Percentage of water absorption
W_e	Weight of samples at absorbing equilibrium
wt %	Percentage in weight

LIST OF ABBREVIATIONS

Abbreviation	**Description**
ASTM	American Society for Testing and Materials
BFF	Banana Frond Flour
CH_4	Methane
CNT	Carbon Nanotubes
CO_2	Carbon Dioxide
MMT	Montmorillonite
SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
HMTA	Hexamethylenetetramine
HNT	Halloysite Nanotubes
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PET	Poly ethylene tetraphtalate
PVA	Polyvinyl alcohol

PVC	Polyvinyl chloride
PMMA	Poly methyl methacrylate
US	Unted States
UV	Ultraviolet
WVT	Water Vapor Transmission
WVTR	Water Vapour Transmission Rate

PENYEDIAAN DAN SIFAT ADUNAN FILEM BIOURAI BERASASKAN POLIVINIL ALKOHOL/TEPUNG KACANG SOYA

ABSTRAK

Dalam kajian ini, adunan polimer baru berasaskan tepung kacang soya (SBF) dan polivinil alkohol (PVA) telah disediakan dengan menggunakan kaedah penuangan larutan. Pertama sekali, PVA telah diadun dengan 10-40% berat SBF. Kekuatan tegangan dan pemanjangan pada takat putus filem adunan PVA/SBF adalah lebih rendah, tetapi modulus tegangan adalah lebih tinggi, berbanding filem PVA sahaja. Ini adalah kerana kehadiran SBF dalam adunan filem tersebut. Filem adunan PVA/SBF juga menunjukkan sifat halangan air yang lebih tinggi dengan peningkatan kandungan SBF. Ujian penguraian bio membuktikan bahawa kehadiran SBF mempengaruhi kadar penguraian filem tersebut dengan penurunan berat filem PVA/SBF selepas tempoh ujikaji penguraian dijalankan. Kedua, keberkesanan heksametilenatetramina (HMTA) sebagai ejen sambung silang pada filem adunan PVA/SBF telah dikaji dan dibandingkan dengan filem PVA/SBF tidak disambung silang. Filem PVA/SBF yang disambung silang mempamerkan sifat tegangan dan halangan air yang lebih baik. Ini disebabkan keberkesanan HMTA di dalam adunan. Ujian pencuacaan semula jadi menunjukkan bahawa kehadiran HMTA tidak memberi kesan ketara kepada ketahanan filem adunan PVA/SBF terhadap cuaca, tetapi ujian penanaman dalam tanah menunjukkan filem adunan yang tidak disambung silang mengalami penurunan berat sampel yang lebih tinggi berbanding filem disambung silang . Ketiga, tepung pelepah pisang (BFF) dan tiub nano halloysite (HNT) telah ditambah sebagai pengisi untuk membentuk sistem gabungan ternari. Filem adunan PVA/SBF/HNT menunjukkan sifat tegangan dan halangan air yang lebih baik kerana HNT mempunyai nisbah aspek yang lebih tinggi dan menyediakan lebih tapak interaksi. Peratusan berat kedua-dua filem adunan telah meningkat dengan peningkatan penambahan pengisi selepas dikenakan ujian penguraian. Akhir sekali, BFF telah diubahsuai menggunakan kaedah rawatan alkali. Sifat-sifat tegangan dan halangan air yang lebih baik telah diperolehi oleh filem adunan PVA/SBF/BFF terubahsuai. Kajian ini menunjukkan BFF yang diubahsuai mempunyai keserasian dan interaksi yang lebih baik antara BFF dan matrik PVA/SBF. Di samping itu, sifat halangan air yang lebih baik oleh filem adunan PVA/SBF/BFF terubahsuai telah menyumbang kepada pengurangan kadar penguraian filem tersebut.

PREPARATION AND PROPERTIES OF POLYVINYL ALCOHOL/SOYA BEAN FLOUR BIODEGRADABLE FILM

ABSTRACT

In this research, a new polymer blend based on soya bean flour (SBF) and polyvinyl alcohol (PVA) was prepared using solution casting method. Initially, the SBF content was varied from 10 to 40 wt %. Tensile strength and elongation at break of the PVA/SBF blend films were lower, but the tensile modulus was higher than that of unfilled PVA film. This was mainly because of the presence of SBF in the blend. The PVA/SBF blend films showed higher water barrier properties with increasing SBF content. Biodegradability tests revealed that the presence of SBF stimulated the degradation rate and caused the weight loss of the PVA/SBF blend films. Secondly, the effectiveness of hexamethylenetetramine (HMTA) as crosslinker on PVA/SBF blend films was compared to the non crosslinked PVA/SBF blend films. The crosslinked PVA/SBF blend films showed better tensile and water barrier properties. This was attributed to the effectiveness of HMTA in the blend. Natural weathering test revealed that the presence of HMTA did not significantly affect the weatherability of the PVA/SBF blend films. But, in soil burial test the weight loss of non-crosslinked blend films was higher than crosslinked blend films. Thirdly, banana frond flour (BFF) and halloysite nanotubes (HNT) were added as filler to form ternary blend system. PVA/SBF/HNT blend films show better properties in tensile and water barrier because HNT have higher aspect ratio and provided more interaction sites. Degradability for both blend films were increased with increasing filler content after subjected to degradation test. Lastly, BFF was treated by alkaline treatment. Better tensile and water barrier properties were obtained by the treated PVA/SBF/BFF blend films. This result might due to the better compatibility and interaction of treated BFF and PVA/SBF matrix. Besides that, the higher water barrier properties of treated PVA/SBF/BFF blend films were contributed to reduction of the film degradation.

CHAPTER 1

INTRODUCTION

1.1 Overview

Plastics have become one of the most important materials in our lives and also one of the greatest innovations of the millennium (Danjaji, 2000). The usage of plastic materials was started in 1930 when major thermoplastics such as polystyrene (PS), polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP) and polymethyl methacrylate (PMMA) were developed (Brydson, 1989). Since then, plastics have replaced the conventional materials in many applications ranging from transportation, packaging, building, medical appliances, agricultures and communication. The break-up of these applications in Europe is shown in Figure 1.1. From this figure, 39.4% from 45.9 Mtonne of the total plastics demand came from packaging applications (PEMRG, 2013).

Plastics are one of the major polymer materials used in packaging application because of their matchless characteristics such as low price and can easily be produced in big quantity. In addition, they also exhibit favourable properties such as good mechanical strength and applicable in industrial processing (Tharanathan, 2003; Davis and Song, 2006). In spite of this benefits, plastic industry also significantly contributes to the environmental problem. Disposal of plastic waste is a serious environmental problem. From Figure 1.2, PE, polyethylene terephthalate (PET), PP, PVC and PS from packaging application contribute much to municipal solid waste. Realizing that plastics are prevalent in almost every human activity and the non degradable plastics becoming more and more problematic especially where they are use only a short period of time (Moura and Machado, 2012). In agriculture, plastic films in soil have caused a significant drop in yield. Plastics waste, especially plastics packaging that float in rivers, seas and lakes are endangering the animals that live in those habitats and also threatening the operation of hydropower plants and other public works (Ren, 2003).

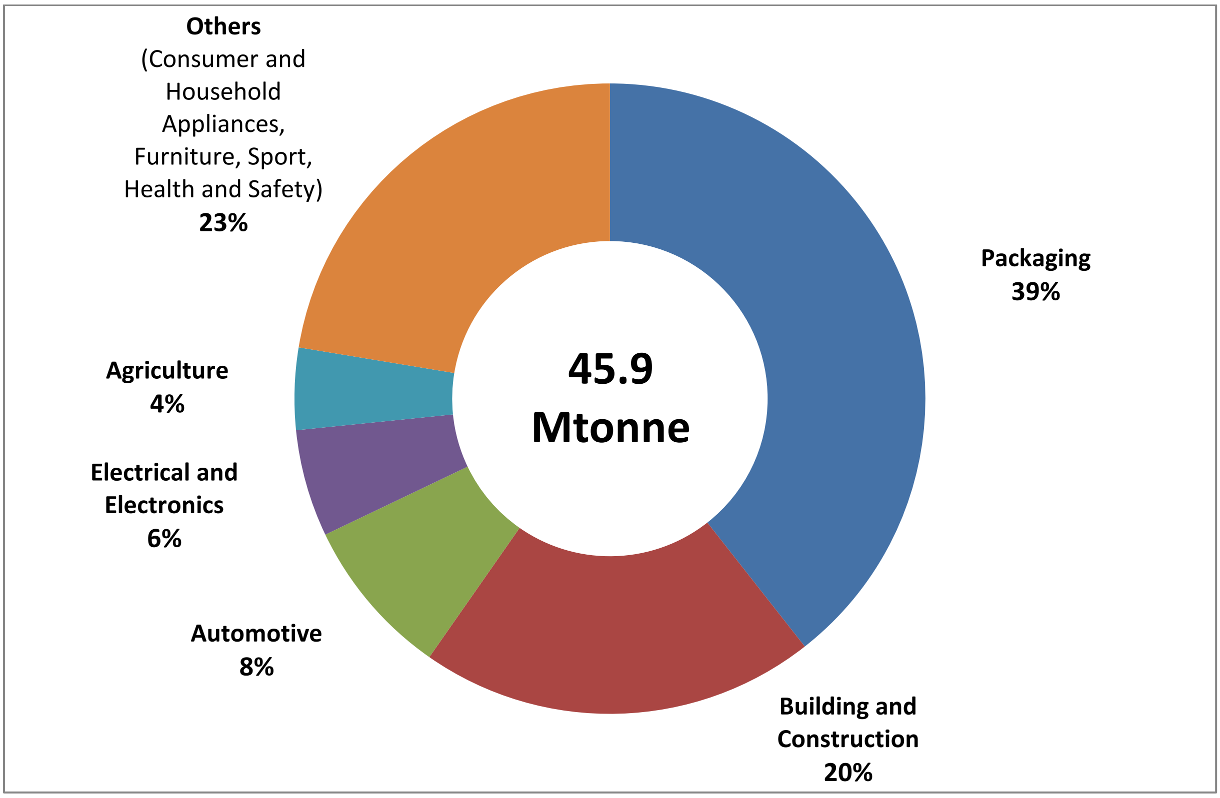


Figure 1.1: European plastic demands by segment in 2012 (PEMRG, 2013).

One of the attempt to overcome the disposal of plastic waste issue is by create a biodegradable polymer. There are several kinds of biodegradable polymers (polylactic acid and polycaprolactone) but polyvinyl alcohol (PVA) is the most promising biodegradable polymer because of its good mechanical properties, excellent chemical resistance, biodegradability, biocompatibility and have potential as water processable polymer (Paradossi *et al*., 2003; Ramaraj, 2007a; Seldarik *et al*., 2007). Matsumura *et al*. (1993) reported that PVA has been confirmed to be biodegradable under aerobic conditions. However, degradation process of pure PVA is quite slow under this condition and the degradation rate of PVA is strongly depends on the residual acetate groups (Corti *et al*., 2002). Another limiting factor of PVA usage is its high cost which has to compete with the low cost conventional plastic in practical application (Ramaraj, 2007b). Hence, in order to enhance the biodegradation rate and reduce the cost, polymer blending has been introduced. For this purpose, the highly polar and water soluble of PVA typically used to blend with more biodegradable, cheaper and easily processable natural filler or polymers.

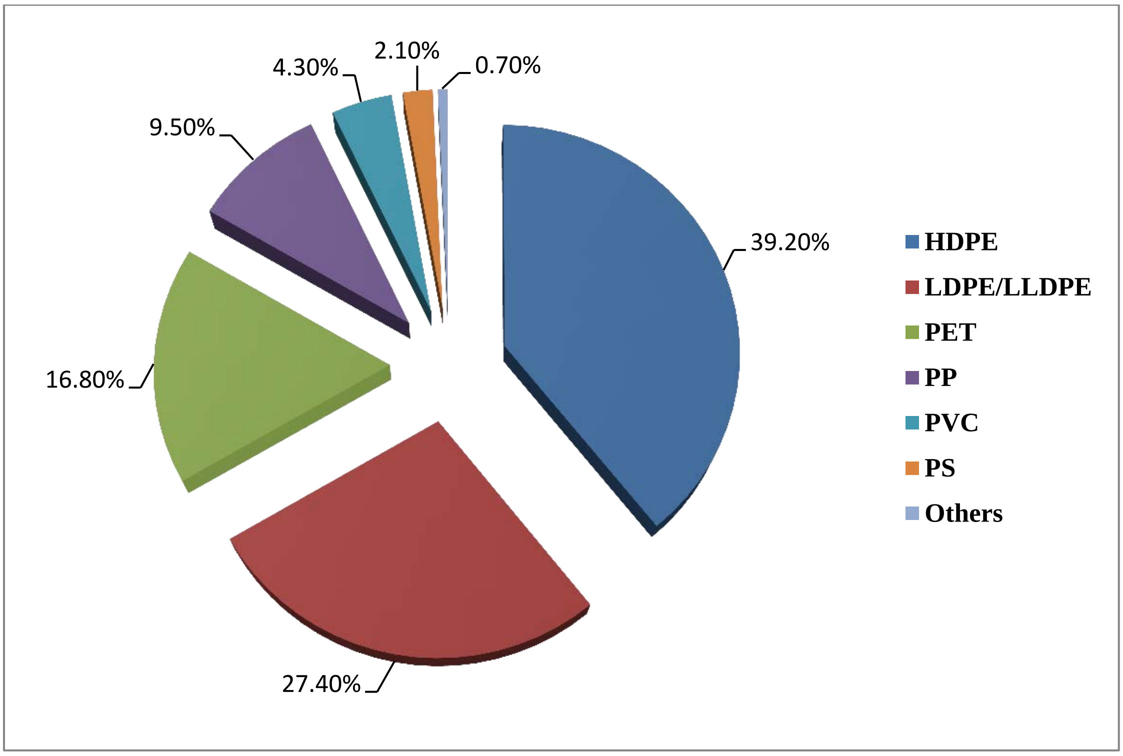


Figure 1.2: Plastic resin in packaging in U.S municipal solid waste stream (PEMRG, 2013).

Various types of starches have been applied in PVA matrices and the biodegradability of the PVA/starches blends has been proven. Beside the starch-based natural polymer, soya protein-based polymer is also a potential natural polymer that can be blended with PVA to reduce the production cost and to accelerate its degradation. Soya bean flour (SBF) actually is a remaining product after removal of soya bean oil (Sam *et al*., 2010). It is not mainly derived from proteins or peptide and less so from carbohydrates (Sam *et al*., 2011). Soya bean is inexpensive, abundantly available and renewability (Jong, 2008). Thus, the investigation of the performance of soya bean products in PVA is a worthwhile effort because the studies of protein in non-food application is still less.

However, the blend of the PVA and SBF has lower tensile properties and water barrier properties. Cajlakovic *et al.* (2002) reported that PVA must be crosslinked in order to be useful for wide variety of application and the crosslinking agents for PVA 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 PVA to form the macromolecular network. In addition, Zhou *et al*. (2008) mentioned that the crosslinking agents were usually added into aqueous solution of PVA/starch mixture followed by casting method in order to improve their physical and mechanical properties. Therefore, by preparing the PVA/SBF blend films, the weak tensile properties will be improved through crosslinking reaction. In this study, hexamethylenetetramine was used to create linkages between the hydroxyl group of the PVA and SBF in order to compare the improvement of tensile properties and water barrier properties.

Recently, ternary composite systems have attracted many researchers attention because of their potential to enhance the present of the composite system. The system can be developed either by polymer blend plus filler or hybrid of filler with polymer matrix. In this research, two different types of filler (banana frond flour and halloysite nanotubes) were added to PVA/SBF blend to form ternary blend films. 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. 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) for the preparation of low cost biodegradable polymer. In this research, banana frond flour (BFF) has been used. Banana frond (*Musacea* family) is known to have high content of cellulose, which can be the substrate for microorganisms reactions. Agricultural activity involving banana generates large amounts of residues, because each plant produces only one bunch of bananas. After harvesting the fruits, banana frond and stem are cut and usually left in the soil plantation to be used as organic material (Abdul Khalil *et al*., 2006). Therefore, by utilizing these wastes, it is hoped to be a way of disposing the waste, it is hoped to be a way of disposing the waste instead of forgo them. Moreover using banana frond/stem can significantly reduce the cost of the biodegradable film production as it is cheap and widely available. Besides agricultural waste, incorporation of nanofiller will hopefully enhance the mechanical and thermal properties of the blend films and decrease the water uptake. The addition of halloysite nanotubes (HNT) will improve the performance of PVA/SBF blend films. HNT are inorganic clay minerals with a unique tubular structure (Liu *et al.*, 2007). The HNT are formed by the hydrothermal alteration of aluminosilicate minerals. These HNT have very high aspect ratios which are critical to the polymer binding process. Alumina and silica groups are located on the surfaces of HNT especially on their crystal edges (Zhou *et al*. 2010).

From the previous series of study, PVA/SBF/HNT blend films show better tensile properties and water capabilty compare to the PVA/SBF/BFF blend films. Therefore, alkaline treatment is needed to impart the properties of PVA/SBF/BFF blend films. Alkali treatment is a common method to clean and modify the fiber surface and enhance interfacial adhesion between a natural fiber and a polymeric matrix. Mohanty *et al*. (2006) reported that fibers are treated with sodium hydroxide (NaOH) to remove lignin, pectin, wax substances and natural oils that cover the surface of the fiber cell wall. Previous studies by several researchers (Edeerozeey et al., 2007; El-Shekeil *et al.,* 2012) have been discussed which alkaline treatment has significantly improved the tensile properties of natural fiber reinforced polymer composites.

1.2 Problem Statement

Today, the petroleum-based plastic takes a long time to degrade, thus caused a serious waste disposal problem to our environment. This is because of the molecular bonds and structure that make them so durable and resistant to natural processes of degradation. Polyolefin are very resistant to hydrolysis and are totally non-biodegradable. As a consequence, the landfill area will have abundance with the plastic waste and definitely lead to another issue including the shortage of landfill availability and soil contamination. Moreover, there are some problems existences from recycling of plastic waste. It was reported that, the recycling process implied to the difficulties of the collection, separation, cleaning and possible contamination on the plastic and hard to find economical viable outlet, where incineration may emit some toxic gas (Averous and Halley, 2009).

As a viable alternative, much effort has been focused in recent years to develop environmental friendly polymer products by incorporating renewable materials. As an added advantage, renewable materials are comparatively less expensive, environmentally friendly and naturally biodegradable. This new polymer cannot replace synthetic polymers in every application but they can result in specific products, especially for those applications in which recovery of plastics is not economically feasible, viable and controllable like one time use plastic (Doane *et al*., 1993).

Polyvinyl alcohol (PVA) is one of biodegradable synthetic polymers. However, the high production cost and slow biodegradation rate of PVA become limiting factor to compete with the low cost synthetic thermoplastic materials especially in commodity usage. In this regards, PVA is well suited to be blended with the low cost natural polymer, agricultural waste and/or byproducts to overcome the limiting factor. In conjunction of economical and ecological issue has led to the idea of waste utilization. The applications of proteins are commonly in food science. However, the studies of protein in non-food application is still less. From all the point above, an attempt is done in this research to investigate the incorporation of soya bean flour (protein) could enhance the biodegradability of biodegradable polymer.

1.3 Research Objectives

The aim of this research is concerned with the biodegradability of polyvinyl alcohol and soya bean flour (PVA/SBF) blend films by using solution casting method. The primarily objectives for this research work are:

i. To determine the effect of adding SBF on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.

ii. To study the effect of hexamethylenetetramine (HMTA) as crosslinker on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.

iii. To investigate the effect of two different types of filler (banana frond flour (BFF), and halloysite nanotubes (HNT)); on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF blend films under natural weathering and soil burial.

iv. To determine the effect of surface treatment on the tensile properties, water barrier properties, morphological studies and degradability of the PVA/SBF/BFF blend film under natural weathering and soil burial.

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 a brief introduction of research background, problem statement and the objectives of this research.

- **Chapter 2** presents an overview of current issue related to the plastic and development of biodegradable films. This chapter also introduces the literature review of this study and will explain in details about biodegradable polymer, polyvinyl alcohol, polyvinyl alcohol blend, soya bean flour, crosslinking agent, filler addition, and modification of the filler. It also discuss about the research that have been done by other researcher.

- **Chapter 3** contains the information about the materials and equipment used in this research. This chapter also contains the methodology and characterization that related to this research.

- **Chapter 4** presents all the results and discussion of this research. The effect of soya bean flour, crosslinker, various fillers and surface treatment will be explained and discussed in term of its tensile properties, water barrier properties and biodegradability. The films were further characterized by using Fourier transform infrared and scanning electron microscope.

- **Chapter 5** presents some concluding remarks on the present study as well as some suggestion for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable Polymers

Biodegradable polymers are one alternative to the non-degradable of petroleum based polymers in order to decrease the solid waste problems created by the plastic waste. The definition of biodegradable polymer varies greatly among scientists, manufactures and consumers. A biodegradable polymer is defined as a plastic that is degraded primarily by the action of naturally occurring microorganisms, such as bacteria, fungi and algae. The indiscriminate discarding of plastics has increased and the waste does not degrade rapidly because synthetic are inert to the immediate attack of microorganisms. The use of biodegradable polymers provides a promising solution to this problem and this theme has been an objective of many researchers (Rutkowska *et al.*, 2002; Stevens, 2002; Utracki, 2002).

Biodegradable polymers can be divided into two main categories which are natural and synthetic biodegradable polymers. Natural biodegradable polymers or biopolymers are polymers that formed in nature during growth cycles of all organisms (Chandra and Rustgi, 1998), including polysaccharides (starch, cellulose, chitin/chitosan and alginic acid); polypeptides of natural origin and bacteria polyesters (polyhydroxybutyrate). Simple sugar such as glucose, fructose and maltose are the basic units in this compound (Danjaji *et al.*, 2000). Some polyester such as polyhydroxylalkanoates is also natural biodegradable polymers. Others naturally occur polymers including proteins, gelatin, silks, shellac and poly (gamma-glutamic acid).

Synthetic biodegradable polymers are normally polymers with hydrolysable backbone or polymers that are sensitive toward photo degradation. Among them aliphatic polyesters, polycaprolactone, polyamides, polyurethanes and polyureas, polyanhydrides and poly (amide-enamine)s (Chandra and Rustgi, 1998). Interestingly, some polymers with carbon backbones such as polyvinyl alcohol (PVA); also categorized as synthetic biodegradable polymers. These polymers (e.g., vinyl polymers) require an oxidation process for biodegradation because they are not susceptible to hydrolysis in general. Most of biodegradable vinyl polymers contain an easily oxidizable functional group and catalysts are added to promote their oxidation or photo oxidation, or both.

2.1.1 Mechanism of Biodegradation

Biodegradation is a chemical degradation of materials provoked by the action of microorganisms. It is expected to be the major mechanism of loss for most chemicals released into the environment (Leja and Lewandowincz, 2010). Its refers to the process of degradation and assimilation of the polymers by living microorganisms to produce degradation products. Fungi, bacteria and algae are the most important organisms in biodegradation (Gautam *et al*., 2007).

Natural polymers such proteins, polysaccharides, nucleic acids are degraded by oxidation and hydrolysis in biological systems (Kyrikou and Briassoulis, 2007). Biodegradable materials degrade into biomass, carbon dioxide and methane. In the case of synthetic polymers, microbial utilization of its carbon backbone as a carbon source is required (Jayasekara *et al*., 2005). The biodegradation process can be divided into aerobic and anaerobic degradation (Figure 2.1).

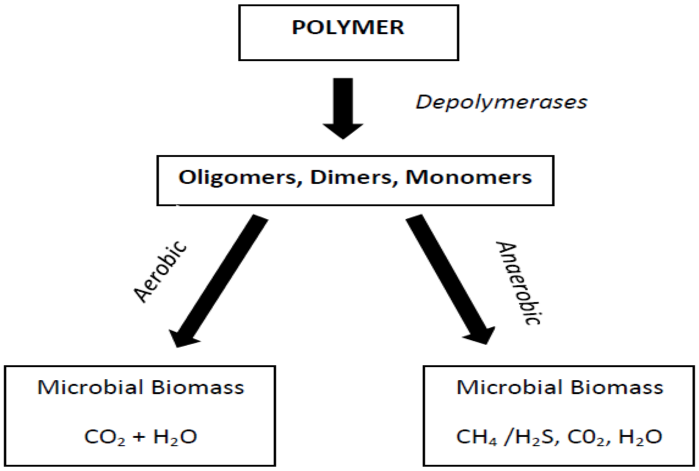


Figure 2.1: Scheme of polymer degradation under aerobic and anaerobic conditions.

Aerobic biodegradation:

$$\text{Polymer} + O_2 \rightarrow CO_2 + H_2O + \text{biomass} + \text{residue(s)} \quad \text{.......} (2.1)$$

Anaerobic biodegradation:

$$\text{Polymer} \rightarrow CO_2 + CH_4 + H_2O + \text{biomass} + \text{residue(s)} \quad \text{.......} (2.2)$$

An aerobic biodegradation (Equation 2.1) occurs with the presence of oxygen and carbon dioxide is produced. Whereas, an anaerobic degradation (Equation 2.2) occurs when there is no oxygen presence and methane is produced instead of carbon dioxide (Kyrikou and Briassoulis, 2007; Grima *et al*., 2002; Gu, 2003; Swift, 1998). Mineralization is a conversion process of biodegradable materials to gases (carbon dioxide, methane, and nitrogen compounds), water, salts, minerals and residual biomass occurs. Mineralization is complete when all the biodegradable materials or biomass are consumed and all the carbon is converted to carbon dioxide (Kyrikou and Briassoulis, 2007). Biodegradable materials have the proven capability to decompose in the most common environment where the material is disposed, within one year, through natural biological processes into non-toxic carbonaceous soil, water or carbon dioxide.

2.1.2 Factors Affecting Polymer Biodegradability

At this present, there are two main types of plastics degradation being researched which are chemical, physical and both are closely inter-connected. Chemical degradation included the reactions of oxidation and hydrolysis (Tidjani *et al*., 1997; Usarat *et al*., 2006; Baljit and Nisha, 2008) while physical degradation involved environmental stress cracking and plasticizer migration and loss (Baljit and Nisha, 2008). Polymer structure, polymer morphology, radiation, chemical treatments and molecular weight are the several factors that affecting the degradability of the polymers.

Polymer structure (amorphous, crystalline and semi crystalline) are really affected the degradability of the polymers. Bastioli (2005) and Lee (2007) mentioned that other chemical properties including the chemical linkages in the polymer backbone, the position and chemical activity of the pendant groups and the chemical activity of the ends groups also important in affecting polymer degradability. Some polymers degrade at a faster rate than others because of their different chemical structures. The chemical structures of the common commodity plastics like polyolefin, which contain the carbon-carbon single bonds in their backbones makes them particularly resistance to degradation (Steven, 2002). Nevertheless, polyvinyl alcohol (PVA) also have the carbon-carbon single bond in their backbone chain, but the presence of hydroxyl groups on the alternate carbon atoms make it hydrophilic. Thus, this hydrophilicity helps to promote degradation of PVA through hydrolysis mechanism.

According to Chandra and Rustgi (1998), morphology will affect the biodegradability of the polymer too. Synthetic polymers that have a short repeating unit will enhance the crystallization to make the hydrozable groups inaccessible to the enzymes. Shape, size and number of the crystallites will pronounced effect on the chain mobility of the amorphous regions and thus affect the biodegradation rate.

The molecular weight distribution of the polymer can have a dramatic effect on rates of degradation. This effect has been demonstrated for a number of polymers, where a critical lower limit must be present before the process will start. The molecular origin for this effect is still subject to speculation, and has been attributed to a range of causes such as changes in enzyme accessibility, chain flexibility, fits with active sites, crystallinity, or other aspects of morphology (Bastioli, 2005; Lee, 2007).

Photolysis, irradiation and oxidation affect the polymer biodegradability by the chain scission and the reduction of molecular weight. The biodegradability rate increase until most of the fragment polymer is consumed. Crosslinked polymer will show a lower biodegradability rate due to the crosslink network present (Chandra and Rustgi, 1998).

2.1.3 Ways to Increase Biodegradability of Polymer

Most of synthetic polymers have very high molecular weights and contain only carbon-carbon bonds. Thus, these types of polymers show little or no susceptibility to enzyme-catalyzed degradation reactions. ‘Weak links’ can be attached or inserted within the polymers that are not readily degraded due to the high molecular weight. These weak links are designed to control the degradation of an initially high molecular weight and hydrophobic polymer into a lower molecular weight oligomer that can be attacked and consumed by the microorganism through the biodegradation process (Chandra and Rustgi, 1998; Baljit and Nisha, 2008). Figure 2.2 shows the inserting main chain ester groups into vinyl type polymers.

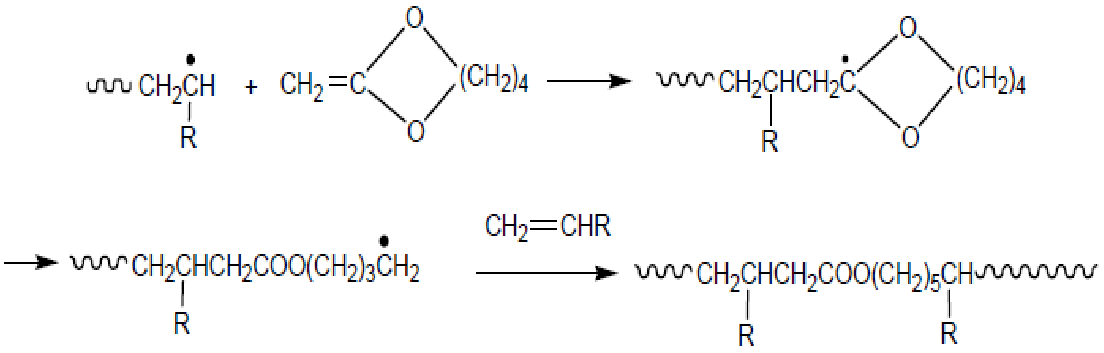


Figure 2.2: Insertion of ester group into vinyl polymer (Baljit and Nisha, 2008).

Preparation of the photodegradable copolymer follows by oxidation is shown in Figure 2.3 and Figure 2.4. These are some of the methods to insert the weak link into a high molecular weight and hydrophobic polymers.

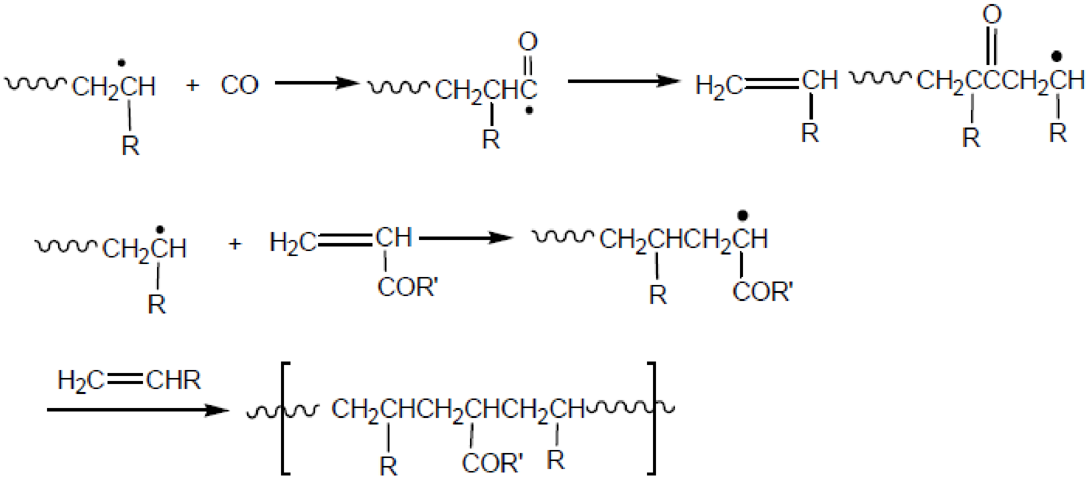


Figure 2.3: Insertion of ketone group into vinyl polymer (Baljit and Nisha, 2008).

From Figure 2.4, Norrish I is the free radical generation and no chain cleavage, and Norrish II is the chain cleavage. Ketones are introduced onto the backbones of polymers by photo oxidation. Under exposure to light, these ketone groups absorb photons of appropriate energy; break the carbon-carbon bonds, and scission the polymer backbone (Feldman, 2002).

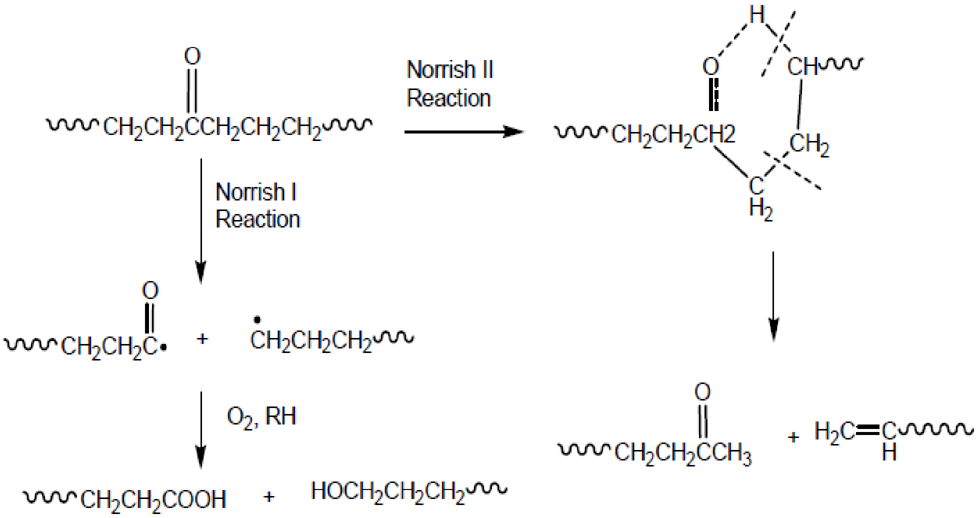
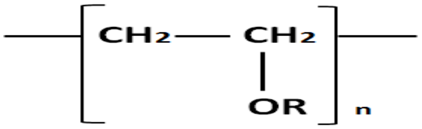


Figure 2.4: Norrish I and Norrish II reaction mechanisms for the degradation of copolymers of ethylene (Baljit and Nisha, 2008).

Blending of biodegradable polymers such as poly (ε-caprolactone) and starch with an inert polymer such as polyethylene is another method to produce a degradable polymer. The idea in this concept is if the biodegradable component is present in sufficient amounts and it is potentially removed by the microorganism, the plastic or film containing the remaining inert will lose its integrity, disintegrate and disappear (Chandra and Rustgi, 1998; Baljit and Nisha, 2008).

2.2 Polyvinyl alcohol

Polyvinyl alcohol (PVA) was discovered in 1915 by F Klatte and the stoichiometric saponification of polyvinyl acetate with caustic soda to yield PVA was first described in 1924 by W. O. Hermann and W. Haehnel. The name of PVA is based on the repeating structural unit, and it is not monomer based (Stevens, 2002). This is because the polymerization takes place on the principle of free radical polymerization of vinyl acetate, followed by alkaline alcoholysis of the functional acetate groups (Chiellini *et al*., 2003). Unlike most of the polymer, PVA faces difficulties to be formed by its own monomer due to the restriction caused by the unstable vinyl that tends to form stable tautomer of acetaldehyde. Molecular structure of PVA is schematically presented in Figure 2.5 and the scheme for industrial production of PVA is given in Figure 2.6.



$$-\left[CH_2-\underset{\displaystyle OR}{\underset{|}{CH_2}}\right]_n-$$

where R = H or $COCH_3$

Figure 2.5: Molecular structure of PVA

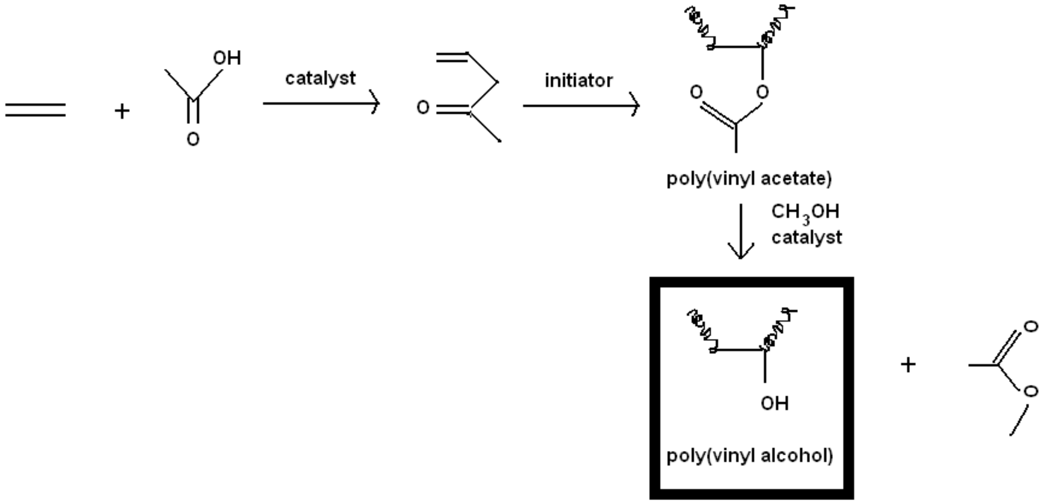


Figure 2.6: Manufacturing route to PVA (Rudnik, 2008**).**

Different grades of PVA were depending on the degree of hydrolysis. Degree of hydrolysis indicates the number of residual acetate group that presence in the polymer which saponification or alcoholysis has not taken place (Goldschmidt and Streitberger, 2003). According to Hutten (2007), there are four different range of hydrolysis are 98 - 99.5 % (fully), 90 – 97 % (intermediate), 86 – 89 % (partially) and 76 - 87.6 % (specialty grades). But, commercially PVA only can be classified into fully or partially hydrolysed as shown in Figure 2.7 (Goswami *et al.*, 2005).

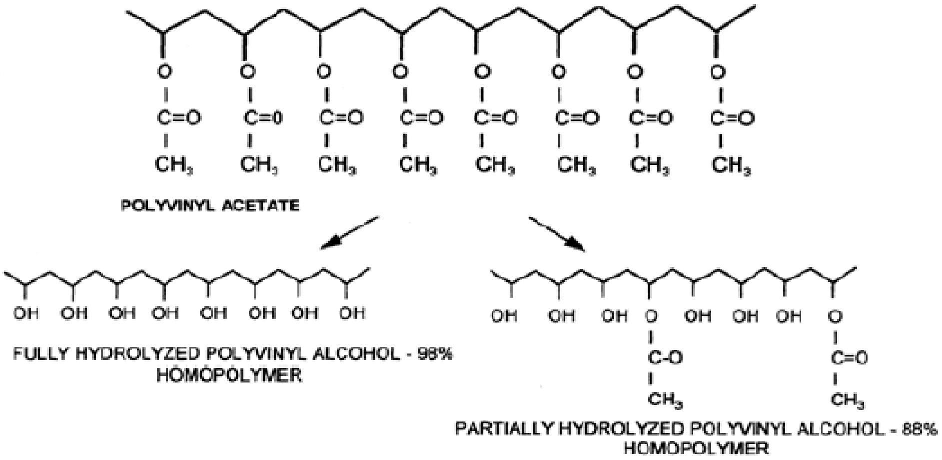


Figure 2.7: Hydrolysis of polyvinyl acetate (PVAc) (Goswami *et al.*, 2005).

The effects of degree of hydrolysis (Hutten, 2007) are shown in Table 2.1. As degree of hydrolysis increased, increment of solvent and water resistance, tensile strength and viscosity can be seen. But, the reduction in stability, hygroscopic and flexibility can be observed as increased in degree of hydrolysis. Figure 2.9 shows a closer look into the effect of degree of hydrolysis on solubility; water molecule would require addition breakage of interchain hydrogen bonding for fully hydrolysed PVA while penetration of water molecule is easy for partially hydrolysed PVA due to the presence of bulky acetate radical which distances the neighbouring chains (Goswami *et al.*, 2005).

Table 2.1: The effect of degree of hydrolysis on the properties of PVA.

Property effect on	Degree of hydrolysis	
	High	Low
Solvent resistance	+	-
Water resistance	+	-
Solubility	-	+
Hygroscopicity	-	+
Tensile strength	+	-
Flexibility	-	+
Viscosity	+	-

Note: "+" indicates the property gets higher or stronger
"-" indicates the property gets lower or weaker

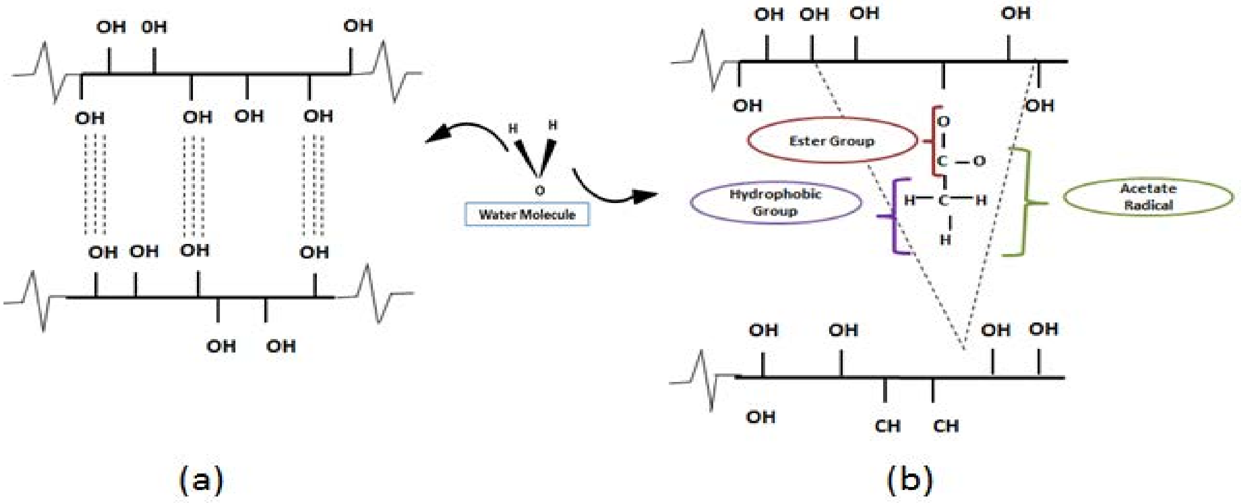


Figure 2.8: Effect of degree of hydrolysis on solubility of PVA; (a) fully hydrolysed segment and (b) partially hydrolysed segment

PVA is a synthetic polymer with its excellent characteristic such as water solubility, good barrier properties to oxygen and oil, good optical and tensile properties, good thermal properties, resistance to organic solvents and oils, non-toxicity and biodegradability under certain conditions (DeMerlis and Schoneker, 2003; Siddaramaiah *et al.*, 2004; Li *et al.*, 2005, Ramaraj, 2007). Siddaramiah *et al.* (2004) reported that PVA also a water processable polymer, thus it allowing the PVA to be produced using solution casting method. Another uniqueness of PVA is its film-forming ability. Therefore, the exceptional properties of PVA have been employed in various application like dip coating, adhesive and solution casting film (Zaikov and Lomakin, 1997; El-Shinawy *et al.*, 1998; Seldarik *et al.*, 2007; Ramaraj, 2007).

PVA is the only synthetic polymers which having carbon-carbon linkages in its backbone and show the biodegradability behavior. This is due to the occurrence of hydroxyl groups on alternate carbon atoms causing enzymatic oxidation of hydroxyl groups from carbonyl groups in the polymer backbone, followed by the hydrolysis of two carbonyl groups causes polymer chain cleavage which resulting to a decrease in molecular weight of PVA (Kale *et al.*, 2007). However, the biodegradability of PVA is low compared to other biodegradable polymer such as poly(lactic acid) and poly(caprolactone) (Ishigaki *et al.*, 1999). The degradation process of pure PVA is quite slow, particularly under anaerobic conditions (Pseja *et al.*, 2006) and the rate of degradation is strongly depends on the residual acetate groups (Corti *et al.*, 2002). However, Lenz (1993) has reported that PVA with an average molecular weight as high as 10^6 could be completely degrade by soil bacteria, especially by *Pseudomonads.*

There are two technologies involved in PVA film production from viscous water solution casting and blown extrusion. Traditionally, most of the plastic are produced by casting method. Recently, with the development in polymer compounding, PVA can be melt-processed. Yang *et al.* (2008) and Zou *et al.* (2008) have applied this process in the extrusion technique for PVA film productions. However, processing at high temperatures is very sensitive to the degradation of PVA. Both solution casting and blown extrusion has its own advantages when it comes to production of PVA film. Solution casting only allows small scale of production and often takes longer time to dry the film. However, it would provide better optical properties, stiffer instant-quenched-film and better gauge control. On the contrary, blown film will have larger variation of 3 % to 4 % of gauge control range as compared to solution casting of only 1 % to 2 %. Furthermore, blown film would be able to produce biaxial orientation with lesser scrap and also permits some post-processing in one continuous process such as heat seal and winding up for stock keeping (Giles *et al.*, 2005).

2.3 Polyvinyl Alcohol Blend

The commercial development of polymer blends was rapid growth in the late 1960’s by gaining major interest for many researchers, especially in polymer industry since the polymer blend could potentially offer a large number of different commercial products with the desirable properties (Robeson, 2007). The main reason for blending is to meet the desirable properties with adjusting the cost-performance balance and tailor with the current technology to fabricate product for end use application. According to Utracki (2002), there are several important factors that contribute to the interest in polymer blends. Polymer blends offer useful and economic means of upgrading recycled and off-specification polymers. Polymer blending is a way to develop a new product by blending of two or more commercially available polymer. This is more cost-effective way than totally develop a new polymer which involving high research and cost to meet the customer and market requirements. Moreover, polymer blending allows custom production of different blends in a wide range of production volumes. Contrarily, the polymerization plant for a new polymer is not as flexible and not economical for small volumes production. Polymer blending can be done at relatively low cost conventional equipment compared to new polymer requires high investment risk to develop intensive plant and reactor for the production and research purpose. Other than that, polymer blends can be generated, formulated, optimized and even commercialized at a faster rate than new polymer.

Developments of environmental friendly polymer material have been classified into two categories based on their raw material; degradable synthetic polymer and renewable natural polymers (Yang *et al.*, 2004). The renewable natural polymers include starch, gelatin, protein, cellulose, chitosan are tested alone or blend with other polymer to enhance the polymer properties and biodegradability.

2.3.1 Polyvinyl Alcohol Blend with Starch

PVA/starch blend plastics are one of the most popular types for biodegradable plastics application, and are widely used in packaging and agricultural mulch films (Bastioli *et al.,* 1993). Many researchers have been developed for PVA/starch blend and improvements have been done in the formulation to increase its compatibility, strength and modulus of the film (Chen *et al.,*