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PREPARATION, CHARACTERIZATION AND PROPERTIES OF DEGRADABLE LINEAR LOW DENSITY POLYETHYLENE/SOYA POWDER BLENDS

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2011

PREPARATION, CHARACTERIZATION AND PROPERTIES OF DEGRADABLE LINEAR LOW DENSITY POLYETHYLENE/SOYA POWDER BLENDS

by

SAM SUNG TING

Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

August 2011

ACKNOWLEDGEMENTS

I would like to express my deepest and sincere gratitude to my supervisor, Prof. Dr. Hanafi Ismail. His wide knowledge has been of great value for me. His understanding, encouragement and personal guidance have provided a good basis for the present thesis. I wish to express my warm and sincere thanks to my co-supervisor Associate Prof. Dr. Zulkifli Ahmad. His comments and suggestions are useful in my thesis.

I would also like to thank the Dean of School of Materials and Mineral Resources Engineering, Prof. Dr. Ahmad Fauzi bin Mohd Noor for his concern and valuable help during my study. Special thanks to Mr. Segaran a/l N.B. Dorai, Mr. Shahril, Muhammad Sofi, Mr. Mohammad bin Hassan and Mr. Rashid Selamat, Mr. Mohd. Faizal Mohd. Kassim and Mdm. Fong Lee Lee. They are willing to help students in conducting experiment in lab. They had also taught me a lot of technical knowledge. I wish to extend my warmest thanks to Associate Prof. Dr. Sudesh Kumar in School of Biological Sciences USM and Nucleur Malaysia for providing testing facilities in my research.

I owe my loving thanks to my parents, brother, sister and my wife, Teoh Wan Yeong. Without their encouragement and understanding it would have been impossible for me to finish this work. My special gratitude is due to my postgraduate friends. They let me own a happy life in USM.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CS	Cobalt stearate
DSC	Differential Scanning Calorimetry
EB	Electron beam
E_b	Elongation at break
ENR 50	Epoxidised natural rubber with 50 mol% epoxidation
FTIR	Fourier Transform Infrared Spectrometer
GPC	Gel Permeation Chromatography
LLDPE	Linear low density polyethylene
PE-g-MA	Polyethylene grafted maleic anhydride
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis

LIST OF SYMBOLS

ΔH_m	Melting enthalpy
ΔH_f^0	Heat of fusion
ΔH_f*	Heat of fusion for the semicrystalline
M_n	number molecular weight
M_w	weight molecular weight
$T_{-5\%}$	Temperature at 5% degradation
$T_{-30\%}$	Temperature at 30% degradation
T_c	Crystalline temperature
T_m	Melting temperature
W_i	Weight before degradation
W_f	Weight after degradation
wt%	percentage in weight

LIST OF PUBLICATIONS

International Peer Review Journal

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PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT ADUNAN POLIETILENA LINEAR BERKETUMPATAN RENDAH/SERBUK SOYA TERBOLEHURAI

ABSTRAK

Polietilena linear berketumpatan rendah (LLDPE) diadun dengan serbuk soya dengan menggunakan pengadun dalaman Haake pada suhu 150^{o}C dan kelajuan rotor 50 rpm. Sifat tegangan adunan diuji dengan menggunakan tensometer Instron. Sifat-sifat terma adunan dianalisis dengan menggunakan kalorimeter pengimbasan pembezaan (DSC). Kestabilan termal adunan ditentukan dengan analisis termagravimetrik (TGA). Kandungan serbuk soya telah divariasikan dari 5 hingga 40 wt%. Dua jenis agen pengserasi iaitu maleik anhidrida tergraf polietilena (PE-g-MA) dan getah asli terepoksida dengan 50 mol% (ENR 50) telah digunakan untuk meningkatkan lekatan antara muka adunan LLDPE/serbuk soya. Kekuatan tegangan dan pemanjangan pada takat putus (E_b) menurun dengan peningkatan kandungan serbuk soya. Penambahan PE-g-MA sebagai agen penserasi telah meningkatkan kekuatan regangan, E_b dan modulus adunan. Selain daripada itu, kekuatan regangan, E_b dan kestabilan terma telah diperbaiki dengan penambahan ENR 50. Dalam ujian pencuacaan dan penanaman tanah semulajadi selama 1 tahun, penambahan serbuk soya didapati telah meningkatkan tahap degradasi selepas pengujian. Bagaimanapun, adunan terserasi dengan PE-g-MA menunjukkan tahap degradasi yang lebih rendah daripada adunan tanpa agen penserasi berdasarkan pengajian sifat-sifat tegangan, indeks karbonil, kehabluran, kehilangan berat dan perubahan jisim molekul. Adunan terserasi dengan ENR 50 menunjukkan tahap degradasi yang lebih tinggi berbanding adunan tanpa penserasi.

Adunan terserasi dengan ENR 50 telah diiradiasi dengan alur elektron (EB) pada dos tetap 30 kGy. Kandungan gel didapati meningkat selepas radiasi EB. Namun, peningkatan kandungan serbuk soya telah menghalang peningkatan kandungan gel

adunan. Kekuatan regangan dan modulus Young adunan ditingkatkan oleh EB manakala nilai E_b didapati menurun. Analisis lanjutan adunan diradiasi menggunakan spektrum FTIR menunjukkan bahawa peningkatan produk teroksida selepas rawatan radiasi. Suhu lebur adunan menurun selepas radiasi EB manakala kehabluran meningkat. Radiasi juga meningkatkan kestabilan terma adunan. Selepas ujian pencuacaan dan penanaman tanah semulajadi, degradasi aduan diradiasi didapati lebih rendah daripada adunan tidak diradiasi.

Kobalt stearat (CS) digunakan sebagai pro-oksidan. Berdasarkan keputusan ujian tegangan, morfologi, kehabluran dan kehilangan berat, didapati tahap degradasi adunan dengan penambahan CS lebih tinggi daripada adunan tanpa CS. Tempoh pencuacaan dan penanaman tanah semulajadi dijalankan selama 6 bulan. Ini kerana adunan yang dicampurkan dengan CS mudah terdegradasi dan hancur selepas didedahkan selama 6 bulan.

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CHAPTER 1

INTRODUCTION

1.1 Overview

Today, the production of the polyolefins such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polystyrene (PS) contributed 23,000 kilo tons annually from 2004-2008 based on Global Commodity Polymer Capacity (Nayak, 2009). The application of the polyolefin includes container, bottle, tubing and plastic bag. The advantages of using polyolefin are light weight, durable and cheap. Therefore, it becomes an important material for human being in 21st century.

Polyolefins are non-degradable polymer as they are chemically and thermally stable. They create a lot of solid waste problems to the environment. Therefore, a degradable polymer is needed to overcome the problem. One of the alternatives is to replace the non-degradable plastic with biopolymer. As well known, biopolymers are polymers produced from the biomass such as potatoes, wheat, corn or sugar beets. The biopolymers are not only biodegradable and some compostable, they are also renewable and sustainable. A lot of research has been done of these biopolymers in recent years based on the review of Madhavan Nampoothiri et al. (2010). These biopolymers have been achieved comparable rheological, mechanical, thermal and physical properties as polyolefin. Though, the cost of these materials is far expensive compared to conventional polyolefin products. Thus, most of the biopolymers are used in medical application rather than packaging purpose.

In order to produce a low cost and degradable polymer, polysaccharides based materials are commonly used in blends or as filler in polyolefin. The polysaccharides which are regularly incorporated in polyolefin are corn starch, rice starch, sago

starch, tapioca starch and banana starch. Some researchers (Sangawar et al., 2009; Borghei et al., 2010; Bikiaris et al., 1997) studied on the effect of microbial degradation of LDPE/starch blends using soil burial test. When these blends are buried into soil, various microorganisms consume the starch and leaving the blends with a lot of voids. This allowed the blends easier to be fragmented into small pieces and create bigger surface area for the degradation.

Another approach is to partially replace the polyolefins with protein based natural polymer. Until today, most of the application of protein was focusing in food sciences (Swain et al. 2004). The protein based natural polymer can be extracted from soya bean. Soya bean contribute a huge agricultural production since hundred years ago. World Agricultural Supply and Demand Estimates (2010) reported that soya bean exports are increased 50 million bushels to 1.485 billion in 2010 indicating increase in global import demand, especially for China. From the statistic, one can be deduced that soya bean is available abundantly and easily renewable natural resources. Thus, research need to be developed to maximized the usage of the soya bean products. Basically soya bean is not only used to produce oil products, but other value added products such as defatted soya flour, proteins concentrate and protein isolate. Defatted soya flour (soya powder) has the most protein constituent in composition and has been used in current research.

In current study, polyethylene grafted maleic anhydride (PE-g-MA) was used as a compatibiliser. This compatibiliser was first used to compatibilise the polyolefin and protein based natural polymer. Previously, it was used in compatibilising thermoplastic sago starch and low density polyethylene (LDPE) (Ning et al., 2007), nanoclay and PE (Sheshmani et al., 2010), esterified lignin and lignocellulosic filler and high density polyethylene (Zabihzadeh, 2010). Despite of using grafted type

compatibiliser, an elastomeric type of compatibiliser was also used in present study. Epoxidised natural rubber with 50 mol% epoxidation (ENR 50) has been applied to compatibilised PE and soya powder. There is not much study in the utilization of ENR 50 as a compatibiliser in polyolefin. Commonly, ENR 50 was used to compatibilise the elastomer-elastomer blends or elastomer-polyolefin blends. Kantala et al. (2009) used ENR to compatibilise natural rubber (NR)/ nitrile butadiene rubber (NBR) blends whereas Yong et al. (2007) studied the effect of ENR as a compatibiliser in ethylene vinyl acetate (EVA)/Natural rubber (SMR L) blends.

Apart from using compatibiliser to enhance the interfacial adhesion between polyolefin and soya powder, radiation technology has commonly been used to enhance the physical and mechanical properties of plastic materials due to the chemical reaction between polymer molecules under irradiation. In this study, electron beam (EB) irradiation was used to irradiate the blends due to the following advantages (a) high dose rate achievable, (b) safe and easy to operate, and (c) radiation dose and rate are easy to be controlled (Riganakos et al., 1999). EB irradiation has been used in polymer technology to improve the compatibility between polymer blends, for examples PP/epoxidised natural rubber blends (Meligi et al., 2009), starch modified polypropylene blends (Senna et al., 2008) and low density polyethylene (LDPE)/ plasticized starch blends (Senna et al., 2010). However, not much work is reported on polyethylene/protein based polymer blends.

Pro-oxidants are normally used for the initiation of degradation include organosoluble transition metal ions, aromatic ketones, dithiocarbamates, acetyl acetonates which act as thermal or photo-oxidant for the polymer . Pro-oxidant act as initiators for the oxidation of the polyolefins, consequently cleaved the chain of polymer to a lower molecular weight products. The smaller segment of polymer

chain can become nutrient for microorganism (Reddy et al., 2009). Based on the study of Roy et al. (2007), cobalt stearate has contributed the highest degradability to LDPE compared to other cobalt carboxylates namely palmitate and laurate. Therefore, cobalt stearate has been applied as pro-oxidant in present study.

1.2 Problem Statement

Today, polyolefin caused a serious solid waste disposal problem to our environment due to its behavior of high resistant to environmental influences. Polyolefin are highly sustained to the sunlight, humidity, heat and microorganism because their backbones are solely made of carbon and hydrogen atoms. Among the polyolefin, PE is the most common contributor to the plastic waste as it has been used in various packaging application. Many efforts have been done on recycling the PE in few options includes mechanical recycling, feedstock recycling and energy recovery. However, the plastic waste that success to be recycled is not in satisfactory amount. In order to solve the landfill problem that brought by plastic waste, a replacement is needed.

The partially replacement of polyolefin with soya products is essential to produce a degradable plastic materials and consequently resolve the landfill problem resulted from non-degradable plastic. However, compatibilisation is one the challenge when the soya products used in blends with polyolefin. Soya powder is hydrophilic materials due to the hydroxyl functional group in its compositions. On the other hand, polyolefin such as PE is hydrophobic due to its hydrocarbon structure. Therefore, both materials are not compatible naturally. Compatibiliser is needed to compatibilise both materials in order to improve some properties of the blends.

The degradability of the polyolefin/natural polymer blends was always an issue

among researchers. One claim that natural polymer is the only component in polyolefin/natural polymer blends that can be degraded during degradation test. At the same time, the non-degradable component is still remains. Nevertheless, the present study has been overcome this issue by incorporating the pro-oxidant in the blends.

1.3 Objectives of Study

1. To study the effect of soya powder content on the properties of LLDPE/soya powder blends
2. To utilize PE-g-MA and ENR 50 in compatibilising LLDPE/soya powder blends.
3. To study the degradability effect of LLDPE/soya powder blends by natural weathering and natural soil burial test.
4. To improve the blending efficiency of LLDPE/soya powder blends by using EB irradiation
5. To investigate the effect of cobalt stearate on LLDPE/soya powder blends in natural weathering and natural soil burial.

1.4 Organization of Thesis

This thesis contains 8 chapters and the information is based on research interest as following:

Chapter 1 introduces briefly the coverage of the thesis. It includes introduction about research background, problem statement, and objective of the research work.

Chapter 2 reviews the previous research findings that have been done on degradability of petroleum based polymers and natural polymer blends. This chapter

includes the methods and materials that can be applied to improve the degradability.

Chapter 3 includes information about the material's specifications, equipments and the testing procedures in current research.

Chapter 4 discusses the effect of soya powder content and PE-g-MA as a compatibiliser in LLDPE on rheological, tensile, morphological, physical and thermal properties. This chapter also reviews the degradability of uncompatibilised and compatibilised blends via natural weathering and natural soil burial test.

Chapter 5 reviews the effect of soya powder content and ENR 50 as a compatibiliser in LLDPE on rheological, tensile, morphological, physical and thermal properties. This chapter also discusses the degradability of uncompatibilised and compatibilised blends via natural weathering and natural soil burial tests.

Chapter 6 discusses the effect of EB irradiation on the ENR 50 compatibilised LLDPE/soya powder blends. Natural weathering and natural soil burial tests were also used to evaluate the degradability of EB irradiated blends

Chapter 7 reviews the degradability of LLDPE/soya powder blends with the addition of cobalt stearate and ENR 50 via natural weathering and natural soil burial test

Chapter 8 deduces the findings in the research carried out. Some recommendations of has been proposed to enhance the quality of future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Solid Waste Issue

In 21st century, solid waste is becoming a critical issue globally. The rapid growth of population and urbanization contribute to the significant decrease of landfill space. At the same time, there is around 90% of the municipal solid waste (MSW) was disposed by landfilling (Susan et al., 2004). The MSW disposal is a very crucial problem especially in the area near to cities. According to Kathirvale et al. (2004), an average of 2500 ton of municipal solid waste (MSW) is collected every day for the city of Kuala Lumpur and is being dumped at one of the housing area for landfilling. The quantity of MSW is increasing years over years. There are several published reports shows the composition of MSW (Figure 2.1). From the data shown (Figure 2.1), packaging materials is one of the contributors to the MSW. As well known, a lot of packaging materials are produced from plastics. Thus, the effort in reducing the plastic waste is required in order to reducing the burden of landfilling.

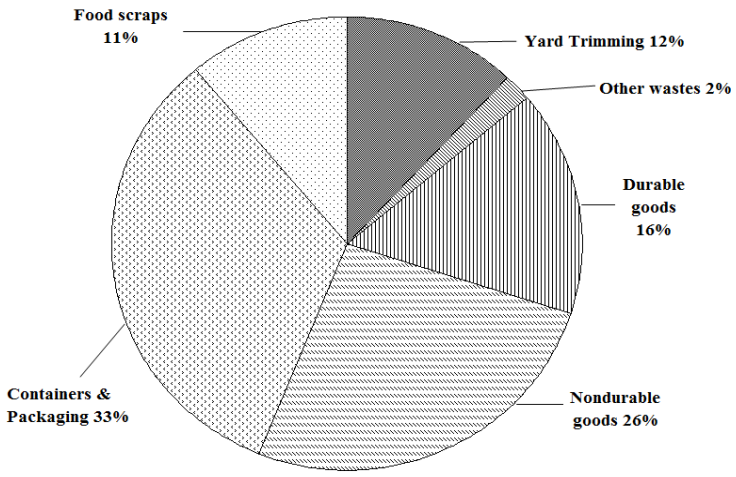

Figure 2.1: The products contributed to municipal waste (Susan et al., 2004)

PE is one of the most widely used polymers due to its wide applications such as bottles, containers and consumer goods. For bottles and container application, high density polyethylene (HDPE) is an interesting source of recycled material because of two main factors, (1) it cannot be used again in alimentary applications and (2) it is very difficult to make direct transformation via injection molding due to its high melting viscosity. There are a few potential application for recycled HDPE such as boxes or pallets, whenever the thermal, mechanical and impact properties of the recycled polymer are close to virgin material (Sánchez-Soto et al., 2008). On the other hand, low density polyethylene (LDPE) is mostly used in plastic film products, for example plastic bag. Basically, recycling of LDPE packaging is directed at stretch wrap, collected from business, at merchandise sacks and collected from consumers through drop-off sites located at stores. There is only little recycling of LDPE postconsumer products because the plastic bags of LDPE is very difficult to be collected. According to Susan et al. (2004), the most common products from recycle LDPE are plastic lumber, merchandise bags, bubble wrap and housewares.

Although plastic recycling is a good technology to reduce the plastic waste in the environment, there are a lot of difficulties during recycling. The cost of recycling is sometimes higher than the production of virgin products. It is because contamination of the postconsumer products is not easy to be controlled. In the aspect of technology, the design of many plastic containers was brilliant. Some of the containers are produced using multiple layers of lightweight, micro-thin plastic sheets with each layer a different plastic serving a different purpose. Therefore, these containers are very difficult to go through recycling process.

Apart from plastic recycling, environmental degradable polymer need to be developed in order to reduce the plastic based MSW in the environment. In recent

years, numerous numbers of researches have been developed on environmental degradable polymer. There are few types of polymer which can degrade in the environment such as biopolymers, modified biopolymers and polymer blends. Among the biopolymers, polyesters play an important role due to their potentially hydrolysable ester bonds. Biodegradable polyesters that are available commercially includes polyhydroxyalkanoate (PHA), polyhydroxyhexanoate (PHH), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polylactic acid (PLA), polycaprolactone (PCL), polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA). PLA is petroleum derived products that can be produced on a mass scale by the microbial fermentation of agricultural by-products mainly the carbohydrate rich substances (John et al., 2006). The blends of non-degradable polymer and polysaccharide based natural polymer have been the subject of research interest. The blends of polyolefins with various starches (Kang et al. 1996, Mani and Bhattacharya, 1998, Ramkumar and Bhattacharya, 1997) can meet to some extent of requirement of mechanical properties, thermal properties and processing behavior close to virgin polymers. Therefore, the non-degradable polymer/natural polymers blends are very popular in degradable plastic industry.

2.2 Degradable Polymer

Basically, degradable polymers are polymers that can undergo significant change in its chemical structure under specific environmental condition, the changes in properties can be measured by appropriate standard test method as a function of exposure time (Albertsson and Huang, 1995). Generally, degradable polymer can be divided in three major categories which are natural polymer, biopolymer and degradable polymer blends and composites.

2.2.1 Natural polymer

Nature can provide an impressive array of polymers that can be used in various forms such as fibers, adhesives, coating, gels, foams, thermoplastics and thermoset resins. Most of the naturally occurring polymer are derived from renewable resources are available for various material applications. Natural polymer can be classified according to their physical character. Starch granules and cellulose fibers are the most common polysaccharides that were classified into different group according to their chemical structure (Long Yu, 2009).

Starch is polysaccharides that are produced by higher plants as energy storage. The starches that are available in the market are corn, rice, wheat, potato and tapioca. Starch granules are heterogeneous materials as it contains both linear and branched structures. Physically, it was formed by both amorphous and crystalline regions. Figure 2.2 shows the common structures of starch. The left hand side is linear structures of starch whereas the right hand side is branch structures (Long Yu, 2009)

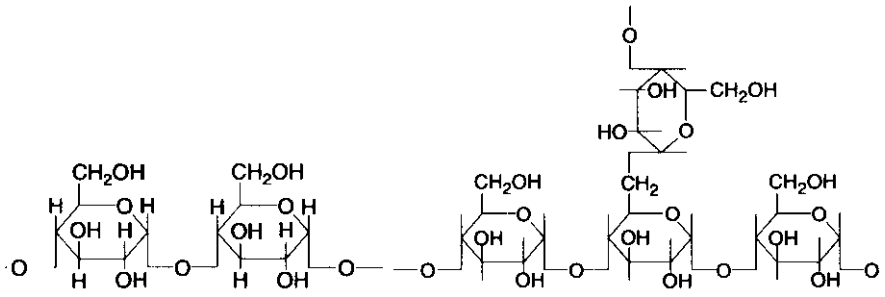

Figure 2.2: Chemical structures of amylase (left) and amylopectin (right) in starch molecules (Long Yu, 2009)

Most starches are semicrystalline with a crystallinity of 20-45%. The amorphous region was formed from amylose and the branching of amylopectin. The main crystalline component in starch was the short branching chains in the amylopectin.

Weight-average molecular weight (M_w) of amylopectin can be determined using high-performance size-exclusion chromatography. Stevenson et al. (2006) has studied the structure and amylopectin of apple starch. According to the research, the polydispersity (M_w/M_n) of molecular weight of Granny Smith, Jonagold and Royal Gala amylopectin was lower than other common starches. The apparent and absolute amylose contents of starch can be determined by measuring iodine affinities of defatted whole starch and of amylopectin fraction using a potentiometric autotitrator (Stevenson, et al., 2006). From their measurement, the absolute amylose content was not much different among the apple cultivars. The iodine affinities of apple whole starch and of amylopectin were larger than that of most local starches reported. The high iodine affinity of the amylopectin implied that the amylopectin molecules consisted of long branch-chains. Based on the calculation, the absolute amylose contents of apple starches (26.0–29.3%) were considerably higher than that reported for starch from corn (21.4–22.5%), potato (16.9–19.8%), rice (20.5%) and wheat (21.6–25.8%). From the analysis by Van Hung and Morita (2007), the actual amylose contents of famous starch, kudzu, was 22.2–22.9%. However, the kudzu starch from Vietnam had lower apparent amylose content than the others.

Some of the agricultural byproducts such as cornhusks, corn stalks, pineapple and banana leaves, and coconut husks have been processed to obtain natural cellulose fibers. Reddy and Yang (2006) had used the rice and wheat straw on the production of high-quality natural cellulose fibers because they are cheap and abundant. Cotton stalks were also used to produce natural cellulose but the surface is coarser than that of cotton and linen due to the presence of short single cells and the formation of the fibers by a bundle of single cells results (Reddy and Yang, 2009). Cotton stalk fibers have medium modulus in between cotton and linen, therefore fibers obtained from

cotton stalks is not flexible as cotton but not as rigid as linen. Moisture regain of cotton stalk fibers is similar to that of cotton and lower than that of linen (Reddy and Yang, 2009).

Chitin is one of the abundant natural polymers after cellulose. Chitin can be found in many invertebrate animals such as insects and crustaceans. Crabs and shrimps are the source of the most easily isolated chitin for marine crustaceans. This material is important in many life forms as their structural component. Generally, when the deacetylation of chitin approaching 50%, it becomes soluble in dilute acid and formed chitosan. A representative chemical structure is shown in Figure 2.3 (Long Yu, 2009). Chitin and chitosan have various applications in medical, food industry and waste water treatment. Therefore, research need to be developed in order to fully explore the potential of these biomacromolecules.

Besides the polysaccharides, protein is one of the important classes of natural polymer. It is one of the three essential macromolecules in biological system and can easily be isolated from natural resources. The source, macromolecular structure and further development of protein based natural polymer will be discussed in section 2.6.

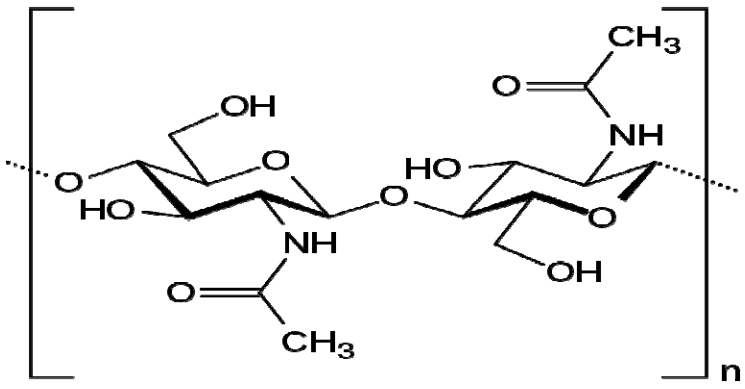

Figure 2.3: Chemical structure of chitin (Long Yu, 2009)

2.2.2 Synthetic Biopolymers

Nowadays, synthetic polymers using bio-derived monomers are practically important for the production of biodegradable polymer from renewable resources. One of the most promising polymers in this regard is poly (lactic acid) (PLA) is one of the most popular biopolymer that is using in various applications. The source of PLA was obtained from agricultural products and is readily biodegradable (Long Yu, 2009). The monomer of the poly (lactic acid), 2-hydroxypropionic acid (CH_3–CHOHCOOH), is the most widely occurring hydroxycarboxylic acid due to its versatile uses in food, pharmaceutical, textile, leather and chemical industries. The monomer is a natural organic acid that can be produced by chemical synthesis or fermentation. There are two chemical routes for chemical synthesized lactic acid. The common process is the hydrolysis of lactonitrile by strong acids, which provide only the racemic mixture of d-and l-lactic acid. On the other hand, lactic acid can also be obtained by base catalyzed degradation of sugars; oxidation of propylene glycol; reaction of acetaldehyde, carbon monoxide, and water at elevated temperatures and pressures (Madhavan Nampoothiri et al., 2010).

The general molecular structure of PLA is shown in Figure 2.4. The lactic acid can be easily converted to polyester via a polycondensation reaction due to the existence of both a hydroxyl and a carboxyl group. However, molecular weight of lactic acid is not significantly increase via conventional condensation polymerization unless organic solvents are used for azeotropic distillation of condensation water and prolong of polymerization time. The esterification process can be accelerated by the addition of acidic catalysts, such as boric or sulfuric acid accelerates, yet side reaction was catalyzed at high temperatures. Crystallization of PLA in the form of stereo complex leads to a brittle mechanical behavior (Sarasua et al., 1998). PLA is a

clear, colorless thermoplastic when quenched from the melt and the physical appearance is similar to polystyrene. PLA can be processed into fiber and film as common thermoplastic. The melting temperature of PLLA can be increased 40–50°C and its heat deflection temperature can be increased from approximately 60–190°C by physically blending the polymer with PDLA. Therefore, PDLA and PLLA can form a highly regular stereo complex with high crystallinity (Sarasua et al., 1998).

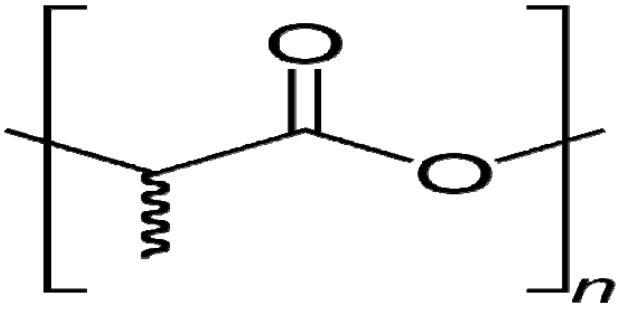

Figure 2.4: Molecular structure of PLA (Sarasua et al., 1998)

PLA can also be blended with other polymers in order to improve some properties or reduce the production cost. PLA is frequently blended with starch to increase biodegradability and reduce costs. The starch content in PLA–starch blend is important to determine mechanical and thermal properties of blends. Natural fibers have been incorporated into the PLA in order to improve some of the mechanical properties. Tanaka et al. (2010) has investigated the use of jute fiber into PLA to form composites. The impact strength of PLA was improved by the addition of jute fiber. Van Den Oever et al. (2010) found that the incorporation of agrofiber can accelerate the degradation properties of PLA. Singh et al. (2010) has improved the tensile strength and elongation at break of PLA by blending PLA and LLDPE. Nevertheless, the compatibiliser is needed in most of the PLA blends and PLA composites to further improve the mechanical strength.

Polyhydroxyalkanoates (PHA) are of one of the hydroxyalkanoates polyesters which are synthesized by many gram-positive and gram-negative bacteria from at least 75 different genera. These polymers are accumulated to levels as high as 90% of the cell dry weight under nutrient stress conditions and act as a carbon and energy reserve poly(3HB), a low molecular weight non-storage PHA have been detected in the cytoplasmic membrane and cytoplasm of Escherichia coli. There around 100 different types monomer have been recognized as constituents of the storage PHA. Figure 2.5 shows the chemical structure of PHA. Therefore, there is flexibility in producing the biodegradable polymers with an extensive range of properties. The molecular weight of PHA ranged from 50,000 to 1,000,000 Da. The PHA are produced from natural resources which are non-toxic and biocompatible with high degree of polymerization and crystallinity (Reddy et al., 2003).

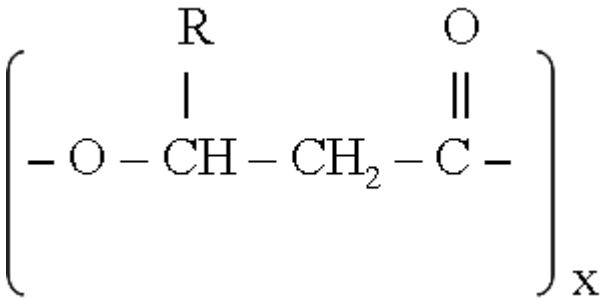

Figure 2.5: Chemical structure of PHA

PHA can be degraded upon exposure to soil, marine sediment or outdoor weathering. Many factors can affect the biodegradation of the PHA such as moisture, temperature, pH and exposed surface area (Boopathy, 2000). According to Lee (1996), the polymer composition and crystallinity can affect the biodegradation of PHA. Hydroxyacids, a kind of microorganisms secrete enzymes can cut down the

polymer into its molecular building blocks and turn to a carbon source for growth. The process of biodegradation of PHA under aerobic conditions can produce carbon dioxide and water, whereas in the degradation products of anaerobic conditions are carbon dioxide and methane. PHA can degrade in different environment condition includes wide range of temperature, moisture and pH (Johnstone, 1990; Flechter, 1993).

There is another earliest biopolymer which was synthesized by the Carothers group in the early 1930s called polycaprolactone (PCL). PCL is naturally hydrophobic and semi-crystalline. The crystallinity PCL decreased with increasing molecular weight. The number average molecular weight of PCL samples is ranging from 3000 to 80,000 g/mol (Wooddruff and Hutmacher, 2010). The molecular weight, molecular weight distribution, end group composition and chemical structures of PCL are much dependent on the polymerization mechanism (Okada, 2002).

There are some issue occurs between biodegradability and bioresorsabability of PCL. Bioresorbability reflects total elimination of the initial foreign materials and bulk degradation products by-products (low molecular weight compounds) with no residual side effects (Vert et al., 1992). PCL is the material that is easy degradable but the bioresorsability is relatively low. Nevertheless, PCL can only be biodegraded by bacteria and fungi, yet they are not biodegradable in animal and human bodies because of the lack of suitable enzymes. Therefore, the bioresorbability of PCL is quite low in human body as it takes longer time to be moved away from human body.

In intracellular degradation study, low molecular weight PCL (Mn, 3000 g/mol) powders were used. According to Albertsson and Karlsson (1997), the powdered PCL was quickly degraded and absorbed within 13 days inside the phagosomes of macrophage and giant cells, and the remaining sole metabolite was 6-hydroxyl

caproic acid. The mechanism of hydrolytic degradation of PCL was shown in Figure 2.6. Hydrolysis intermediates 6-hydroxyl caproic acid and acetyl coenzyme A are formed prior entering the citric acid cycle and then being eliminated from the body (Albertsson and Karlsson, 1997)

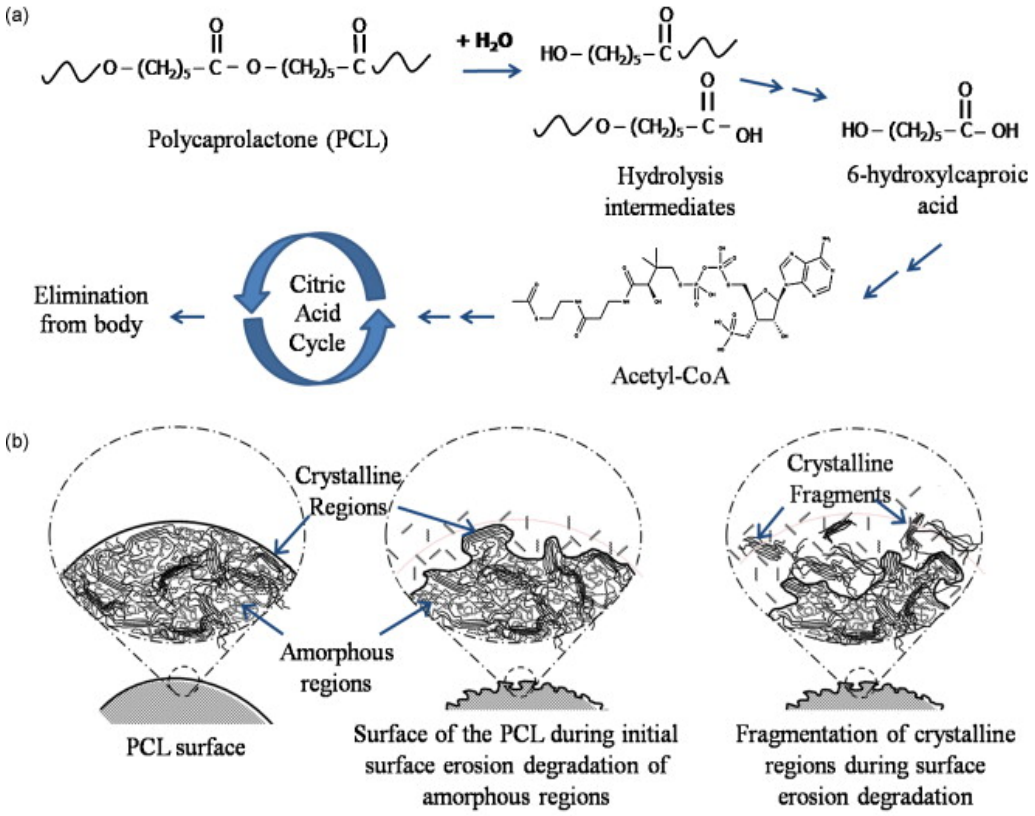

Figure 2.6: Schematic diagram of PCL degradation via hydrolysis intermediates 6-hydroxyl caproic acid and acetyl coenzyme A, which are then eliminated from the body via the citric acid cycle (a) crystalline fragmentation (b) accelerated degradation of PCL over 5 weeks in NaOH (Wooddruff and Hutmacher, 2010)

2.2.3 Degradable Polymer Blends

There are many disadvantages of using natural polymer in producing plastic materials especially in thin film due to the brittleness, hydrophilic nature and deterioration of mechanical properties upon environmental conditions. Therefore, natural polymer needs to be blended with other synthetic polymers to overcome these

problems. The most common natural polymer used in blends with polyolefin is starch. On the other hand, many polymers are hydrophobic and they are immiscible with hydrophilic starch, therefore the mechanical mixing may result in poor mechanical properties. The introduction of new functional group into the polymer or starch can reduce this problem (Kalambur and Rizvi, 2006).

In 1972, the blends which comprised from polyolefin and starch first appeared in Griffin's patent. In the patent, much research on the compatibilisation of polyolefin and starch. These researches indicated that compatibility between polyolefin and starch can be improved by incorporating of coupling agent, reactive compatibiliser and non-reactive compatibiliser. Polyolefin/starch blends are not a biodegradable blends, but it is degradable polymer blends. In recent years, many investigations have been done on the polyolefins/ starch blends to improve the mechanical properties, compatibility, thermal properties and degradability. Wang et al. (2004) studied the effects of glycerol and polyethylene-grafted maleic anhydride (PE-g-MA) on the morphology, thermal properties, and tensile properties of LDPE and rice starch blends. They found that although rice starch has a small granular size, the tensile properties of LDPE/rice starch blends were lower due to inherent multigranular agglomeration. The addition of glycerol enhanced the distribution of rice starch in LDPE matrix and resulted in tensile strength improvement, presuming a result of a stronger interaction between starch and glycerol under the processing conditions. However, glycerol did not improve the interfacial properties between rice starch and LDPE because interaction between LDPE and glycerol is weak. The interfacial adhesion LDPE/rice starch was improved with the incorporation of PE-g-MA. Liu et al. (2003) investigated the properties of LDPE/corn starch blends. They reported that the miscibility between granular corn starch and LDPE was improved by the

incorporation of PE-g-MA. The thermal properties, morphology, and tensile analyses suggest that the improved compatibility was attributed to a chemical reaction between hydroxyl groups in starch and anhydride groups in PE-g-MA and the physical interaction between the PE in PE-g-MA and LDPE. In the investigation of Bikiaris et al. (1997), the effect of ethylene-acrylic acid copolymer (EAA) and plasticized starch (PLST) upon the thermo-oxidative degradation of LDPE was studied using TGA technique. They suggest that TGA can be a very useful technique for the fast study of thermo-oxidative stability of LDPE-starch blends. By using TGA technique, only a small amount of sample required, the great sensitivity to weight changes and the short analysis times needed for the incubation experiments.

2.3 Degradation of Plastics

Degradation is a main issue for plastic product in its service life and the postconsumer waste. Most of the synthetic plastic can undergo photolytic and photo-oxidative through UV light, and thermo-oxidative reactions. Apart from degradation, biodegradation is one of the attractive alternatives for environmental waste management (Sings and Sharma, 2008). Degradation referred to the changes in plastic properties includes mechanical, thermal, morphological and physical properties. According to Grassie and Scott (1985), polymer degradations can be classified as few categories. In the literature, the discussion is only focused on the photo-oxidative, thermal degradation and biodegradation which are related to the current research.

2.3.1 Photo-oxidative degradation

Photo-oxidative degradation referred to the decomposition process of the plastic by the action of light at ambient conditions. Synthetic polymers such as PE and PP are susceptible to UV and visible light degradation. Based on the study of Nagai et al. (2005), photo-oxidation occurs mainly in the ether parts of the soft-segments, in which the generated products are ester, aldehyde, formate and propyl end groups. Furthermore, C–C bond can be cleaved under exposure of UV radiations. UV wavelength is one of the factors that affect the degradation of plastics. The wavelength that can achieve maximum degradation for PE is 300 nm whereas the PP is 370 nm. Photo-degradation can change the physical and optical properties of the plastic. The indicators of the degradation are visually yellowing, reduction of mechanical properties, changes in molecular weight and weight loss. During the UV radiation exposure, PE and PP films lose their extensibility, mechanical integrity and strength along with decrease in their average molecular weight. On the other hand, mechanical integrity of polystyrene (PS) is reduced through extensive chain scission during photo-degradation (Nagai et al., 2005).

The degradation mechanisms of polymer can be determined by their extraneous groups or impurities, which absorb light quanta and form excited states. Basically the photo degradation of polymer can be explained with two developed reactions which are Norrish Type 1 reaction and Norrish Type 2 reaction. Norrish Type 1 reaction is that the excited triplet states cleave the polymer chains and form radical pairs. However, the formation of saturated and unsaturated chain ends by hydrogen transfer is Norrish Type II reaction (Carlsson et al., 1976). Based on the study of Carlsson et al. (1976), the formation of the polymer radicals can consequently add molecular oxygen to peroxy radicals, abstract hydrogen and form hydroperoxide groups. The

group can absorb UV light or become excited and leads to the break of weak O–O bonds. The formation of alkoxy and hydroxyl radicals may react in various ways through hydrogen abstraction, chain scission, rearrangement and thus accelerate photo-degradation.

The schematic diagram (Figure 2.7) shows the photo-oxidative degradation of polymer. There are three processes involved in the degradation includes initiation, propagation and termination. The initiation starts with the absorption of UV light and leads to the breakage of polymer main chain in a condition that the energy is sufficient. The reaction involves the formation of initial radical. Each polymer has different initiation steps depends on the chemical structure. The process will be followed by the propagating reaction which involves auto-oxidation cycle. Hydroperoxide species is generated through this reaction lead to backbone degradation through cleavage of hydroperoxide O–O bond followed by β-scission. Normally, amorphous phase is the scissioning site for semi-crystalline polymers. The oxidative reactions are only initiated if the hydrogen is removed through a photoreaction. In polystyrene, the free radical reacts with oxygen to form peroxy radical. The radical can abstract a proton from some other labile positions, consequently forming hydroperoxides and a new radical site. The ultimate product from the decomposition is ketones and olefins (Singh and Sharma, 2008). During the last stage of degradation i.e termination, the free radical form inert products through combination free radicals in the plastic. The combination of macroalkyl radicals may resulted in the formation of crosslinked, branched or disproportionated product.

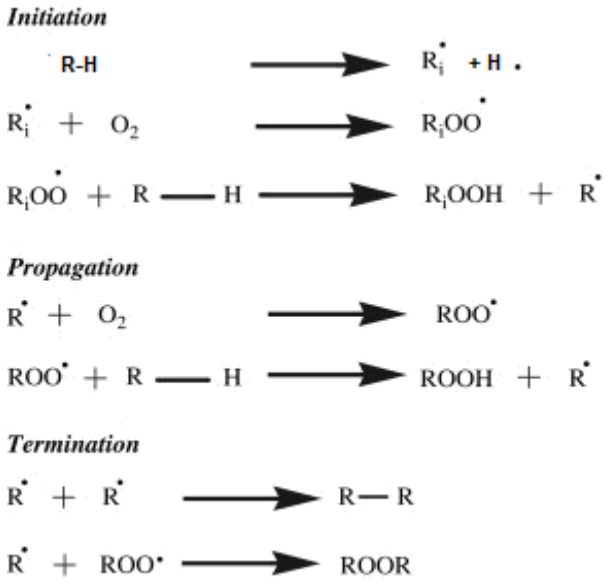

Figure 2.7: The typical photo-degradation process of polymer (Singh and Sharma, 2008)

2.3.2 Thermal Degradation

There are similarities between photochemical and thermal degradations in the normal condition. The difference between the two degradation processes is the sequence of initiation steps. According to Tyler (2004), thermal reactions take place throughout the bulk of the polymer, whereas degradation of photochemical reactions occurs only on the surface. During thermal degradation, the depolymerization reaction imperfections in the chain structure to form a weak link. Many addition polymers can be depolymerized at elevated temperature, for example, polymethylmethacrylate (PMMA) has been converted almost quantitatively back to the monomer and PE has been decomposed into longer olefin fragments. According to Khabbaz et al. (1999), the purities generated during manufacturing resulted in polyolefins susceptible to thermal oxidation. There are few factors affect the thermal degradation includes heating rate, pressure, reaction medium, and reactor geometry. The final products from thermo-oxidative degradation are formaldehyde, acetaldehyde, formic acid, acetic acid, CO_2 and H_2O.

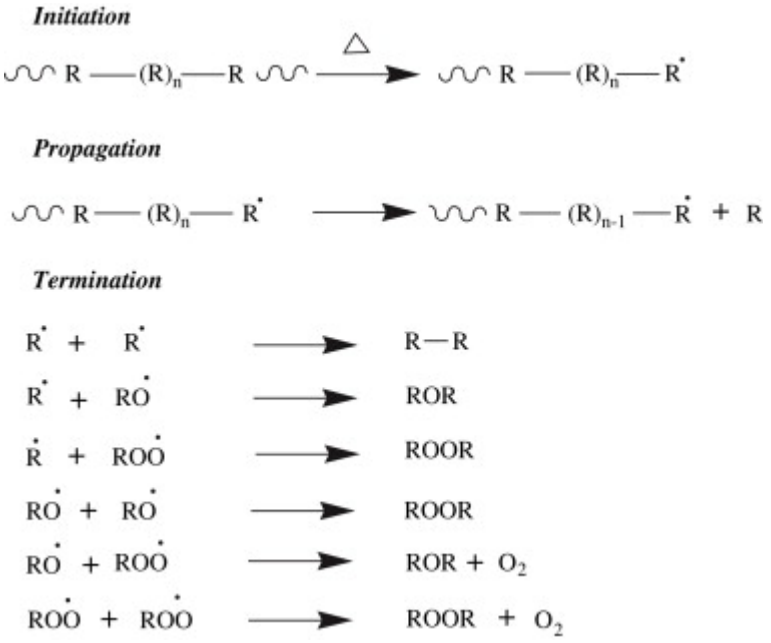

Figure 2.8: Degradation steps of thermal degradation (Khabbaz et al., 1999)

The mechanism of thermal degradation includes two distinct reactions, which are a random scission of links and chain-end scission of C–C bonds products. Murata et al. (2002) found that the chain-end scission takes place at the gas–liquid interface in the working reactor. Based on the study from Starnes (2002), during polymerization thermal dehydrochlorination of poly(vinyl chloride) (PVC) begins with internal allylic chloride and formed tertiary chloride structural defects, ordinary monomer units are converted into internal allylic chloride defects by a mechanism that may include the abstraction of hydrogen by triplet cation diradicals derived from polygene intermediates during thermal degradation. Generally, initiation reaction occurs by random chain scission or chain end initiation. After that, monomer formed during de-propagation step and followed by termination through radical coupling and radical disproportionation as shown in Figure 2.8 (Soto-Oviedo and Lehrle, 2003)

2.3.3 Biodegradation

According to European Committee to standardization (CEN), biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material. In German Institute for Standardization 103.2, it defined biodegradation as process, caused by biological activity, which leads under change of the chemical structure to naturally occurring metabolic products. Under aerobic conditions, carbon dioxide and water are produced from the mineralization of organic compounds. Biodegradation is also depends on the abiotic effect. For example, abiotic hydrolysis, photo-oxidation and physical disintegration of polymers may increase the surface area for microbial colonization or by reducing molecular weight (Palmisano and Pettigrew, 1992). The biodegradation of plastic materials can be determined by loss of mechanical strength, assimilation by microorganisms, degradation by enzymes, backbone chain breakage followed by the reduction in the average molecular weight of the polymers. In nature, biological degradation in chemical mechanism, however the source of the attacking chemical is from microorganism i.e enzyme. The enzymatic degradation can be affected by type of enzyme, availability of a site in the polymers for enzyme attack, and the presence of coenzyme.

Figure 2.9 shows the typical biodegradation of plastic materials. Microorganisms are unable to transport the polymeric material directly into the cells because of the size of the polymer molecules and water-solubility. Therefore, if the polymers molecular weight can be sufficiently reduced to generate water-soluble intermediates, the mineral can be transported into the microorganisms. Biodegradation is also known as surface erosion process because the extracellular enzymes are only attack polymer surface as they are too large to penetrate deeply into the polymer material.