DEVELOPMENT OF A MULTICOMPONENTS DEGRADABLE PLASTICS, THROUGH THE COMBINATION OF THE SAGO STARCH AND POLYETHYLENE/POLY (ε-CAPROLACTONE) BLENDS

by

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Special Dedications

To my beloved parents

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LIST OF SYMBOLS

ε	epsilon
M_t	Total moisture Uptake
W_d	Weight of sample before immersed in water
W_w	Weight of sample after immersed in water
T_g	Glass transition temperature
T_m	Melting temperature
Wt%	Weight percent

LIST OF ABBREVIATIONS

DMA	Dynamic mechanical analyzer
DSC	Differential Scanning Calorimetry
EAA	Poly(ethylene-co-acrylic acid)
EB	Elongation At Break
EMA	Ethylene maleic acid
ENR-50	Epoxidised natural rubber with 50 mol% epoxidation
GCMS	Gas chromotograph mass spectrometer
FTIR	Fourier Transform Infra-red Spectroscopy
HPS	Hyroxypropylated starch
LLDPE	Linear low density polyethylene
LDPE	Low Density Polyethylene
MAH	Maleic anhydride
MFI	Melt Flow Index
MnS	Manganese stearate
NMR	Nuclear magnetic resonance
PCL	Poly(ε-caprolactone)
PE	Polyethylene
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Polylactic acid
PP	Polypropylene
PVA	Poly(vinyl alcohol)
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
SS	Sago starch
TGA	Thermogravimetry analysis
TOA	Thermo-oxidative ageing
TPS	Thermoplastic starch
TS	Tensile strength
UV	Ultraviolet
XRD	X-ray diffraction

LIST OF APPENDICES

A1 Paper 1 (abstract) – Mechanical Properties and Morphology of Low Density Polyethylene/Polycaprolactone/Sago Starch Blends. *14th Scientific conference EMSM, 5th - 7th December 2005, Penang, Malaysia: EMSM.*

A2 Paper 2 (abstract) – Effects of Ultraviolet Irradiation On The Degradation Of Sago Starch Filled Low Density Polyethylene/Poly(ε-caprolactone) Blends. *Post Graduate Research Papers, School Of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (2005/2006)*

A3 Paper 3 (abstract) – Effects of Accelerated Soil Burial On Low Density Polyethylene/Poly(ε-caprolactone)/Sago Starch Blends. *Post Graduate Research Papers, School Of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (2005/2006)*

A4 Paper 4-abstract- Changes in Chemical Structure, Mechanical Properties and Morphology of LDPE/PCL/SS Blends after Exposure to Ultraviolet Radiation and Incubation in Soil at 50^{o}C. *1st International Conference of Young Chemist, Penang, Malaysia(2006)*

A5 DSC results

LIST OF PUBLICATIONS & SEMINARS

1 Mechanical Properties and Morphology of Low Density Polyethylene/Polycaprolactone/Sago Starch Blends. *14th Scientific conference EMSM, 5th - 7th December 2005, Penang, Malaysia: EMSM.*

2 Effects of Ultraviolet Irradiation On The Degradation Of Sago Starch Filled Low Density Polyethylene/Poly(ε-caprolactone) Blends. *Post Graduate Research Papers, School Of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (2005/2006)*

3 Effects of Accelerated Soil Burial On The Degradation Of Sago Starch Filled Low Density Polyethylene/Poly(ε-caprolactone) Blends. *Post Graduate Research Papers, School Of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (2005/2006)*

A4 Changes in Chemical Structure, Mechanical Properties and Morphology of LDPE/PCL/SS Blends after Exposure to Ultraviolet Radiation and Incubation in Soil at 50^{o}C. *1st International Conference of Young Chemist, Penang, Malaysia (2006)*

DEVELOPMENT OF A MULTICOMPONENTS DEGRADABLE PLASTICS, THROUGH THE COMBINATION OF THE SAGO STARCH AND POLYETHYLENE/POLY (ε-CAPROLACTONE) BLENDS

ABSTRACT

In this research, sago starch (SS), poly(ε-caprolactone) (PCL) were incorporated into low density polyethylene (LDPE). Poly(ethylene-co-acrylic) acid (EAA) was added into the blend to study the effect on thermo-oxidative ageing (TOA). Pro-oxidants such as manganese stearate (MnS) and elastomers, epoxidized natural rubber with 50 mol% epoxidation (ENR-50) and styrene butadiene rubber (SBR) were added to increase the degradability of the blends. The compounding of the blend was done by using Brabender Plasticorder internal mixer at 160^{o}C and 30 rpm for 6 minutes. The blends were then compressed into 1 mm thick film using Kao Tieh Go Tech moulding machine. Dumb-bell shape samples were cut and used throughout the whole research. TGA shows that the decomposed temperature was shifted lower as the pro-oxidants were added intbo the blends. This shows that the pro-oxidant helped to increase the degradability of the blends. Tensile strength (TS) and elongation at break (EB) decreased as SS and pro-oxidants were added into LDPE/PCL. This was due to the agglomeration of SS (supported by Scanning Electron Microscope) and incompatibility of the PCL, SS and the additives added (supported by Dynamic Mechanical Analyzer). This is supported by using Dynamic Mechanical Analyzer (DMA) and scanning electron microscope (SEM). Young's modulus increased as SS was added into LDPE/PCL. This is because SS is stiffer that LDPE and PCL. LDPE/PCL/SS blends samples were immersed in water for 24 weeks. Reduction in TS and EB were observed after the water absorption test. This is due to the swelling effect of the SS leading to voids and cracks were observed after water absorption by using SEM. Increased in TS and EB was observed after drying the

immersed samples in oven for 24 hours. This is due to less plasticizing effect as there was no moisture in the blends.Ultra-violet (UV) ageing test was performed by using QUV Accelerated Weathering Tester. Reduction in TS, EB and melt flow index (MFI) were observed. Fourier transform infra-red (FTIR) spectrum shows increment in carbonyl index which indicating increment in carbonyl group formed in samples. SEM micrograph shows that cracks in the form of mosaic pattern were formed on the surface of the LDPE/PCL/SS blends which explain the dramatically reduction in EB. TOA test shows reduction in TS, EB and MFI. FTIR spectrum shows increased in carbonyl index indicating increased in carbonyl group formed as the duration of TOA increase. Two types of soil burial tests were done. LDPE/PCL/SS blends were incubated in soil and in oven at 50^{o}C for 3 months. Increment in carbonyl index was observed. Voids were formed on the surface of the LDPE/PCL/SS blends after 3 months of incubation showed attack of micro-organisms to the SS and PCL particles. The other type of soil burial test was done in the natural environment where LDPE/PCL/SS blends were buried in the soil at natural environment. Reduction in TS and EB were also observed after the natural soil burial test due to the voids formed after the assimilation of PCL and SS particles on the surface of LDPE/PCL/SS blends.

PEMBANGUNAN PENGHASILAN PLASTIK TERBIODEGRADASI YANG PELBAGAI KOMPONEN MELALUI KOMBINASI KANJI SAGO, POLIETILENA/POLI(ε-CAPROLACTONE)

ABSTRAK

Pencampuran fizikal merupakan satu cara yang pantas dan menjimatkan dalam penghasilan polimer terisi kanji. Dalam kajian ini, kanji sago, poli(ε-caprolacton) (PCL) telah dicampuradunkan dengan polietilena berketumpatan rendah (LDPE). Poli(etilena-co-acrylic) asid (EAA) telah ditambah ke dalam komposit tersebut untuk mengkaji kesannya terhadap degradasi terma. Manganese stearate (MnS) dan elastomer seperti getah asli terepoksi (ENR-50) dan getah stirena butadiena (SBR) juga dicampurkan ke dalam formulasi tersebut untuk meningkatkan kesan kemerosotan komposit tersebut. Proses pencampuran komposit dilakukan dengan menggunakan pencampur dalaman Brabender Plasticorder pada suhu 160^{o}C, 30rpm dalam masa 6 minit. Komposit tersebut akan diproses dengan menggunakan mesin Kao Tieh Go Tech bagi meghasilkan filem dengan ketebalan 1.00 mm. Sampel berupakan bentuk Dumbell disediakan dan digunakan dalam seluruh kajian ini. Keputusan Thermogravimetry analyzer (TGA) menunjukkan penurunan dalam suhu pemerosotan apabila MnS dan elastomer dicampurkan ke dalam komposit tersebut. Ini menunjukkan bahawa MnS dan elastomer membantu meningkatkan pemerosotan dalam komposit tersebut. Kekuatan tensil (TS) dan pemanjangan takat putus (EB) menurun apabila kanji sago dan additif dicampurkan ke dalam komposit LDPE/PCL. Ini kerana sifat ketidakboleh campuran PCL dan agglomerasi dalam kanji sago. Keputusan ini disokong oleh keputusan yang diperolehi oleh Dynamic Mechanical Analyzer (DMA) dan Scanning electron microscope (SEM). Modulus Young meningkat apabila kanji sago ditambah ke dalam LDPE/PCL. Komposit LDPE/PCL/SS telah direndamkan dalam air selama 24 minggu. Penurunan dalam TS

dan EB diperolehi akibat pembengkakan kanji sago. Retakan kecil berlaku selepas rendaman dalam air menyebabkan penurunan dalam TS dan EB. Peningkatan TS dan EB berlaku apabila sampel yang direndamkan dalam air dikeringkan semula dalam oven selama 24 jam. Walau bagaimanapun, peningkatan TS dan EB adalah sedikit akibat penggurangan sifat pemplastikan. Ujian pancaran ultraviolet (UV) dijalankan ke atas komposit LDPE/PCL/SS dengan menggunakan mesin "QUV Acclerated Weathering Tester". Penurunan dalam TS, EB dan "melt flow index (MFI)" berlaku. "Fourier Transform infra-red (FTIR)" menunjukkan peningkatan dalam karbonil index selepas ujian pancaran UV. Retakan berbentuk mosaik telah berbentuk di atas komposit LDPE/PCL/SS selepas pancaran UV. Retakan tersebut menyokong penurunan mendadak dalam EB selepas menjalankan ujian pancaran UV. Ujian pemerosotan terma (TOA) dijalankan ke atas sampel komposit LDPE/PCL/SS dan penurunan dalam TS, EB dan MFI diperhatikan. Peningkatan dalam karbonil index turut didapati. Dua jenis ujian penanaman dalam tanah telah dijalankan. Komposit LDPE/PCL/SS yang ditanam dalam tanah pada suhu 50^{o}C selama 3 bulan menunjukkan peningkatan dalam index karbonil. Bagi sampel yang ditanam dalam tanah secara semulajadi pula menunjukkan penurunan dalam TS dan EB selepas 3 bulan. Lubang kecil telah ditemui pada permukaan sampel selepas 3 bulan dan ini menunjukkan terdapat aktiviti mikro-organisma terhadap kanji sago dan PCL.

CHAPTER ONE
INTRODUCTION

1.1 Plastics and the Environment

Plastics have become one of the most important materials in our lives and also one of the greatest innovations of the millennium (Danjaji I.D., 2000). The usage of plastic materials was started in 1930 when major thermoplastics such as polystyrene, poly(vinyl chloride), the polyolefins and poly(methyl methacylate) were developed (Brydson J.A. ,1989). Since then, plastics have been found useful in applications ranging from transportation, packaging, building, medical appliances, agricultures and communication. The break-up of these applications is shown in Fig. 1.1.

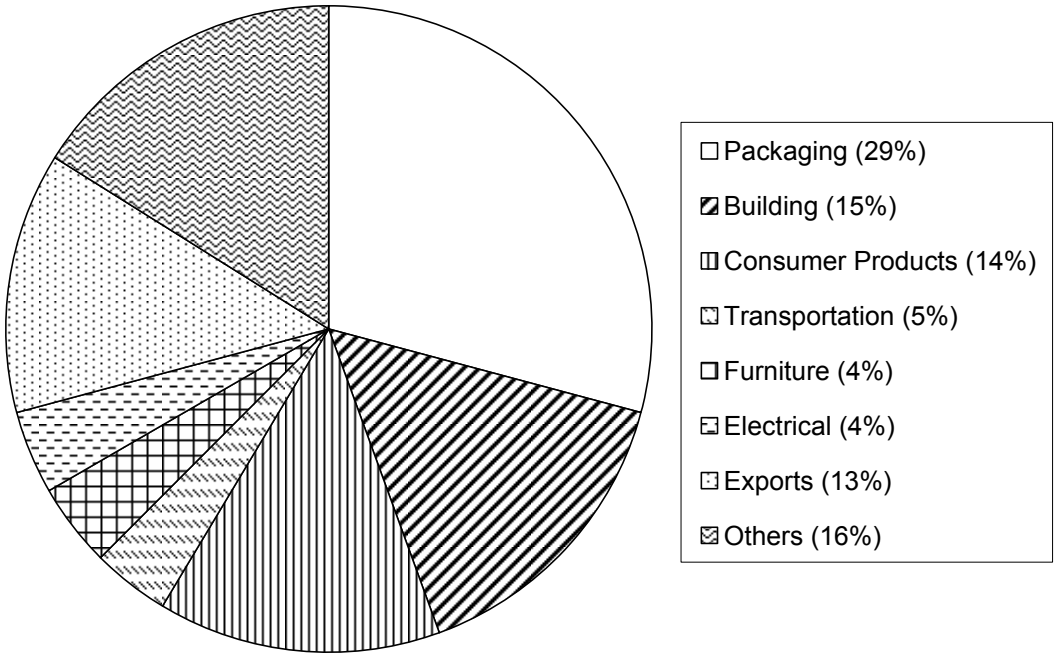

Figure 1.1: Uses of Plastics produced in United States (Stevens E.S., 2002)

Plastics are one of the major polymer materials used in packaging. The main reasons why plastics have been chosen are that plastics are cheap, not susceptible to loss of strength when wet, they improved product protection and do not contribute to

land subsidence or methane gas production (Andrady L. A., 2003). In addition, plastics have good mechanical properties and transparency. Polystyrene, poly(vinyl chloride), polyethylene terephatalate and the polyolefins such as polyethylene and polypropylene are the major plastic resins used in the packaging industries (Susan E.M.S., 2003).

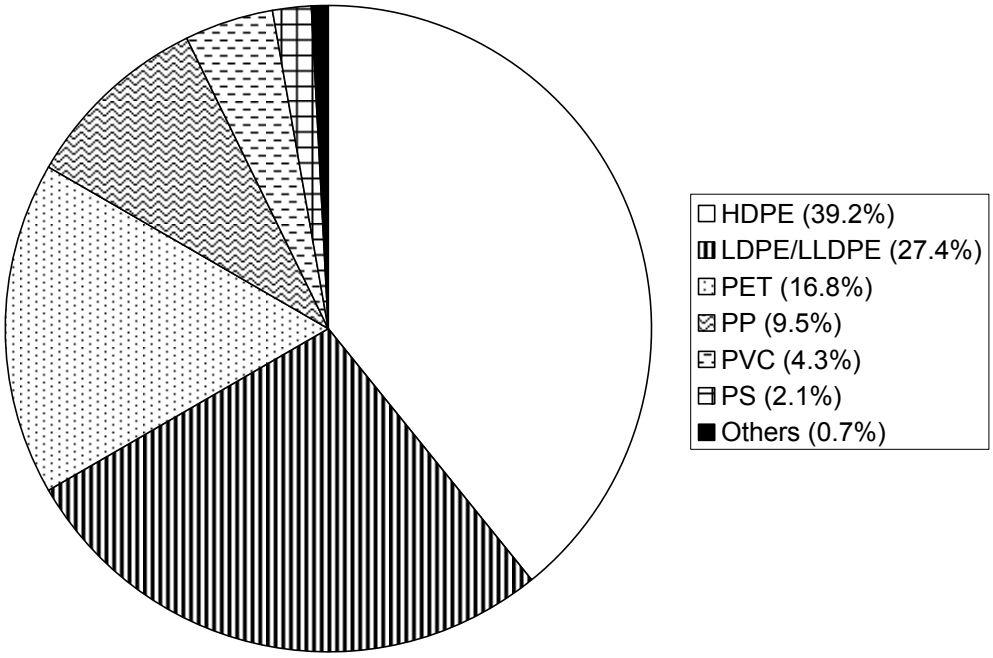

Figure 1.2: Plastics resin in packaging in U.S. municipal solid waste stream (Susan E.M.S., 2003)

Polyethylene (PE) is the most used plastic resin in plastic packaging as shown in Figure 1.2. Polyethylenes are so widely used because of their wide range of physical properties, suitability to most of the commercial thermoplastics fabrication process. The most important properties found in PE resin is because of the cheaper price that can give them a competitive edge compared to other materials (both polymeric and non polymeric) (Peacock A.J., 2000).

Plastics are prevalent in almost every human activity. However, the resistance to natural biodegradation has becoming more and more problematic especially where they are use only a short period of time (Vert M. *et al.*, 2002). 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. Not only that, they are also threatening the operation of hydropower plants and other public works. (Ren X., 2003)

World wide, about one half of all discarded plastic come from packaging. Out of this, almost one-third of them come from single-used-packaging which are discarded soon after use (Stevens E.S., 2002). Plastics create so much pollution and landfill crisis that various attempts have been made to solve these problems. One of these attempts is to create a biodegradable plastic by adding natural biodegradable materials into the plastics.

1.2 Degradable Polymers

Biodegradable polymers are an alternative replacement for traditional petroleum-based non biodegradable polymer. After the useful life of the degradable plastics, they will simply fall apart and get assimilated by microorganisms. They return to the natural ecosystem without causing any pollution or harm to the nature environment (Stevens E.S., 2002).

Biodegradable polymers can be divided to naturally occurring biodegradable polymers and synthetic biodegradable polymers. Starch is a naturally occurring biodegradable polymer which is cheap, abundant, renewable and can be added as a filler in blends with other polymers. Examples of synthetic biodegradable polymers are polycaprolactone, poly(lactic acid) and poly(vinyl alcohol). In the degradation of polymers, there are a lot of factors need to be considered. Sunlight, heat, oxygen, humidity, microorganisms are some of the agents that work synergistically towards the degradation of polymers. A photodegradable polymer can be obtained when chromophores or photosensitive materials are added into the polymers. Starch, natural fillers which contain hydrolysable groups, is cheap and readily biodegradable. It has been mixed into the thermoplastics to increase the biodegradability (as starch is

biodegradable and ready be consumed by mico-organisms) and reduce the cost of the material (Shah P.B. *et al.,* 1994).

In the early 1970s, Griffin used granular starch as filler in polyethylene to increase biodegradability (Bikiaris D & Panayiotou C., 1998). Microorganisms enzymatically hydrolyzed the starch granules leaving voids and pits on the surface of the LDPE/starch blends. The mechanical properties of the blends also determined (Chandra R., & Rustgi R., 1998)

1.3 Problem Statement

Normal commodity resins are used in packaging are resistant to degradation thereby causing to a lot of pollution and landfill problems. There is a need to find degradable plastics resin to overcome pollution and landfill crisis problems. However, the price of raw biodegradable plastic resins in the market is very high compared to normal commodity plastic resins. Petroleum based commodity resins cost only an average of $0.50 per pound (Douglas B.E. *et al,* 1995). The most common thermoplastics used in packaging, low density polyethylene (LDPE) cost less than $0.90 per pound.

Table 1.1 shows the price of biodegradable materials and their major producers. As can be seen, biodegradable plastics cost at least twice the normal commodity plastics. Another reason why polyolefins were initially selected for development as degradable polymers rather than natural products such as cellulose is that although cellulose is known to be slowly biodegradable, it suffers from a number of technical deficiencies. Other than that, the extraction of cellulose from natural products is both energy intensive and polluting. Furthermore, the modification of cellulose by acetylation to give technologically acceptable products sharply reduces the environmental biodegradability of the base polymer (Scott G., 2002)

Table 1.1: Major biodegradable materials producers (Narayan R., 1993).

Company	Base polymer	Feedstock	Cost, USD/lb
Cargill, Minneapolis, MN	Polylactide acid(PLA)	Renewable resources, corn	1.00-3.00
Ecochem, Wilmington, PE	Polylactide copolymers	Renewable resources, cheese whey, corn	<2.00 proj'd
Flexel, Atlanta GA	Cellophane (Regenerated cellulose)	Renewable resources	2.15
Zeneca (Business unit of ICI)	Poly(hydroxybutyrate-co-hydroxyvalerate), PHBV	Renewable resources-carbohydrates (glucose), organic acids	8.00-10.00
Novamont/Ferruzzi-Montedison, New York, NY & Italy	Starch synthetic polymer blend containing approx. 60% starch	Renewable resources + petrochemical	1.60-2.50
Novon Product (Warner-Lambert Div), Morris Plains, NJ.	Thermoplastic starch polymer compounded with 5-25% additive	Renewable resources, starch	2.00-3.00
Union Carbide, Danbury, CT	Polycaprolactone (Tone polymer)	Petrochemical	2.70
Air Products & Chemicals, Allentown. PA	Polyvinyl alcohol (PVOH) and thermoplastic PVOH alloys (VINEX)	Petrochemical	1.00-1.25 (PVOH) 2.50-3.00 (VINEX)
National Starch & Chemical, Bridgewater, NJ	Low ds starch ester	Renewable resources, starch	2.00-3.00
Planet Packaging Technologies, San Diego, CA.	Polyethylene oxide blends (Enviroplastic)	petrochemical	3.00

Starch was used as filler in polyethylene in 1977 by Griffin. Starch is inexpensive, abundant and renewable biopolymer (Liu W. *et al.*, 2003; SE-Pierre N. *et. al*., 1997; Psomiadou E. *et al*., 1997). However, starch is not suitable to be used on its own due to its hydrophilic behavior. Native starch will swell when absorbed water with their free hydroxyl groups. As a result, it will become very brittle and it supports the growth of mold. Due to these reasons, native starch alone is not suitable to be used as a packaging material. The introduction of granular starch into plastics via melt-mixing has become the simplest and cheapest way for preparing starch-plastics composites (Danjaji I.D *et al*., 2002).

1.4 Objectives

The primary objectives of this study are:

1. To determine the optimum loading, reinforcement efficiency and mechanism of sago starch in the LDPE/PCL blends. Malaysia produces tonnes of sago starch per year and mostly this sago starch is used as food resources. The incorporation of sago starch in LDPE/PCL blends is expected in lower the cost and increases the degradability of the LDPE/PCL blends. The optimum loading of sago starch needs to be determined so as to improve the degradability of the material without adversely affecting the mechanical property too much.
2. To study the effects of pro-oxidants on the properties of the LDPE/PCL/SS blends. A previous study had shown that pro-oxidants such as epoxidised natural rubber (ENR), styrene butadiene rubber (SBR) and manganese stearate (MnS) increased the degradability of LDPE/starch blends. The incorporation of pro-oxidants into the LDPE/PCL/SS blends is hoped to increase the degradability of the current blends too.
3. To study the effect of adding ethylene acrylic acid (EAA) to the blends. Previous studies had shown that EAA can act as a compatibilizer or pro-oxidant in LDPE/starch blends. It is now hoped that the incorporation of EAA into the blends will increase the in mechanical strength but at the same time also increase the degradability of the blends.
4. To study the (bio)degradability of the LDPE/PCL/SS blends. Several tests such as thermo-oxidative ageing, soil burial and ultra-violet radiation will be done to determine the (bio)degradability of the LDPE/PCL/SS blends. Previous studies had shown that incorporation of starch increased the degradability of the LDPE/starch blends.

1.5 Outline of Thesis structure

Chapter 1 starts with an introduction of the usage of commodity plastics and its impact on the environment. Related issues, which help to generate this research work, are also stated. The objectives and the general flow of the whole research program are outlined.

Chapter 2 discusses the issues of pollution and landfill problems caused by commodity thermoplastics. Waste management and the degradable plastics materials are discussed as possible solutions to the pollution and landfill problems. This is followed by a literature survey on various published works on degradable polyethylene and starch filled thermoplastics, particularly those related to this work.

Chapter 3 describes the materials, experimental procedures, equipments and tests to generate data in the present study.

Chapter 4 reports the effects of adding SS, EAA and various pro-oxidants on the LDPE/PCL composites. Data, graphs and charts of the mechanical, degradation and thermal properties of these composites are presented here. Discussion based on the data analysis is presented in this chapter as well.

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

CHAPTER TWO
LITERATURE REVIEW

2.1 Effect of Plastics to Environment

2.1.1 Plastics Waste

Human is the only species in the world to developed technologies to access the Earth's fossil fuel, petroleum. Plastic is the greatest invention from petroleum resources. Since plastics have started been used in 1930, it has become one of the most important part in our daily life. Fig. 2.1 shows the production of thermoplastics resins is increasing year by year.

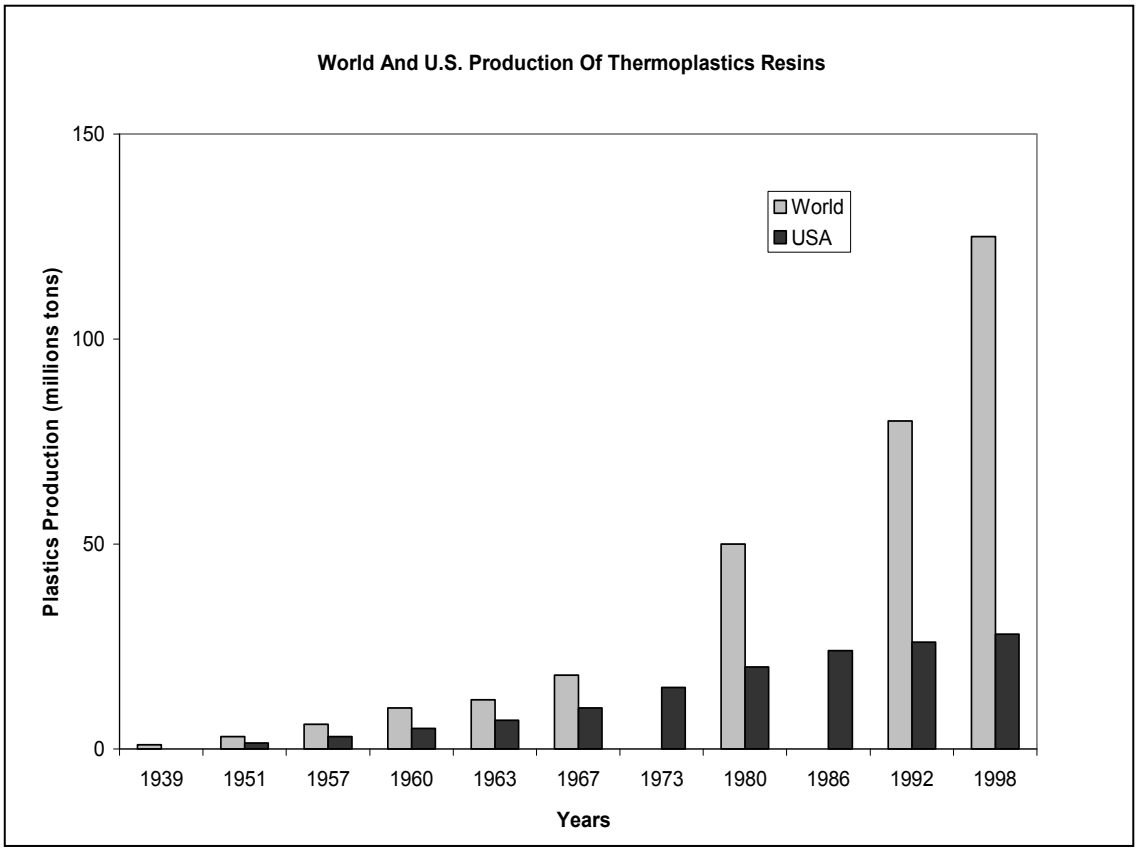

Fig. 2.1. World and U.S. production of thermoplastics resins (Anthony L. A., 2003).

People have started to concern about the impact of plastics wastes to the environment when the usage of the plastics increased year by year. Worries about the plastics waste was started since 1960s. Over 60 billion pounds of plastics are discarded into the waste stream each year in U.S. (Stevens E.S., 2002). Many

countries have the “landfill crisis” due to the shortage of landfill space and the increase of the municipal solid waste. Plastics take up a large volume of municipal solid waste leading plastics industries to come under severe attack in the last few years (Ehrig R.J. & Curry M.J.,1992).

Plastics are manufactured and designed to resist the environmental degradation. Plastics are economical than metal, woods and glasses in term of manufacturing costs and energy required (Samuel J.H.,1995). Due to these issues, plastics resins have become one of the most popular materials used in packaging. Plastics packaging has a life cycle less than a year and continuously enter the waste stream on a short turnout of time. The continuous growing of plastics industries have lead to the increase volume of plastics wastes going to the landfills (Ehrig R.J. & Curry M.J., 1992). To overcome this problem, a properly plan waste management is needed.

2.1.2 Plastics Waste Management

In the early stages, “Reduce-Reuse-Recycle” is the motto of overcome the plastics waste problems. Source reduction refers to the reduction of the amount of materials entering the waste stream by redesigning patterns of production or consumption. There are proposals to replace plastic packaging with other materials such as metals, papers or glasses but they are environmentally or economically less attractive (Stevens E.S., 2002).

Reuse strategy also has its limitation. Many plastic applications are not designed to reuse because of the impurities and contamination. Food packaging, disposable diapers, medical appliances and agricultural covers are the most common ones. These examples are the plastic wastes that enter the waste streams quickly (Stevens E.S., 2002).

Plastics manufacturers have long been recycling internal scraps generated during production. However, recycling of plastic wastes also has limitation. Technology of sorting, collecting and recycling the plastic wastes is still being developed. Plastics

wastes that enter the waste stream were normally contaminated by dirt, food scraps and waste. Cleaning of the plastics has become one of the major problems in plastics recycling. Furthermore, deterioration of the materials during recycling also leads to reduction in mechanical properties of the plastics itself. Not all plastics can be recycled. For examples, thermosetting plastics which cannot be softened and reshaped through heating are not suitable for plastic recycling. Plastics recycling suffered from unfavorable economical factors; unsteady market and development of the plastics recycling technology which lead to limitation in plastics recycling (Stevens E.S., 2002).

When the 3R motto cannot meet the requirement, another idea was created by the scientist. Incineration or sometimes referred as energy recycling was introduced to overcome the landfill problems. Energy generation by incineration of plastics waste is a way to recovered plastics waste since hydrocarbon polymer is made of fuel and can be replace fossil fuel and reduce CO_2 burden in the environment (Scott G., 2000). Japan is expected to take care up to 70 percents of the polymer waste by incineration (Samuel J.H.,1995). Although incineration look more benefit to harm, incineration is still not acceptable to most of the voting residents in a community. They worried about the toxicity of the pollutant include hydrogen chloride, heavy metals and dioxins. With the help of the latest technology, it can deal safely with such chemicals but the fund to maintain and provide the adequate equipment is very high (Stevens E.S., 2002).

An alternative way to incineration is pyrolysis. In pyrolysis, waste materials are heated in the absent of oxygen, and possibly under pressure as well. The process drives out volatile components and generate usable fuel, other chemical as well as heat. It preserves some materials value of the waste. One of the newest technologies in pyrolysis is directed at cracking waste materials. In this process, the long polymer chains of the plastics are broken into smaller chains and convert the waste plastics into the hydrocarbon building blocks from which the plastics were originally made. It is a form of feedstock recycling as these hydrocarbons will then be reused as polymer

feedstock. However, the technology has not yet been fully developed and the price of the reactors or plant is very expensive (Stevens E.S., 2002).

Finally, the waste plastics will be ended up in the landfills. Again, plastics waste take up a large of space in the landfill even the plastics been compacted. As landfill become full, the problems of finding a new landfill, establishing disposable fees and getting the site approval have become majoring problems in most of the developing countries (Stevens E.S., 2002). Fig. 2.2 summarizes the polymer waste management options.

Although plastics are not to be blame for responsible for the entire waste management problem, however they are part of it. To prevent this problem to get worst, ideas of creating a more environmental friendly plastic emerged.

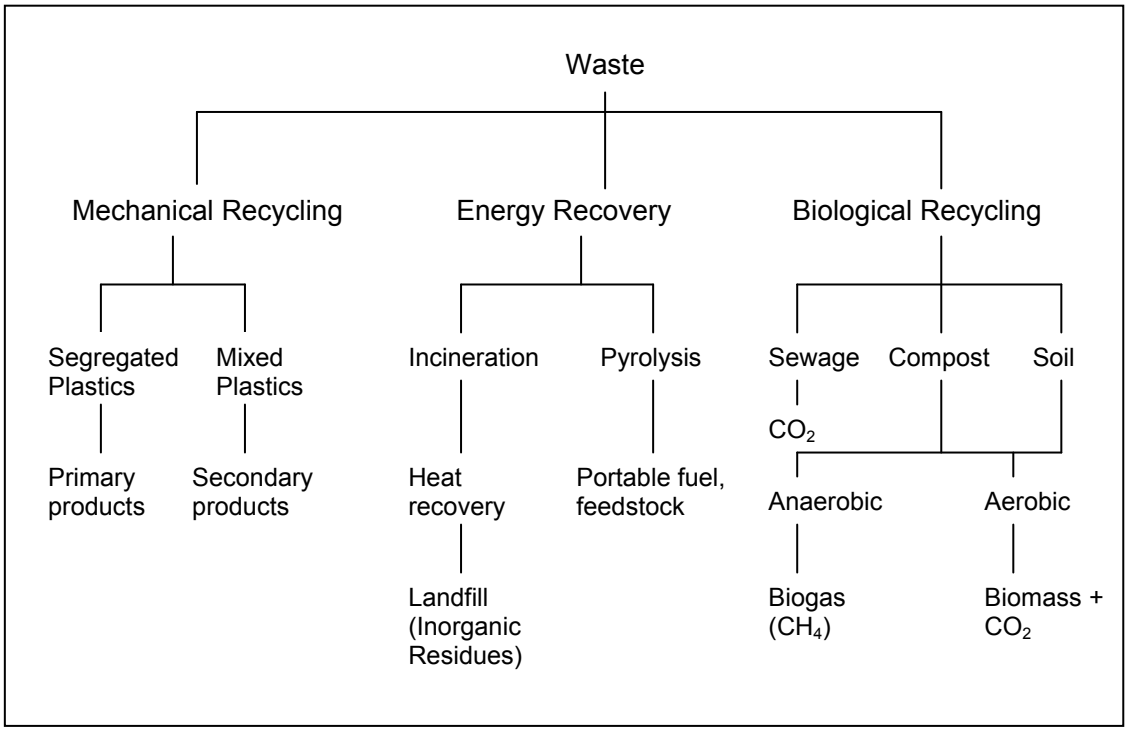

Fig 2.2 Polymer waste management options (Scott G., 2000).

2.1.3 Environment Friendly Plastics

Environmentally degradable polymers can be generally divided into biodegradation, hydrolytic degradation, photodegradation and oxidative degradation. In the American Society of Testing and Materials (ASTM), the definitions of the environmentally degradable polymers are as below:

A *degradable polymer* is designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of properties that may vary as measured by standard tests methods appropriate to the polymer and the application in a period of time that determines its classification.

A *biodegradable polymer* is a degradable polymer in which the degradation results from the action of natural-occurring micro-organisms such as bacteria, fungi and algae (Swift G., 1995). Enzymes produced by the micro-organisms will degrade the plastic under aerobic or anaerobic conditions. Microbial population, moisture temperature and oxygen are the key elements that control the rate of the degradation (Wool R.P. *et al.,* 2000).

A *hydrolytically degradable* polymer is a degradable polymer in which the degradation results from hydrolysis (Swift G., 1995).

An *oxidative polymer* is a degradable polymer in which the degradation results from oxidation (Swift G., 1995). Oxidants and peroxides catalyzed oxidation of the double bonds, produce peroxides which decompose into highly active free radicals and thus attack the polymer chains. This will cause chain scissoring follow by polymer degradation (Wool R.P. *et al*., 2000).

A *photodegradable polymer* is a degradable polymer in which the degradation results from the action of natural daylight (Swift G., 1995). The ultraviolet (UV) from the sun will leads to the decompositions of the plastic molecules. Incorporation of photoactive chemical groups into the polymer chain or by adding the photoactive additives will enhance the photodegradation. By reducing the molecular weight and

introducing oxygen groups on the polymer chain will help to increase the chemical degradation and thus, lead to biodegradation of the polymer (Wool R.P. *et. al*., 2000)

Fig. 2.3 shows the schematic pathways and further events beyond initial degradation may occur in the environment. The degradation will initially produce fragments which remain in the environment as recalcitrant pieces or completely biodegraded (Swift G., 1995).

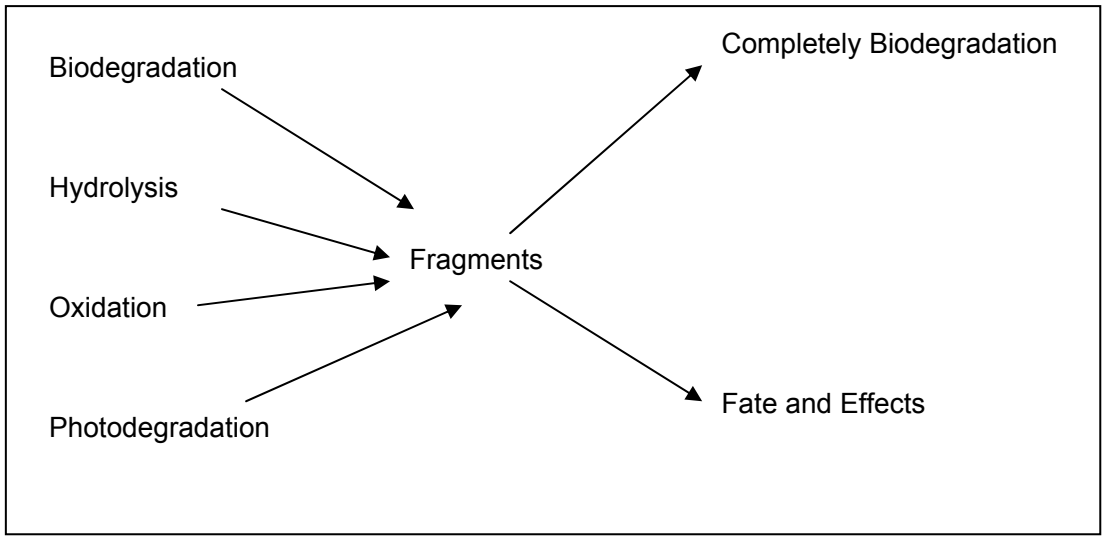

Fig 2.3 Pathways for environmentally degradable polymers (Swift G., 1995).

2.2 Biodegradable Polymers

Biodegradable polymers are an alternative to the petroleum based non-biodegradable polymers. It decreases the solid waste problems created by plastics waste. Biodegradable polymers can be divided to two main categories which are naturally occurring biodegradable polymers and synthetic biodegradable polymers.

Naturally occurring biodegradable polymers including polysaccharides such as starch, cellulose, chitin/chitosan, pullulan, levan, konjac and elsinan. In this compound, simple sugar such as glucose, fructose and maltose are the basic units (Danjaji I.D, 2000). Some polyester such as polyhdroxyalkanoates is also naturally occurring biodegradable polymers. Others naturally occurring biodegradable polymers include

proteins – collagen/gelatin, casein, albumin, fibrinogen, silks, elastins, natural rubbers, lignin, shellac, and poly(gamma-glutamic acid).

Synthetic biodegradable polymers are normally polymers with hydrolysable backbone or polymers that are sensitive to photodegradation. Polyesters are the polymer with hydrolysable backbone. Examples of polymers that in the family of polyesters are poly(glycolic acid), poly(glycolic acid co-lactic acid), polycaprolactone, polyether-polyurethane (I), polyether-polyurethane (II) and poly(amide-enamide)s. Plastics that allegedly biodegradable are listed in Table 2.1.

Table 2.1: Biodegradable materials

Commercial name	Composition	Producer
BIOMER	polyhydroxyalcanoate	Biomer
BIOPOL*	Poly(β-hydroxybutyrate-co-β-hyroxyvalerate)	Monsanto Europe S.A
AEROMYL-Chips	starch	Südstärke
BIOPAC	starch	Franze Haas Waffelmaschinen Indutriegesel. GmbH
BIOPUR	starch	Biotech GmbH
GREEENPAC	starch	Folag (Nasional Starch and Chemical Comp. USA
FRAMFILL	starch	Hubert Loick vnR gmbH
NOVON	starch	Ecostar GmbH
PARAGON	starch	Avebe
RENATUR	starch	Storopack Hans Rechenecker GmbH & Co
Paragon	starch	Avebe
Evercorn	starch modified	Japan Corn Starch Co Ltd.
Vegemat	Corn + natural additives	Vivadour Group
FASAL	saw dust binder	Ifa
Ecoplast	saw dust starch + binder	Groen Granulat
Coffi-Colagenfolie	protein	Naturin GmbH & Co
ACEPLAST RT ACEPLAST LS	cellulose acetate DS=2.25 cellulose acetate DS=2.40	Acetati

BIOCETA	cellulose acetate DS=2.00	Mazucchelli 1849 Spa (Prod.: Tubize Plastics) Franz Rauscher GmbH (Prod.: Tubize Plastics
SCONACELL	starch acetate DS>2	BSL-Olifinverbund
Cohpol	starch ester	VTT Chemical Technology
Ecoplast	poly(lactic acid)	Cargill
LACEA	poly(lactic acid)	Neste Chemicals
BIOPLAST BIOFLEX	starch+poly(-caprolactone)	Biotec
MATER-BI Z-grade	starch+poly(-caprolactone)	Novamont
MATER-BI Y-grade	starch+celluloseacetate	Novamont
MATER-BI N-grade	starch+copolyester	Novamont
Greenpol	starch+aliphatic polyester	SK Corporation
BIONOLLE	poly(butylene adipate-co-butylene succinate-co-ethylene adipate-co-ethylene succinate	Showa Denko (Europe)
SKY GREEN	poly(butylene adipate-co-butylene succinate-co-ethylene adipate-co-ethylene succinate	Sunkyong Ind.
CAPRA 650	poly(-caprolactone)	Solvay
TONE P787	poly(-caprolactone)	Union Carbide
Lunare SE	aliphatic polyester	Nippon Shokubai CO,LTD
EASTAR BIO 14766	aliphatic -aromatic copolyester	Eastman Chemical Europe
ECOFLEX	aliphatic -aromatic copolyester	BASF
BIOMAX	poly(ethylene terephtalate) derivative	Dupont PET Resins and Chem.
BAK 1095* BAK 2195*	poly(ester-amide)	Bayer
PETROCOMP	poly(-caprolactone)+Estane	Petroplast
AQUANOVON	PVA/NOVON	Ecostar
ELVANOL 71-30	PVA insol. high DH	Du Pont
Hydrofilm	PVA	Hydroplst
BIOSOLO	polyethylene+starch	Indaco manufacturing Ltd
DEGRA-NOVON ECOSTAR +	polyethylene+starch+additives	Ecostar
EPI CP530 EPI CP560 EPI CP590	polyethylene+starch+additives	Technicoat Ltd (EPI Envir. Prod. Inc)

* The production has stopped; the material is not available on the market anymore.

(*Resources are taken from www.nf-2000.org/publications/SMT4-2187FinalSynthesis .pdf, 2002)*

2.2.1 Factor Effect The Biodegradability Of Polymers

Biodegradation is defined as process carried out by biological systems (bacteria or fungi) wherein a polymer chain is cleaved via enzymatic activity. It might involve hydrolysis and oxidation process (Kaplan D.L *et. al.,* 1993). Polymer structures, morphology, radiation and chemical treatments and molecular weights are the factors that affecting biodegradation.

Natural macromolecules such as starch and cellulose are generally degraded by hydrolysis and followed by oxidation. The hydrophilic-hydrophobic character of synthetic polymers will affect the biodegradability of the polymer. This is due to the enzyme-catalyzed reactions mostly occurring in the aqueous media. Polymer that has both hydrophobic and hydrophilic segments seems to have a higher biodegradability than those polymers that containing only hydrophobic or hydrophilic structures (Chandra R. & Rustgi R., 1998).

Morphology will bring effect to the biodegradability of the polymer. Synthetic polymers that have short repeating units which enhance the crystallization will make the hydrozable groups inaccessible to enzymes. Size, shape and number of the crystallites will pronounced effect on the chain mobility of the amorphous regions and thus affect the rate of biodegradation (Chandra R. & Rustgi R., 1998).

Photolysis, irradiation and oxidation will cause effect to the biodegradability of the polymers by chain scission and decrease in molecular weight. The rate of the biodegradation increase until most of the fragment polymer is consumed. A lower rate of degradation should be occurred due to the crosslink of the polymer (Chandra R. & Rustgi R., 1998).

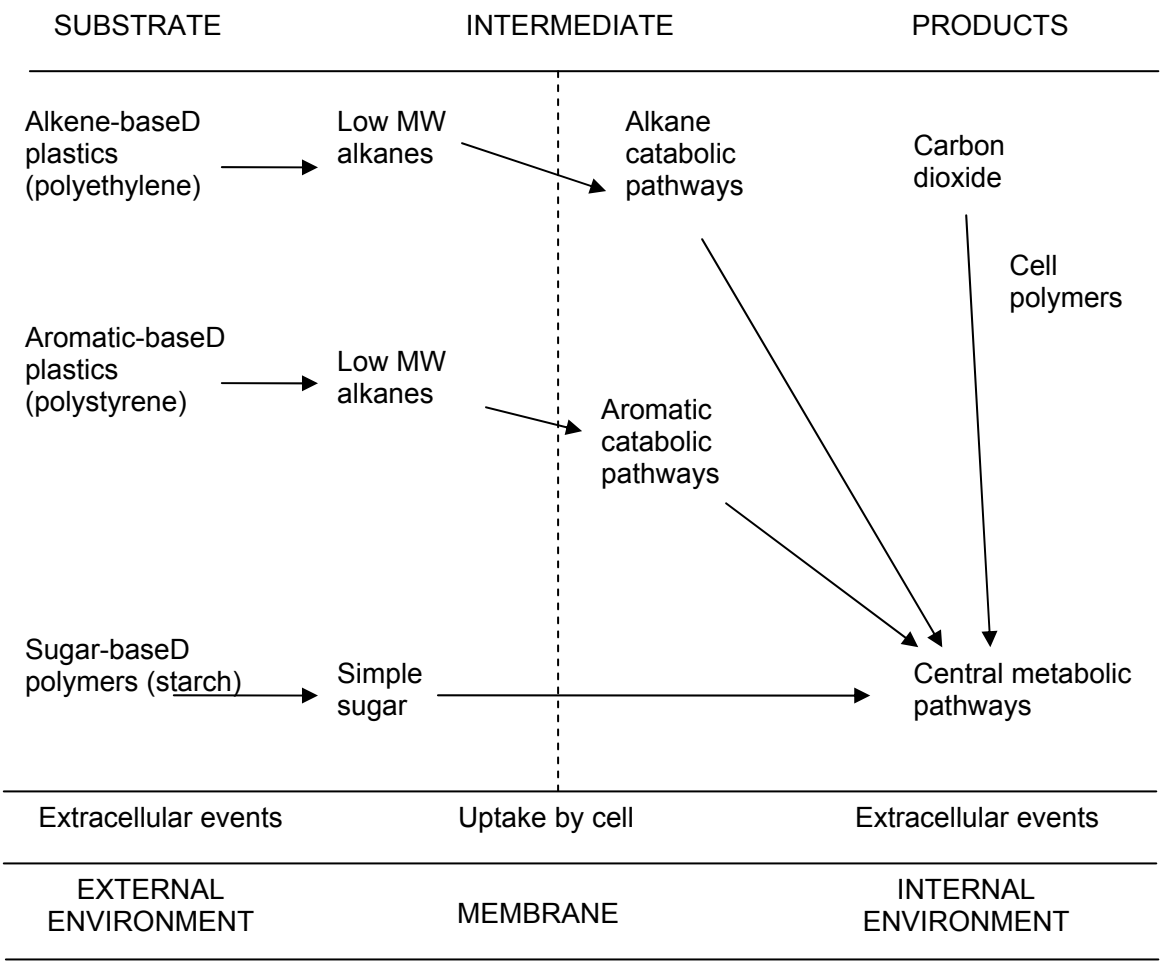

Fig 2.4 : Pathways for polymer biodegradation (Chandra R. & Rustgi R, 1998).

2.2.3 Key Elements To The Biodegradability

The three key elements to the biodegradability of the polymers are organisms, substrates and environment. The biodegradation will not be possible if one of the elements is not present. Suitable microorganisms with the appropriate biochemical machinery to synthesis enzymes specific to the target polymer are needed in biodegradation process. The organisms not only depolymerize the polymer but also mineralize the polymer. The type of organisms (e.g., aerobic or anaerobic, facultative), the nature of the enzymes in these organisms (e.g., hydrolytic, oxidative), the level of enzyme production (e.g., constitutive, inducible), the stability and location of the enzyme (e.g., intracellular, extracellular, periplasmic space), the kinetics of the process

and the influence of inhibitors or inducers in the process are the factors to determine the rate of the biodegradability of the polymers (Kaplan D.L *et. al.,* 1993).

Temperature, moisture (liquid or vapor), salts (concentration and type), oxygen (aerobic to anaerobic), availability of alternative electron acceptors, trace metals trace nutrients, pH, redox potential, environmental stability or flux, pressure, predators (e.g., protozoa), inhibitors, alternate carbon, and light (intensity, energy range, cycle) are the factors on environments that determine how fast is the biodegradable process can be occurred. All these elements have to be present within the window of acceptability for the organisms to produce the enzyme to degrade the polymer (Kaplan D.L *et al.,* 1993).

For the substrate, at the lowest level of the hierarchy, the polymer chain must contain chemical bonds susceptible to hydrolysis or oxidation by enzymes for biodegradation process to initiate. The degree and type of branching, rate of hydrophobicity or hydrophilicity, stereochemistry and molecular weight distribution will bring impact to the depolymerization of the polymer and thus affect the biodegradability. At a higher hierarchy, degree of crystallinity and morphology will affect the accessibility of the enzymes and affect the degradation of the polymer. At the higher level of complexity, coating and interaction of the polymers (blends) will bring into the consideration. Coating and polymers blend might prevent the moisture and permeability of the oxygen to the organisms and thus making the biodegradation impossible (Kaplan D.L *et al.,* 1993). The summary of the elements that affect the biodegradation is stated at Fig. 2.5.

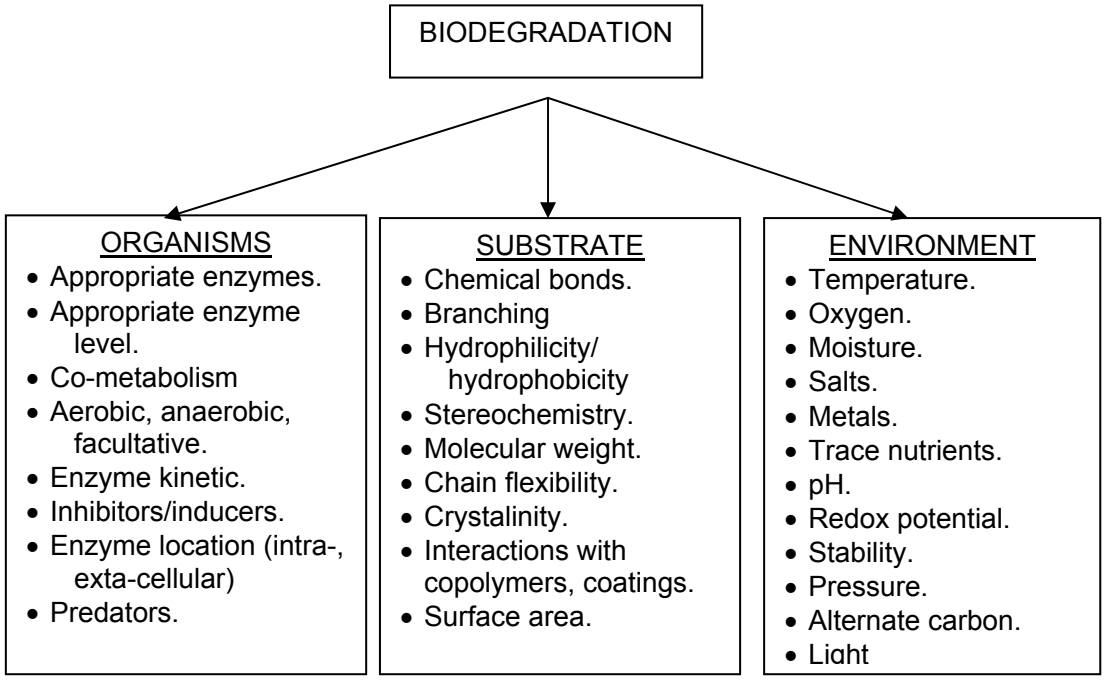

Fig. 2.5: Key elements in the biodegradation process (Kaplan D.L *et al.,* 1993).

2.2.4 Ways To Increase The Biodegradability Of Polymers.

Most of the synthetic polymers contain only carbon-carbon bonds and have very high molecular weights. These types of polymers show little or no susceptibility to enzyme-catalyzed degradation reactions. 'Weak links' was attached or insert within the polymer that are not readily biodegradation. These 'weak links' are designed to control the degradation of an initially high molecular weight, hydrophobic polymer into a lower molecular weight oligomer that can be consumed by the microorganisms through the biodegradation process (Chandra R. & Rustgi R, 1998). Inserting main chain ester groups into vinyl type polymers is shown in Fig. 2.6.

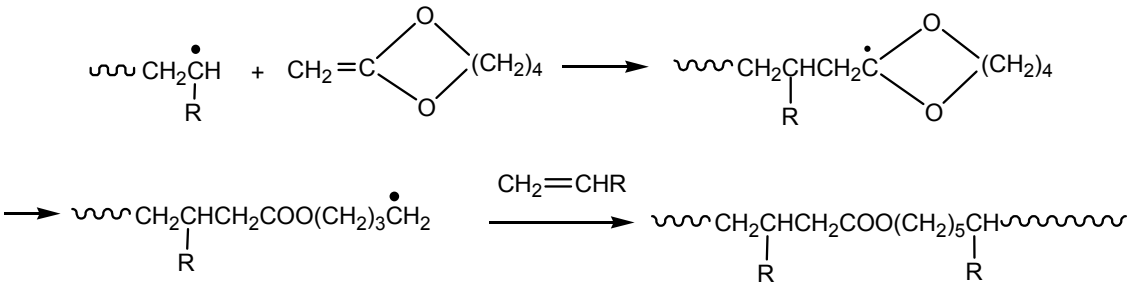

Fig. 2.6 Insertion of ester group into vinyl polymer (Chandra R. & Rustgi R, 1998).

Preparations of the photodegradable copolymer follow by oxidation are shown in Fig. 2.7 and Fig 2.8. These are some of the methods to insert the 'weak links' into a high molecular weight and hydrophobic polymers (Chandra R. & Rustgi R., 1998).

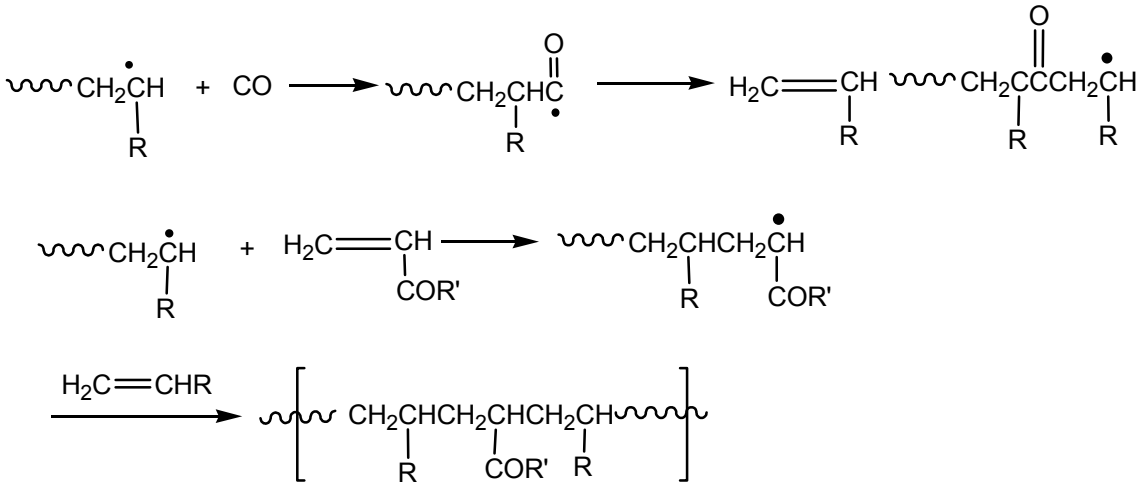

Fig. 2.7 Insertion of ketone group into vinyl polymer (Chandra R. & Rustgi R., 1998).

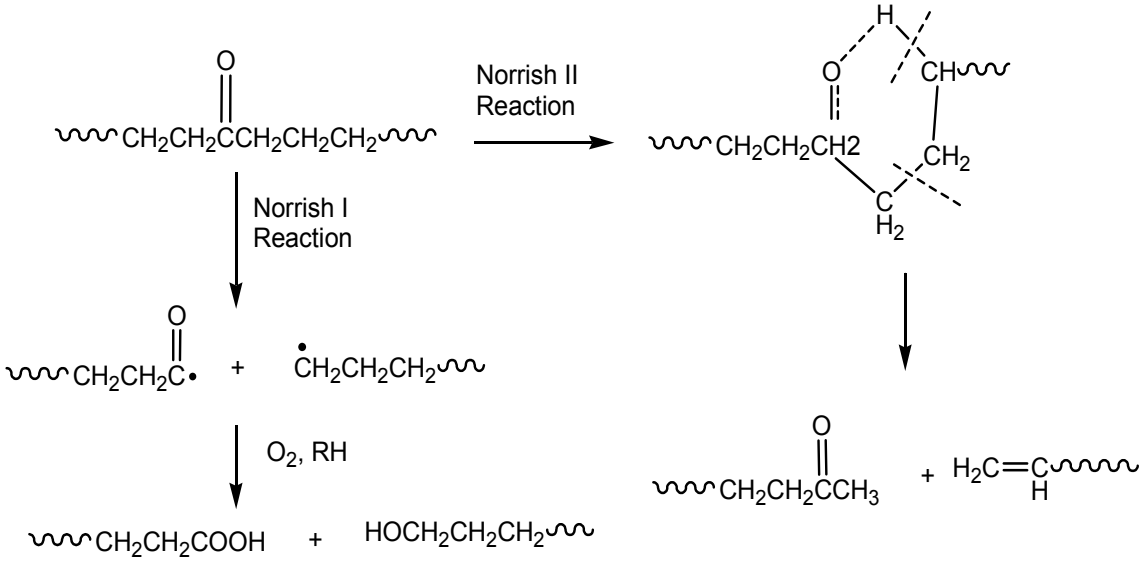

Fig. 2.8 Norrish I and Norrish II reaction mechanisms for the degradation of copolymers of ethylene (Chandra R. & Rustgi R., 1998).

Blending of biodegradable polymers such as poly(ε-caprolactone) and starch with inert polymers such as polyethylene is another method of producing a degradable polymers. The idea in this principle is if the biodegradable component is present in

sufficient amounts and it is removed by the microorganisms, the plastics or film containing the remaining inert will lose its integrity, disintegrate and disappear (Chandra R. & Rustgi R., 1998).

2.2.5 Starch Filled Polymers

Incorporation of starch into the synthetic polymer is hoped to increase the biodegradability of the synthetic polymer when the starch is consumed by microorganisms. It is believed that under a rapid enzymatic hydrolysis, starch will be degraded leading to a void-containing matrix, the reduced of mechanical properties and might be promote the biodegradation of the synthetic polymer due to the increased surface area available for interaction with microorganisms as the molecular weight decrease (Chandra R. & Rustgi R., 1998).

Amylase and amylopectin were the two major components in starch. The linear amylose portion represents about 30% of common cornstarch and has a molecular weight of 200,000-700,000, whereas the amylopectin molecules have molecular weight ranging at 100-200 million. The particles sizes of selected starches were shown in Table 2.2 (Iman S.H. *et al.,* 1999).

Table 2.2 Particles size of selected starches (Iman S.H. *et al.,* 1999).

Starch types	Average diameter, m	Shape
Potato	50	Prolate, ellipsoid and small spheres
Sago	30	Prolate, some truncation
Maize	15	Facetted spheres
Casava	15	Smooth spheres
Rice	5	Heavily facetted spheres
Tairo	2-6	Heavily facetted spheres
Cowcockle	0.5-1.6	Facetted spheres

2.2.5.1Starch Filled Polyethylene (PE)

The idea of incorporation starch to LDPE was first introduced by Griffin. The degradation of starch/polyethylene was observed in composting municipal solid waste (MSW) and this led to the realization that some of the component in the MSW was responsible to the degradation of starch/LDPE. The chain breaking and followed by the biological attack on the fragments of LDPE/starch was caused by unsaturated cooking oil; which selectively absorbed by the LDPE under warm condition (Chandra R. & Rustgi R., 1998).

Normally, there have been three basic approaches of preparing starch filled polymer in lab. The first approach was to prepare a polymer blend consists of starch and synthetic polymers and then formed a films or injection molded articles. An example was the blending of LDPE and starch. On the second approach, starch was blend with other biodegradable polymers such as polyhydroxybutyrate-polyhydroxyvalerate (PHBV) to develop a 100% biodegradable polymer. Thermoplastic polymer chain was grafted on starch or starch was chemically modified in the second approach. Example of starch graft copolymers was starch-poly(methyl acrylate). Recently, the third approach of starch filled polymer was immerged when starch itself has been proposed as a solitary thermoplastic material that can be cast into films or extruded with low molecular weight plasticizers (Gordon *et al.*, 1999).

Starch has been used as filler in thermoplastics since 1977. Griffin is the first who incorporation of starch into synthetic plastic resin. Fatty acid was used as an auto-oxidizable substance to promote the degradability. Griffin claimed that starch filled thermoplastics can achieved the degradability when the starch particles on the surface of the thermoplastics degraded or leached out, thus creating a cellular structure which is readily attacked by the processes of oxidation, hydrolysis, direct enzyme action or combinations of these processes (Griffin, 1977). In Nakamura *et. al.*, different starches such as native, adiapate, acetylated and cassava starch was incorporated in LDPE matrix to obtain a partially biodegradable product, with the aim to decrease the plastics

wastes in the environment. High shearing mixer was used to guarantee the homogeneity of the formulations. Studies on mechanical, morphological and biodegradation properties have been done in this study (Nakamura E. *et al*., 2005).

In Shah *et al.*, the degradation mechanism of starch filled LDPE have been study. LDPE was compounded with native, dry starch using two-roll mill. Strips of LDPE filled starch was obtained by Brabender extruder. Accelerated degradation tests such as thermo-oxidation, enzyme hydrolysis and UV radiation tests were done and the degradation mechanism of the composite has been study (Shah P.B. *et al.*, 1995). Study on using vegetable oil as a compatibilizer in PE-starch blends has been done by Sastry and co-worker. Degradation tests such as thermo oxidative, soil burial, UV light exposure and etc. In this study, it was found that vegetable oil not only acted as plasticizer that can improve the films quality but also acted as pro-oxidant that accelerated the degradation of the PE-starch film (Sastry P.K. *et al.*, 1998). Arvanitoyannis *et. al.* studied the gas/water permeability, mechanical properties and degradability of LDPE and rice or potato starch blends before and after storage. The blends were extruded in the presence of varying amounts of water and hot pressed. On higher starch contents (>30% w/w) there was an adverse effect on the mechanical properties. When starch contents increased, the gas permeability and water vapor transmission rate were increased proportionally. Theoretical and semiempirical calculations for mechanical properties and gas permeability were carried out and possible interpretations were provided for the occasionally observed deviations between the experimental and theoretical values. When the starch content exceed 10% w/w, the biodegradability rate of the blends was enhanced (Arvanitoyannis *et al*., 1998).

Danjaji *et al.* studied the degradation and moisture uptake of sago-starch filled LLDPE composites. After the hydrolysis enzymatic degradation, only the surface starch granules were involved in the hydrolysis, whereas the embedded granules were not easily accessible due to the poor moisture absorption of the matrix. Discoloration,

embrittleness and dimensional changes were observed to the samples after the natural weathering exposure. Soil burial led to a drop in the pH and presence of holes. Mechanical properties decreased with time in the first four months of soil burial and decreased gradually after that. Moisture uptake increased with the increased of starch content and immersion time. Three months were needed for the composites to equilibrate even completely immersed in water. Decreased in mechanical properties were observed with the increasing moisture uptake (Danjaji I.D. *et al.*, 2002). Hakkarainen *et al.* analyzed the susceptibility of starch-filled and starch-based PE to oxygen and air. LDPE containing 7.7% starch and a pro-oxidant formulation in the form of masterbatch (LDPE-MB) was compared to the pure LDPE, LDPE with 7.7% starch (LDPE-starch) and a blend with 70% starch and 30% ethylene maleic anhydride (starch-EMA). Molecular weight changes, formation of carbonyl groups and degradation products were analyzed by FTIR and gas chromograph mass spectrometer (GC-MS) after the samples were subjected to thermal ageing at 80^{o}C in air and water. LDPE-MB has the fastest degradation rate in both environments, although the degradation was faster in air than in water. Etching out or deactivation of pro-oxidant in water explained the slower degradation of LDPE-MB in water. Degradation of pure LDPE and starch-EMA was faster in water. LDPE/starch was the only material that did not degraded during 11 weeks in water at 80^{o}C. Addition of starch to LDPE made the materials even more stable to ageing in air. Molecular weight distribution of LDPE-MB narrowed during the ageing in air but broaden during the ageing in water. Same result was also observed in LDPE-starch samples. This might due to the lower oxygen concentration in water increased the probability for molecular enlargement reactions compare the case in air (Hakkarainen M. *et al.,* 1997).

Yabannavar and Bartha studied the degradability of photosensitized PE, PE-starch, extensively plasticized polyvinyl chloride (PVC) and PP films in aerobic soil for 3 months. Carbon dioxide evolution, residual weight recovery and loss of tensile strength were observed along the degradation duration. Photosensitized PE resulted