PREPARATION AND PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE)/ THERMOPLASTIC SAGO STARCH (TPSS)/KENAF COMPOSITES

ROHANI BINTI ABDUL MAJID

UNIVERSITI SAINS MALAYSIA

2010

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By

ROHANI BINTI ABDUL MAJID

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

2010

Special Dedications To my beloved parents

ACKNOWLEDGEMENTS

First of all, I would like to extend my sincere gratitude to my parents for showering me with encouragements and love. Not forgetting my brothers and sisters that giving me all the encouragements and supports that I need.

I am especially indebted to my supervisor Prof. Dr. Hanafi Ismail for his constant assistance, advices and guidance that molded me into a researcher that armed with skill and knowledge to carry out my research with great perseverance. Sincere thanks are accorded to my co-supervisor, Dr Razaina Mat Taib for spending her valuable time and effort to evaluate my research papers and thesis prior to submission.

Special acknowledgements are also accorded to my friends and my love one, Mohd Firdaus Rusli, Nik Nurazza, Siti Rohana, Noorina Hidayu and Ku Marsilla for giving me a lot of helpful mentally and physically support to help me achieve my goals and sharing all the moments of joy, laugh and sad throughout my study days. My sincere thanks also extended to all postgraduates colleagues for their support, encouragement and invaluable advised.

The advices and opinions obtained from the lab assistants namely Mr. Segar, En. Mohd Hassan, En. Rokman, En. Faizal, En. Shahril and En. Rashid are greatly appreciated. Finally, special acknowledgements are also accorded to School of Materials and Mineral Resources Engineering, Government of Malaysia and Universiti Sains Malaysia for providing research grant and facilities during my study.

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LIST OF SYMBOLS

%	Percent
ºC	Degree Celsius
µm	Micrometer
cm	Centimeter
Deriv.	Derivative
g	Gram
GPa	Giga pascal
hrs	Hours
J	Joule
kg	Kilogram
kJ	Kilo joule
kN	Kilo Newton
kPa	Kilo Pascal
m^2	Square meter
min	Minute
ml	Milliliter
mm	Millimeter
MPa	Mega Pascal
rpm	Revolution per minute
wt%	Percent by weight
wt/v	Weight by volume
wt/wt	Weight by weight
Ic	Carbonyl index

LIST OF ABBREVIATIONS

LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
PP	Polypropylene
PE	Polyethylene
TPSS	Thermoplastic sago starch
TPS	Thermoplastic starch
PE-g-MA	Polyethylene grafted maleic anhydride
MA	Maleic anhydride
EVOH	Polyethylene-vinyl-alcohol
EAA	Ethylene-co-acrylic-acid
PLA	Poly lactic acid
PET	Polyethylene terephthalate
PVC	Poly vinyl chloride
PS	Polystyrene
APS	Aminopropyltriethoxysilane
MPS	γ-methacryloxypropyltrimethoxysilane
TAS	Diethylenetriamminopropyltrimethoxysilane
SEM	Scanning electron microscopy
FTIR	Fourier transform Infra Red
TGA	Thermo gravimetric analysis
DTMA	Dynamic thermal mechanical analysis
DSC	Different scanning calorimetric
DMA	Dynamic mechanical analysis
HDT	Heat deflection temperature
DCP	Dicumil peroxide
TSE	Twin screw extruder
SSE	Single screw extruder
FPTPS	Formamide-plasticized TPS
APTPS	Acetamide-plasticized TPS
UPTPS	Urea-plasticized TPS
EPTPS	Ethylenebisformamide- plasticized TPS
GPTPS	Glycerol-plasticized TPS

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A3 Effects of Soil Burial on Properties of Low Density Polyethylene (LDPE)/Thermoplastic Sago Starch (TPSS) Blends, Journal of Pertanika Science and Technology (vol. 19(1): 189-197, 2011).

A4 Additional of Polyethylene-grafted-Maleic Anhydride: Effects on Properties of Low Density Polyethylene/Thermoplastic Sago Starch Reinforced Kenaf Fiber Composite, Iranian Polymer Journal (vol. 19(7): 501-510, 2010.

PENYEDIAAN DAN SIFAT-SIFAT KOMPOSIT POLIETILINA BERKETUMPATAN RENDAH (LDPE)/TERMOPLASTIK KANJI SAGO (TPSS)/ KENAF

ABSTRAK

Dalam kajian ini, termoplastik kanji sago (TPSS) telah dicampurkan ke dalam polietilena berketumpatan rendah (LDPE). Kandungan termoplastik kanji sago (TPSS) di dalam polietilena berketumpatan rendah (LDPE) di tambah dalam kadar yang berbeza-beza mengikut peratus berat bermula dari 10, 20, 30, 40 and 50%. Kesan penambahan termoplastik kanji sago di kaji dalam beberapa jenis sifat-sifat termasuk dalam sifat-sifat tensil, sifat-sifat morfologi (SEM), sifat-sifat penyerapan air, sifat-sifat pendedahan (jemuran) semula jadi dan sifat-sifat biodegradasi apabila ditanam di dalam tanah. Maleic Anhidrida tercangkuk polietilena telah ditambahkan ke dalam campuran untuk siri yang ke dua untuk mengkaji kesan penambahan agen penserasi terhadap sifat-sifat yang dinyatakan di atas. Untuk siri ke tiga, kenaf telah ditambahkan dengan kadar yang berbeza mengikut peratus berat bermula dari 5, 10, 20, 30 dan 40%, untuk mengenalpasti berat optimum yang diperlukan untuk mendapat sifat-sifat tensil yang terbaik dalam komposit tersebut. Campuran LDPE/ TPSS untuk pencampuran bersama komposit telah ditetapkan dengan kadar berat 80% untuk LDPE dan berat 20% TPSS. Ujian-ujian yang sama telah dijalankan terhadap komposit polietilena berketumpatan rendah(LDPE)/ termoplastik kanji sago (TPSS)/kenaf. Untuk komposit ini, maleic anhidrida tercangkuk polietilena juga telah digunakan sebagai agen penserasi dalam siri yang ke empat. Pemprosesan untuk campuran dan komposit telah dijalankan dengan menggunakan Haake Polidrive.

Campuran dan komposit tersebut kemudiannya telah diacuan mampat menjadi filem berketebalan1 mm. Sampel berbentuk dumbbell dipotong dan digunakan untuk setiap ujian yang dilakukan. Sifat-sifat tensil menunjukkan dengan penambahan termoplastik kanji sago ke dalam polietilena berketumpatan rendah, kekuatan tensil, Young's modulus dan pemanjangan takat putus menurun. Keputusan-keputusan ini ini adalah disebabkan oleh ketidakserasian antara TPSS dan LDPE dalam campuran dan juga disebabkan sifat tensil TPSS itu sendiri yang rendah. Keputusan ujian morfologi menunjukkan penggumpalan termoplastik kanji sago berlaku di dalam campuran dan kadar penggumpalan bertambah dengan penambahan kadar peratusan termoplastik kanji sago. Kadar degradasi di dalam campuran juga bertambah dengan penambahan kadar termoplastik kanji sago. Untuk siri ke dua, sifat-sifat tensil menunjukkan peningkatan dengan penambahan agen penserasi. Ujian morfologi juga mendapati penggumpalan termoplastik kanji sago telah berkurang. Untuk siri ke tiga, penambahan kenaf fiber meningkatkan sifat-sifat tensil jika dibandingkan dengan campuran LDPE/TPSS. Tetapi sifat-sifat tensil ini dapat ditingkatkan dengan penambahan agen penserasi untuk siri yang ke empat. Walaubagaimana pun, sifat-sifat degradasi meningkat dengan penambahan agen penserasi untuk siri yang ke empat ini. Ini mungkin disebabkan oleh kehadiran sebhagian PE-g-MA yang tidak bertindak balas dengan termoplastik sago starch dan kenaf. Kehadiran kumpulan-kumpulan berfungsi ini akan memberikan ruang kepada molekul air semasa ujian dijalankan untuk bertindak balas dan meningkatkan kadar degradasi.

PREPARATION AND PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE)/ THERMOPLASTIC SAGO STARCH (TPSS)/KENAF COMPOSITES

ABSTRACT

In this research, thermoplastic sago starch (TPSS) was incorporated in low density polyethylene (LDPE). TPSS loadings were varied from 10 to 50 wt. % to study the effect of adding TPSS on tensile properties, morphology, water absorption, natural weathering and soil burial properties of LDPE/TPSS blends. Polyethylene grafted maleic anhydride (PE-g-MA) was added into the second series of blends to study the effect of the addition of compatibilizer to the properties of the blends. For the third series, kenaf fiber was incorporated in the blends to study the effect of the addition of natural fiber. Kenaf fiber loading was varied from 5 to 40 wt. % to determine the optimum kenaf fiber loading in the LDPE/TPSS/Kenaf composites. The matrix loading have been fixed with the ratio of 80 wt. % of LDPE and 20 wt. % of TPSS. Same testing has been conducted to the LDPE/TPSS/Kenaf composites with and without the additional of compatibilizer. Preparation of the blends and composites has been conducted in Haake Polydrive with the temperature of 150ºC using rotor speed of 50 rpm. The blends and composites were then compressed into 1 mm thick film using compression molding. Dumbbell shape samples were cut and used throughout the whole research. Tensile properties show that with the addition of TPSS, the tensile strength, Young’s modulus and elongation at break of LDPE/TPSS blends decreased. These results are due to the incompatibility of both materials. SEM micrograph shows that agglomeration of TPSS is higher with the increase in TPSS loading. The degradation properties of the blends also increased with the increase in TPSS loading as well as the degradation time. Tensile properties increased with the addition of PE-g-MA into the blends. This result is due to better interaction and interfacial adhesion between LDPE and TPSS. FTIR analysis also indicated an ester linkage for the compatibilized blends that prove the interaction between the two components. For the LDPE/TPSS/Kenaf composites without the addition of compatibilizer, tensile properties are better compared to the blends but agglomeration still occurred. Better tensile properties were obtained with the addition of compatibilizer as compared to the uncompatibilized composites. However, the degradation rate increased with the incorporation of PE-g-MA. This result might due to the unreactive PE-g-MA that interact with water during natural weathering and soil burial test that can increase the number of carboxylic group in the samples.

CHAPTER ONE
INTRODUCTION

General introduction

Now days, the study on degradable polymeric materials have become one of the major focus for researchers due to the waste management problems. With some additional of other additives or blending the common hydrocarbon polymer with other biopolymer might accelerate the degradable mechanism. In addition, low cost biopolymer such as starch is available due to the natural renewable polysaccharide from a great variety of crops. There are types of raw biodegradable plastic materials in markets but the price is very high if compared to the common hydrocarbon plastic materials.

In the case of hydrocarbon plastic materials such as polyethylene (PE), the degradability and the chemical interactions for degradation are very slow. El Rehim et al., 2004 reported that adding certain additives such as starch to the PE increases polyethylene chain oxidation reactions. Microbial consumption of starch increases polyethylene surface area by creating pores and enhances oxygen based reaction. With the addition of low-molecular-weight plastic additives like plasticizers and fillers make the polymer more susceptible to microbial attack. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened polymer. The microbes, in turn, release nonspecific oxidative enzymes that could attack the synthetic polymer. Also, the gradual degradation of the natural polymer leads to increased surface area by erosion and pitting. This will accelerate the degradation of the synthetic polymer by diffusion of O_2, moisture, and enzymes into the porous polymer

Research now days have focus on the use of native starch. Native starch commonly exists in the form of single granules with about 15-45% crystallinity. Starch in plastic technology can be modified into 3 types of modification which are, chemical modification, starch plasticization and blending with other common thermoplastic. The advantages and disadvantages of starch as well as the modification of starch can be seen in Figure 1.1. The main focus of this research is the plasticization of starch. The starch can be processed like other common thermoplastic materials after the plasticization. There are a lot of plasticizer that can be used in starch modification such as glycerol, urea, formamide and other polyols. During plasticization, hydrogen bonds are formed between plasticizers and starch, replacing the strong hydrogen bonds between the hydroxyl groups of the starch molecules (Hwan-Man et al., 2002).But thermoplastic starch (plasticized starch) itself also does not show any improvement in term of mechanical properties. Common hydrocarbon plastic materials have a very high performance of mechanical properties. Better mechanical and degradation properties can be achieved with the combination of these two types of materials.

In some applications such as in automotives, thermoplastic starch blend with hydrocarbon material does not fulfill all requirements. To preserve renewability and biodegradability as well as improving the mechanical properties of the final products, associations between natural fiber and the blend have been investigated (Averous et al., 2002).

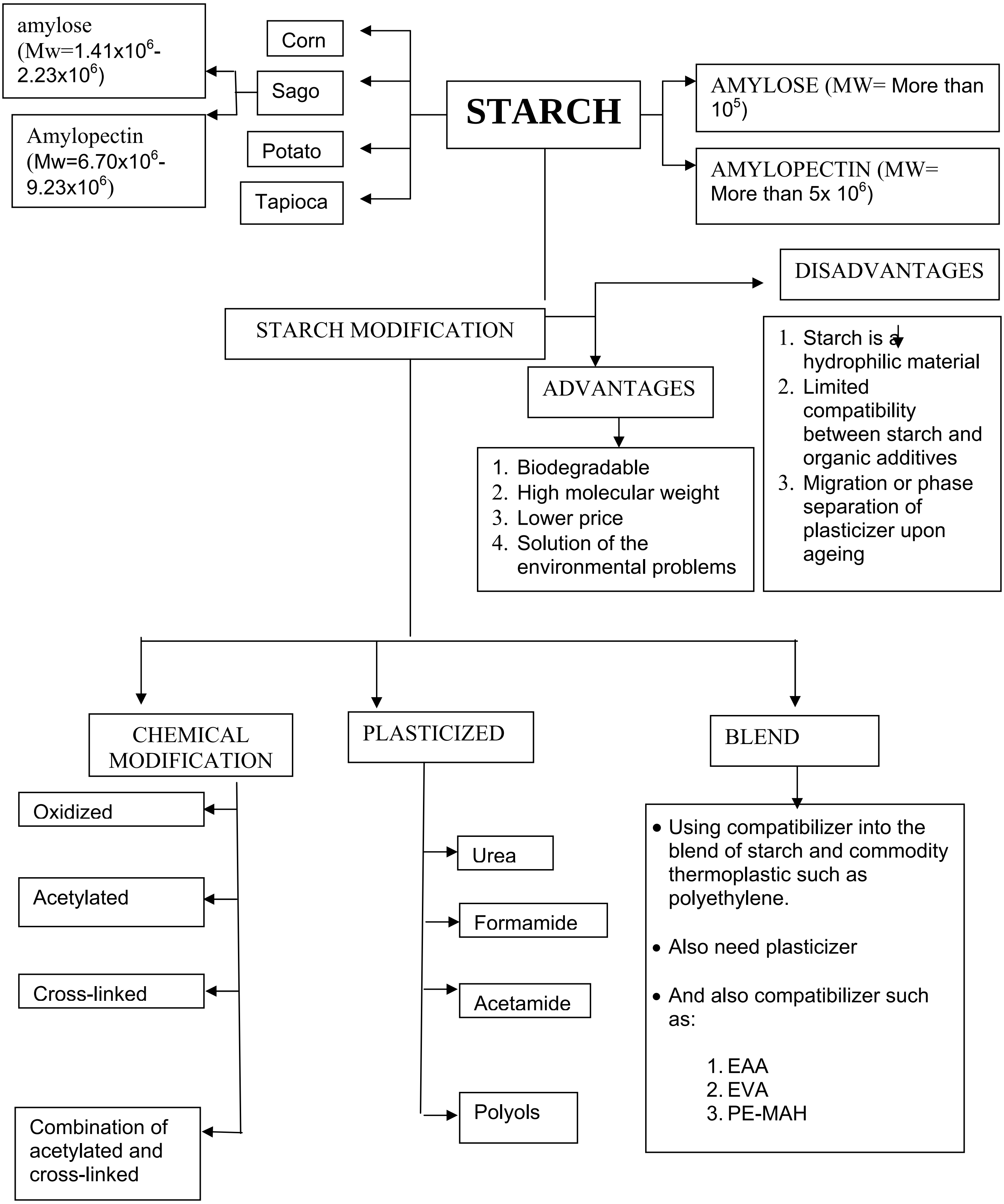

Figure 1.1 Type of starch and modification for industrial uses.

1.1 Problems Statement

Plastic materials usually create problems and disadvantages to the environment because of the long lasting life of these materials (Wang et al., 2004). But the usage of plastic materials keeps increasing years ahead. It was started in 1930 when major thermoplastic such as polystyrene, Poly (vinyl chloride), the polyolefins and poly (methyl methacrylate) were developed (Sangeeta et al., 2007). Since then, plastic have been found useful in applications ranging from transportation, packaging, medical appliances and communications.

However, petroleum based plastics are not degradable materials. Many problems were created because of the non degradable properties of the common hydrocarbon plastic materials. Some examples of the problems created because of the wide usage of plastic materials are shortage of landfill, air pollution due to open burning of the plastic materials and also higher cost for recycling. Some alternatives have been considered to reduce the amount of plastic wastes. One of the popular ways is by the production of degradable plastics.

Now days, degradable plastic materials have been widely produced but the price is higher compared to the common hydrocarbon plastic materials. For commodity uses, the price of the degradable plastic materials in the market cannot compete with hydrocarbon plastic materials. This situation created big problems because the production cost per product was increased. And for higher mechanical properties uses, the used of common fiber and reinforcement will also created problems to the environment. Other than that, introduction of natural fiber as the reinforcing materials is one of the alternatives to reduce the cost and at the same time is environmental friendly. Table 1.1 shows the major biodegradable materials and their prices in the market. Early research of degradable plastic material focused on native starch filled thermoplastic but only low volume of starch can be used due to inherent loss in the mechanical properties at high starch loading (Wang et al., 2004, Sangeeta et al., 2007, Hwan-Man et al., 2002). One of the ways to improve the properties of starch is by using plasticization.

Plasticization of starch allowed the materials to be processed like other common plastic materials. As the thermoplastic starch is 100% degradable material, problems as stated above can be reduced, but other problems were created due to the low mechanical properties and the hydrophilic nature of the materials enhanced the materials to absorbed more water molecules. Because of these problems, research involved thermoplastic starch with incorporation of common hydrocarbon plastic materials and natural reinforcement can be one of the suitable solutions of the problems and at the same time remains the good properties of common hydrocarbon plastic materials.

Table 1.1: Major biodegradable materials and their prices (Narayan, 1993)

Base Polymer	Feedstock	Cost, USD/lb
Polylactide acid (PLA)	Renewable resources corn	1.00-3.00
Polylactide copolymers	Renewable resources cheese whey, corn	<2.00
Cellophane (Regenerated cellulose)	Renewable resource	2.15
Poly(hydroxybutyrate-co-hydroxyvalerate) PHBV	Renewable resource-carbohydrates (glucose),	8.00-10.00

	organic acid	
Starch synthetic polymer blend containing approx. 60% starch	Renewable resources + petrochemical	1.60-2.50
Thermoplastic starch polymer compounded with 5-25% additive	Renewable resources, starch	2.00-3.00
Polycaprolactone (Tone Polymer)	Petrochemical	2.70
Polyvinyl alcohol (PVOH) and thermoplastic PVOH alloys (VINEX)	Petrochemical	1.00-1.25 (PVOH) 2.50-3.00 (VINEX)
Low density starch ester	Renewable resources starch	2.00-3.00
Polyethylene oxide blends (Enviroplastic)	Petrochemical	3.00

1.2 Objectives

The objectives of this study are:

1 To determine the effect of adding thermoplastic sago starch (TPSS) in low density polyethylene (LDPE) on the processing, tensile, morphology and degradation properties of LDPE/TPSS blends.

2 To study the effect of adding polyethylene grafted maleic anhydride (PE-g-MA) on the processing, tensile, morphology and degradation properties of LDPE/TPSS blends.

3 To determine the effect of adding kenaf fiber on the processing, tensile, morphology and degradation properties of LDPE/TPSS/Kenaf composites.

4 To study the effect of adding polyethylene grafted maleic anhydride (PE-g-MA) on the processing, tensile, morphology and degradation properties of LDPE/TPSS/Kenaf composites.

1.3 Outline of Thesis structure

Chapter 1 starts with an introduction of the usage of the common commodity hydrocarbon materials and problems created by the materials, its impact on the environment and the advantages of using degradable biopolymer

Chapter 2 discuss the issues of pollution and landfill problems caused by the use of common hydrocarbon plastic materials. Waste managements 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 plastic materials using starch and also natural fiber as the reinforcing materials, 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 thermoplastic sago starch (TPSS), compatibilizer and natural fiber on the LDPE/TPSS blends. Data, graphs and charts of the mechanical, degradation and morphology of these blends and 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 Degradable Polymer

Degradation is a process where the deterioration in the properties of the polymer takes place due to different factors like, light, thermal, mechanical etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties of the degraded materials. In addition, degradation is an irreversible process leading to a significant change in the structure of a material, typically characterized by a loss of properties and/or fragmentations) (Baljit Singh et al., 2008, Jitendra et al., 2005). Thus, degradable polymers are polymer which went through the degradation process. There are kinds of degradation process which are photo-degradation (degradation preceded by light (UV), bio-degradation (degradation processes in which at least one step is mediated by biological agents), thermal degradation (degradation caused by heat and temperature), ultrasonic degradation (degradation caused by ultrasonic sounds) and high energy degradation (degradation caused by high energy radiations like X-ray, α,β,γ rays) (Jitendra et al., 2005).

Degradable plastics have found most of their popularity in single-use, short-lived items that are difficult to collect and recover by recycling or incineration. Some products being marketed as degradable include disposable diapers, food packaging, shopping bags, compost and sandwich bags, mulch film, six-pack beverage rings, and coatings for paper and paperboard. Plasticizers, chemicals that add flexibility to plastics and enable them to be molded products are increasingly being made of degradable material (Baljit Singh et al., 2008).

2.1.1 Factors affecting the degradability of polymers.

Generally, there are two main types of plastics degradation being researched at present: physical and chemical, and both are closely inter-connected. Physical degradation can involve environmental stress cracking and plasticizer migration and loss (Baljit Singh et al., 2008). Chemical degradation included the reactions of oxidation and hydrolysis (Baljit Singh et al., 2008, Tidjani et al., 1997, Usarat et al., 2006, Youssef et al., 2008]. Polymer structure, molecular weight, morphology, radiation and chemical treatments are the factors that affecting the degradability of polymers (Catia Bastioli, 2005).

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

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

In addition, interactions with other polymers (blends) also affect the degradation properties. These additional materials may act as barriers to prevent migration of microorganisms, enzymes, moisture or oxygen into the polymer domains of interest. The susceptibility of a degradable polymer to microbial attack is sometimes decreased by grafting it onto a non-degradable polymer or by cross linking. On the other hand, in the literature it has sometimes been suggested that combining a non biodegradable polymer with one that is degradable or grafting a degradable polymer onto a non-degradable backbone polymer may result in a degradable system (Catia Bastioli, 2005, Lim Wei Lee, 2007).

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

2.1.2 Ways to Increase degradability of Polymer

Management of plastics waste is a serious problem throughout the world. Plastics recovery technologies include material recovery (mechanical recycling, chemical or feedstock recycling, and biological or organic recycling) and energy recovery (heat, steam, or electricity as substitution for fuel or other fossil resources) (Mohanty et al., 2002, Abd El-Rehim et al., 2004, Averous et al., 2002, Bikiaris et al., 1998, Danjaji et al., 2001, Yew et al., 2005). The use of biodegradable plastics is one of the valuable recovery options (biological or organic recycling) (Gloria et al., 2007, Abd El-Rehim et al., 2004, Hwan-Man et al., 2002, Jeroen et al., 1996, Jiugao et al., 1996, Krishna et al., 1998, Mondragon et al., 2008). Degradable polymers are an alternative to the petroleum based non-degradable polymers.

Most of 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' can be attached or inserted within the polymers that are not readily degraded due to the high molecular weight. These weak links are designed to control the degradation of an initially high molecular weight, hydrophobic polymer into a lower molecular weight oligomer that can be consumed by the microorganisms through the biodegradation process (Lim Wei Lee, 2007). Inserting main chain ester groups into vinyl type polymers in shown in Figure 2.1.

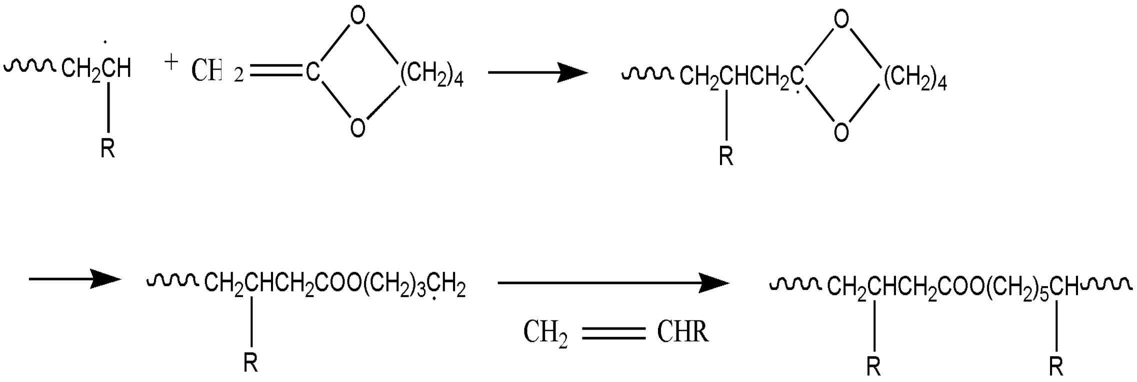

Figure 2.1 Insertion of ester group into vinyl polymer (Baljit Singh et al., 2008).

Preparations of the photodegradable copolymer follow by oxidation are shown in Figure 2.2. These are some of the methods to insert the weak link into a high molecular weight and hydrophobic polymers.

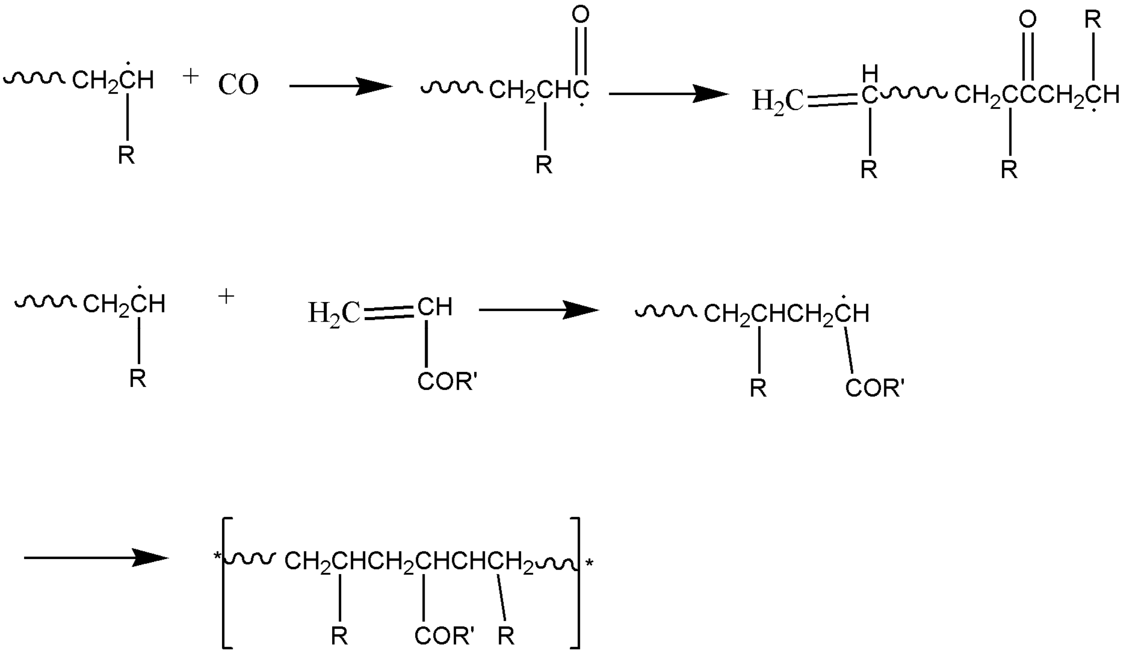

Figure 2.2 Insertion of ketone group into vinyl polymer (Baljit Singh et al., 2008).

Another example of degradation mechanism for ethylene copolymer can be seen in Figure 2.3. From the figures, Norrish I is the free radical generation and no chain cleavage, and Norrish II is the chain cleavage. Ketones are introduced onto the backbones of polymers by photo-oxidation. On exposure to light, these ketone groups absorb photons of appropriate energy, break carbon–carbon bonds, and scission the polymer backbone (D. Feldman, 2002**)**.

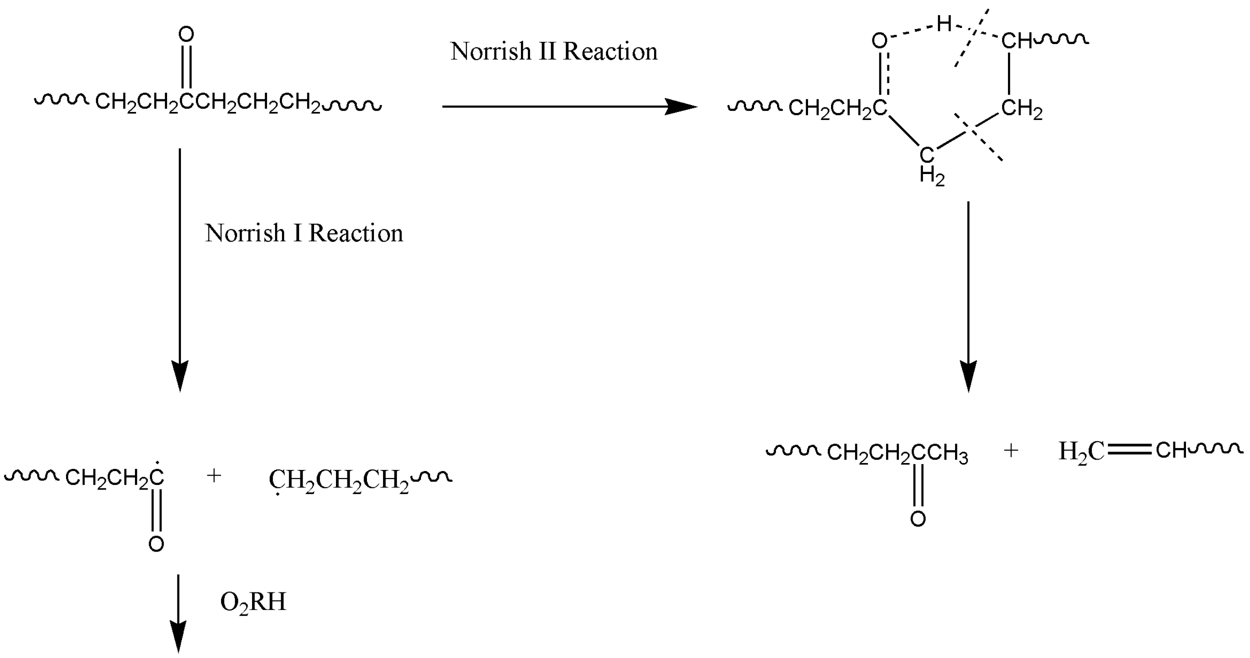

Figure 2.3 Norrish I and Norrish II reaction mechanisms for the degradation of copolymers of ethylene (Baljit Singh et al., 2008) .

Blending of biodegradable polymers such as poly (ε-caprolactone) and starch with inert polymers such as polyethylene is another method of producing 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 (Lim Wei Lee, 2007).

2.1.3 Starch as a Degradable Polymer

Several authors have studied the biodegradability of granular starch-based composites (Danjaji et al., 2001, Yew et al., 2005, Danjaji et al., 2002, Mondragon et al., 2008, Yew et al., 2005) and polymeric blends (Abd El-Rehim et al., 2004, Bikiaris et al., 1998, Hwan-Man et al., 2002). When starch is mixed with biodegradable polymers, a significant improvement in the biodegradation rate can be observed. This has been attributed the faster biodegradation rate/solubilily of starch compared to other biodegradable polymers (Abd El-Rehim et al., 2004). Prinos et al., 1998 reported that LDPE blends prepared with good agreement with the percolation threshold for the starch dispersed particles (volume fraction =0.31 calculated by Peanasky et al., 1991. The addition of a compatibilizer has been reported to produce an adverse effect on the biodegradation extent which means, strong interactions with polar compatibilizers, such as ethylene-acrylic acid copolymer is the lower concentration of starch at the blend surface as it consequence of the better starch domains and its continuity in the bulk. Arends et al, 1992 stated that the presence of same composition in immiscible polymeric systems. That suggests a good alternative to increase the biodegradation extent of starch-based materials.

2.2 Starch

Starch is made up of individual unit of glucose, linked together in chains by alpha 1-4 and occasional alpha 1-6, linkages. The linkage produces linear chains that primarily compressed molecules called amylose, where as the alpha 1-6 linkages serve as branching points to produce branched-chain molecules called amylopectin (Thierry et al., 2007).

Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Chemical structure of amylose and amylopectin can be seen in Figure 2.4 and Figure 2.5 respectively. The relative proportions of amylose to amylopectin both depend on the source of the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none (~3%) (Fringant et al., Doungjai et al., 2007, Gena et al., 2003, Gloria et al., 2007, Van Soest et al., 1996).

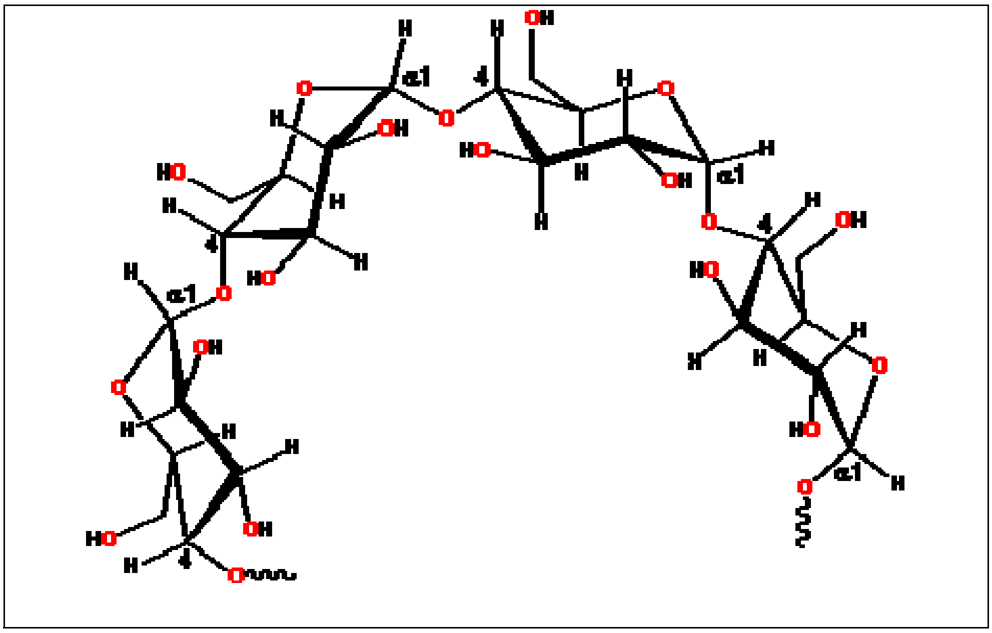

Figure 2.4 Representative partial structure of amylose (Francisco Rodriguez, 2002).

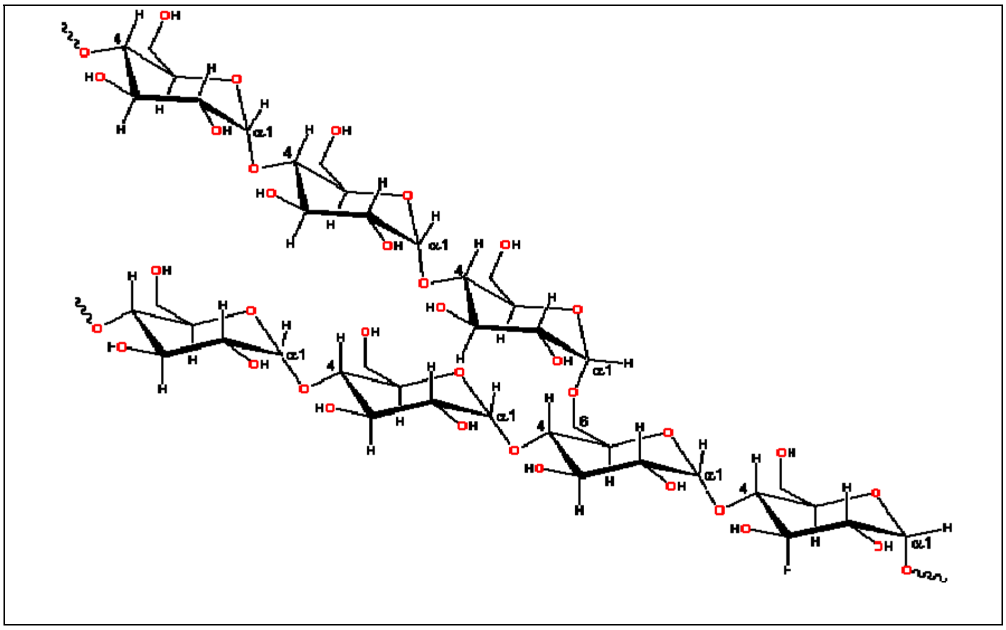

Figure 2.5 Representative partial structure of amylopectin (Francisco Rodriguez, 2002).

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

Starch is a versatile and cheap, and has many uses as thickener, water binder, emulsion stabilizer and gelling agent. Starch is often used as an inherent natural ingredient but it is also added for its functionality. It is naturally found tightly and radially packed into dehydrated granules (about one water per glucose) with origin-specific shape and size (maize, 2-30 µm; wheat, 1-45 µm; potato, 5-100 µm) (Francisco Rodriguez, 2002).

2.2.1 Starch Modification

2.2.1 (a) Thermoplastic Starch

When biodegradability is required, thermoplastic starch (TPS) can be an alternative material for replacement of many petroleum-based products and has gained much attention. The preparation of thermoplastic starch involves the interaction of the native starch and plasticizer. During process, plasticizer molecules entered into starch particles replaced intermolecular and intramolecular hydrogen bonds (Jin-hui et al., 2006).

During the early research, traditional plasticizers have been used such as water and polyols (glycerol, glycol, xylitol and sorbitol) (Jin-hui et al., 2006). But recently there have been other plasticizers that are being use to study the effect of different type of plasticizer content. Other types of plasticizer that can be used are urea, formamide and acetamide (Xiaofei et al., 2004).

Gena Nashed et al., 2003 reported the mixtures of starch, water and glycerol with a water content ranging from 12 –40% and a glycerol concentration up to 75%. Dependent on composition, the enthalpy of gelatinisation ranged from 1.7 – 12.6 J/g (on a dry starch basis), while the onset and peak temperatures varied from 54 to 86 °C and 60 to 90 °C, respectively. As expected, water acted as a plasticiser in that the onset temperature for gelatinisation (T_0) decreased with increasing moisture content. Glycerol, however, increased T_0. It is shown that the T_0 of starch-glycerol-water mixtures may be predicted on the basis of the effective moisture content of the starch fraction of these mixtures resulting from the relative speed of moisture absorption by glycerol and starch, respectively.

Other study on type of plasticizer use has been reported by Xiaofei et al., 2004. Several amide groups-containing plasticizers for thermoplastic starch (TPS), such as formamide, acetamide, and urea, were studied in this paper with glycerol as reference. The hydrogen bond interaction between starch and plasticizers in TPS was tested by Fourier transform infrared (FT-IR) spectroscopy. Both the oxygen of the C-O-H group and the oxygen of the C-O-C group in starch could form hydrogen bonds with these plasticizers. The order of the hydrogen bond-forming abilities is as follows: urea, formamide, acetamide and polyols. The retrogradation of formamide-plasticized TPS (FPTPS), acetamide-plasticized TPS (APTPS) and urea-plasticized TPS (UPTPS) was investigated at three levels of relative humidity (RH=0, 50 and 100%) using X-ray diffractometry. Urea and formamide could effectively improve the resistance of TPS towards retrogradation. The studied mechanical properties demonstrated that FPTPS had a good breaking strain but poor breaking stress, while UPTPS had opposite characteristics. The properties of TPS mainly relied on the hydrogen bond-forming abilities between plasticizers and the starch matrix. On the other hand, the water resistance of TPS mainly depended on the plasticizer. The higher the water absorption of the plasticizer was, the better was the water resistance of the TPS.

Jin-hui et al., 2006 study the used of ethylenebisformamide as a plasticizer where ethylenebisformamide was synthesized and used as a novel plasticizer for corn starch to prepare thermoplastic starch (EPTPS). FT-IR spectra showed that the absorption bands of the C-O groups of the starch molecules were shifted to lower wave numbers, which indicated that a strong and stable hydrogen bond had been formed between ethylenebisformamide and starch. By scanning electron microscope (SEM) native individual corn starch granules were proved to transfer to a continuous phase.

From the previous studies of thermoplastic starch and its plasticizers, it can be summarized that:

Glycerol

- One of the most popular polyol that have been used as thermoplastic starch plasticizer. (Jin-hui et al., 2006).
- But because of the –OH group in the glycerol make the structure has poor water resistant. (Xiaofei et al., 2004).
- If we use glycerol as the plasticizer in thermoplastic starch, it cannot restrain the retrogradation of starch. (Jin-hui et al., 2006).
- But the advantage from using glycerol is that we can get better tensile strength (Jin-hui et al., 2006).

Sorbitol

- Another polyol that can be use as thermoplastic starch plasticizer.
- Most of the properties are just like glycerol.
- It also can improve mechanical properties with less increase in permeability compared to other plasticizers.
- But the drawback is tendency to crystallize over time which resulting reduction in film flexibility and eventually loss of film continuity.

Formamide

- Formamide can restrained the retrogradation of starch compared to conventional glycerol plasticized starch.
- But tensile strength are lower than glycerol
- Water resistance using formamide is better than using glycerol (Jin-hui et al., 2006). This is because formamide formed stronger hydrogen bonds then glycerol which hinder water molecule to combine to the plasticizer (Jin-hui et al., 2006).
- Using formamide such as ethylene bisformamide also can increase elongation at break for tensile properties. This is because ethylene bisformamide contain a flexible –CH2-CH2- chains and enough space is available for the movement for the starch molecules, hence the elongation at break increase with increase in plasticizer contents.

Acetamide

- Acetamide also can be use as plasticizer in thermoplastic starch.

- Hydrogen bonding than will form in thermoplastic starchs is stronger than in glycerol but less strong than formamide because of the stearical hindrance (Xiaofei et al., 2004).

Urea

- Improve the resistance of thermoplastic starch toward retrogradation.
- Water resistance using urea as plasticizer in thermoplastic starch is the best among all type of plasticizers state above (Xiaofei et al., 2004).
- This is because urea can form the strongest hydrogen bonds than other type of plasticizers state above.
- However urea is a solid with little internal flexibility and hence urea-plasticized thermoplastic starch is rigid and brittle.
- Because of that problem urea also can be mixed with formamide to improve their ability (Jin-hui et al., 2006).

2.2.1 (b) Thermoplastic Starch blend with hydrocarbon plastic material

Blending TPS with synthetic polymers have shown the typical characteristics of immiscible polymer blends (St-Pierre et al., 1997). The melt blending of TPS with synthetic polymers has given place to a series of scientific and technologic developments.

In Usarat et al., 2006, preparation and characterization of banana starch blends with LDPE was prepared using extrusion. Chemical structure of the films, morphological properties and thermal properties was studied. Incorporation of compatibilizer was made to improve the interfacial adhesion of the materials. Chemical structure of the film showed a different FTIR spectrum bands after the incorporation of starch as compared to pure LDPE. New bands occurred at 3000-3050, 1640 and 960-1190cm-1 which are designated as O-H stretching, O-H bending and C-O stretching respectively. With the addition of compatibilizer, which in this case is PE-g-MA, even after using the PE-g-MA as a compatibilizer, there was no significant difference between the two spectra. It was anticipated that PE-g-MA which contain an anhydride group could develop hydrogen bonds, with hydroxyl group of starch and form ester group at 1735cm-1.

Danjaji et al., 2001 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 with the increased of starch content and immersion time. Three months were needed for the composites to equilibrate even completely immersed in water.

2.2.1 (c) Starch Modified Chemically

Oxidation is a way of chemical modification, and carboxyl and carbonyl functional groups can be introduced into starch chains. At a suitable temperature and pH value, starch can react with many oxidizing reagents to form oxidized starch. The most valuable oxidized starch is dialdehyde starch.

Shui et al., 2007 reported that a novel method of starch modification was developed to obtain thermoplastic starch plastics with improved comprehensive properties. Corn starch was oxidized under mild conditions using sodium periodate to prepare dialdehyde starch, which had an acceptable average molecular weight. The dialdehyde starch with 35.2% carbonyl content was reacted with different alcohols (methanol, ethanol, and glycol) to prepare a series of novel starch derivatives, whose structures were characterized by 1H-NMR and FT-IR. The thermo gravimetric analysis showed that these starch derivatives had an improved thermal stability compared with dialdehyde starch. Thermoplastic starch and its derivatives were prepared when water and glycerol were added as plasticizers. The modified thermoplastic starch and its derivatives had better mechanical properties than other modified starches, and lower humidity absorption than conventional thermoplastic starches.

Thierry et al., 2007 studied the thermal properties of seven commercial modified cassava starches, including oxidized, acetylated, cross-linked, and combined acetylated and cross-linked starches by differential scanning calorimetric (DSC) in the glassy and rubbery states. Increase in gel hardness in the rubbery state during storage was also monitored, as well as gelatinization behavior. The glass transition temperatures (*T*g) of the modified starches were 3–67ºC significantly lower than that of the non-modified starch. The physical aging peak temperatures were also significantly reduced by 2–37ºC, compared to the non-modified starch, while aging enthalpies increased. Starch modifications did not decrease amylopectin retrogradation significantly. During storage, the oxidized starch gel became significantly harder than the non-modified starch gel, while the hardness of the acetylated and/or cross-linked starch gels was significantly reduced, which confirmed that acetylation or cross-linking can decrease hardness, even when the extent of modification is limited. Different modifications controlled different properties of the starch system, with cross linking and acetylation influencing the gelatinization behavior and the changes in starch gel texture during storage, respectively.

In other study, Byung et al., 2006 reported the use of trifluoroacetic anhydride as a promoter for the acylation of granular starch. Efficient acylation in a homogeneous solution is attained when the carboxylic acid of interest and trifluoroacetic anhydride are added, the latter in at least twice molar excess to the hydroxyl groups of the anhydroglucose residues. This is because it was difficult to find organic solvents for homogeneous reactions of the polysaccharides with acid chlorides or anhydrides as acylation agents. The polysaccharides were not soluble in any single base solvent, such as pyridine or *N*,*N*-dimethylacetamide, and had a limited solubility of , 1% in a solution of dimethyl sulfoxide mixed with such base solvents. In a search of efficient preparative methods, a mixed anhydride system (acyl trifluoroacetate) resulted in a rapid and homogeneous solution of polysaccharide, when freeze-dried material was suspended in a solution of acetic acid in trifluoroacetic anhydride.

2.3 Natural Fiber Composite

Natural fiber composites have found a large dispersal in several areas of technical applications because of excellent characteristics, such as low weight or high strength and stiffness. However, because of increasing environmental consciousness and demands of legislative authorities, the manufacture, use, and removal of traditional