PREPARATION, CHEMICAL MODIFICATION AND DEGRADABILITY OF DURIAN SEED STARCH (DSS) BASED COMPOSITES

by

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LIST OF ABBREVIATION

LDPE	Low Density Polyethylene
DSS	Durian Seed Starch
AAc	Acetic Acid
AA	Acrylic Acid
LA	Lactic Acid
MMT	Montmorilonite
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared
OM	Optical Microscopy

LIST OF SYMBOLS

^{o}C	Degree Celcius
%	Percentage
wt %	Weight percent
Tm	Melting temperature
Xc	Degree of Crystallinity
ΔH_f	Heat of fusion
Wd	Dry weight
Wi	Initial weight
mg	milligram
T_0	Initial degradation
T_{deg}	Final degradation
$Tmax_{deg}$	Maximum degradation
µm	micronmeter

Penyediaan, Pengubahsuaian Kimia dan Degradasi Komposit Kanji Biji Durian (DSS)/Polietilena Berketumpatan Rendah (LDPE)

ABSTRAK

Penyediaan, modifikasi kimia dan degradasi komposit bagi kanji biji durian (DSS)/polietilena berketumpatan rendah (LDPE) telah dikaji. Semua composite telah disediakan dengan menggunakan pencampur dalaman Brabender Plastograph EC pada suhu 150 °C dan 50 pusingan per minit, dan diacuan menggunakan pengacuanan mampatan pada suhu 150 °C. Purata partikel saiz bagi DSS yang digunakan di dalam kajian ini adalah 15 μm. Mikroskop pengimbas elektron (SEM) bagi kedua-dua DSS yang tidak diubahsuai dan diubahsuai telah menunjukkan zarah-zarah adalah berbentuk tidak sekata dan beragglomerak. Analisis Fourier Transform Infra Red (FTIR) bagi kanji yang diubahsuai menunjukkan pengubahsuaian tersebut adalah mudah dikesan dengan terdapat puncak-puncak baru. Kesan kandungan pengisi dan perbezaan modifikasi kimia bagi sifat-sifat mekanikal, morfologi dan sifat-sifat haba bagi komposit kanji biji durian (DSS)/polietilena berketumpatan rendah (LDPE) dikaji. Pelbagai jenis-jenis modifikasi kimia seperti asetik asid (AAc), akrilik asid (AA) dan laktik asid (LA) telah digunakan. Keputusan menunjukkan bahawa penambahan kanji (DSS) ke dalam LDPE mengurangkan kekuatan tensil, pemanjangan pada takat putus, darjah penghabluran (X_c), di mana kestabilan terma dan modulus elastic komposit meningkat. Modifikasi kimia kanji menghasilkan kesan positif ke atas sifat-sifat mekanikal dan terma konposit LDPE/DSS. Komposit LDPE/DSS yang diubahsuai dengan AAc, AA dan LA mempunyai kekuatan tensil, modulus elastic, kestabilan terma, darjah penghabluran (X_c) yang lebih tinggi berbanding komposit tidak diubahsuai. Interaksi antara muka yang lebih baik di antara kanji (DSS) yang diubahsuai dan matrik LDPE telah dibuktikan melalui kajian mikroskop pengimbas elektron (SEM). Spektra FTIR kanji yang diubahsuai menunjukkan kumpulan puncak-puncak baru dari pembentukan ikatan kimia di antara kanji (DSS) dan bahan kimia pemodifikasi. Komposit kanji yang diubahsuai dengan LA mempunyai kekuatan tensil dan pemanjagan pada takat putus yang lebih rendah tetapi modulus elastic, kestabilan terma, Xc lebih tinggi daripada komposit kanji diubahsuai dengan AAc dan AA. Mikrograf SEM komposit kanji diubahsuai dengan LA menunjukkan permukaan yang kasar dan tidak sekata. Sifat-sifat komposit diperkuatkan lagi dengan penggunaan Montmorilonite (MMT) dan Kaolin sebagai pengisi kacuk kepada komposit kanji diubahsuai LDPE/DSS. Nisbah untuk kacukan DSS/MMT dan DSS/Kaolin yang dikaji adalah gabungan 100/0/0, 94/5/1, 88/10/2, 82/15/3 dan 76/20/4. Kedua-dua pengisi kacukan tersebut didapati dapat memberi kesan penguatan bantuan terhadap kanji (DSS). Kacukan dengan MMT menunjukkan sifat-sifat yang lebih baik berbanding kacukan dengan Kaolin. Kedua-dua penambahan pengisi kacukan dan pengserasi telah meningkatkan sifat-sifat regangan serta sifat-sifat pelupusan terma komposit-komposit tersebut. Percirian mikroskop pengimbas elektron (SEM) telah dijalankan untuk mengkaji sifat permukaan rekahan. Ujian pelupusan semulajadi yang ringkas telah dijalankan untuk setiap siri bagi tempoh 9 bulan. Berdasarkan ujian pelupusan tersebut, kanji yang diubahsuai dengan asetik asid (AAc) mempunyai kadar pelupusan yang tinggi berbanding akrilik asid (AA) dan laktik asid (LA). Walaubagaimanapun, kacukan pengisi dengan MMT mempunyai kadar pelupusan yang tinggi berbanding kacukan pengisi dengan Kaolin. Analisis Fourier Transform (FTIR) dan mikroskop optikal (OM) menunjukkan pembuktian pelupusan komposit-komposit tersebut.

Preparation, Chemical Modification and Degradability of Durian Seed Starch Based Composites/LDPE

ABSTRACT

Preparation, chemical modification and degradability of Durian Seed Starch (DSS)/low-density polyethylene (LDPE) composites were investigated. All of composites were prepared using Brabender Plastograph EC internal mixer at temperature of 150 ˚C and rotor speed of 50 rpm, and moulded using compression moulding at temperature of 150 ˚ C. Particle size analysis revealed that average size of DSS used in this research is 15 µm. Scanning electron microscopy (SEM) of unmodified and modified starch were found to be irregular shape particles and shows agglomeration pattern. The Fourier Transform Infra-Red (FTIR) analysis on modified DSS indicates that the modification is easily detected due to the new positions of absorbance peaks. The effect of filler loading and different types of chemical modifications on mechanical properties, morphology and thermal properties of LDPE/DSS composites were studied. The various types of chemical modifications via acetic acid (AAc), acrylic acid (AA) and lactic acid (LA) were chosen in this study. The results showed that the addition of starch into LDPE matrix reduced the tensile strength, elongation at break, degree of crystallinity (X_c), whereas the thermal stability, Young's modulus and percent of degradability of composites increased. The chemical modification of DSS resulted positive effect on mechanical and thermal properties of LDPE/DSS composites. The modified LDPE/DSS composites with AAc and AA have higher tensile strength, Young's modulus, thermal stability, degree of crystalinity (X_c) compared to unmodified LDPE/DSS composites. Improvement in interaction between modified DSS and LDPE matrix was proven by SEM study. The FTIR spectra of modified DSS showed the new functional group from the formation of chemical bonding between DSS and chemical modifying agent. The modified LDPE/DSS composites with LA had lower tensile strength and elongation at break, but higher Young's modulus, thermal stability, X_c than modified LDPE/DSS composites with AAc and AA. The SEM micrographs of modified LDPE/DSS composites with LA exhibit a rough surface. The composites properties were further enhanced with incorporation of montmorilonite (MMT) and Kaolin, as hybrid filler into DSS. The DSS/MMT and DSS/K hybrid ratio is studied at 100/0/0, 94/5/1, 88/10/2, 82/15/3 and 76/20/4 weight percent (wt %). Both hybrid fillers were found to act as reinforcing fillers to the DSS, with for the MMT show better properties than Kaolin. Both additions of hybrid fillers also have improved the tensile properties as well as the thermal degradation properties of the composites. SEM was also done to investigate the fracture surface behavior. Simple biodegradability test was conducted on each series of the composites were taken for 9 month. Based on biodegradability test, the modified LDPE/DSS composites with AAc had higher rate of degradation compare to AA and LA. Meanwhile, hybrid filler of MMT give higher degradability compare hybrid filler of Kaolin. FTIR analysis and optical microscopy was done to determine the degradability of the composites.

CHAPTER 1 : INTRODUCTION

1.1 Introduction

Plastic were first invented in 1860, but have only been widely used in the last 30 years. Global production and consumption of plastics have increased, from less than 5 million tons in the year 1950 to 260 million tons in the year 2007 (Moinuddin, 2011). One the major use the plastics in packaging due to its cheaper price and lightweight. Polyethylene (PE) is one of the majorly used synthetic plastics as shown in Figure 1.1. This is due to its wide range of physical properties and suitability to most of the commercial thermoplastics fabrication process. One of the most important criteria in this resin is its cheaper price that can give a competitive edge compared to other materials; polymeric and non-polymeric materials (Peacock, 2000).

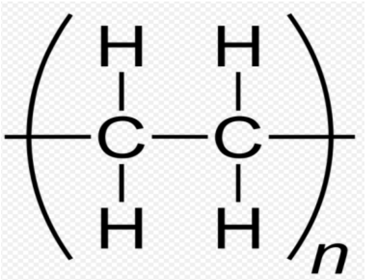

Figure 1.1 : Structure of polyethylene

Low density polyethylene (LDPE) is used in the manufacture of blow-moulded bottles, film bags, food boxes, sacks and sheeting, flexible piping and hosepipes, household articles such as bowls and buckets, telephone cable sheaths, toys and etc. (UNEP, 2009). Their useful physical and chemical properties such as durable, easy to process and characteristically inert have been the main cause of its broad applications in many industrial uses (Mark, 1999). LDPE is known to be hardly degraded after disposal and this can cause pollution to the environment and affects the ecological system (Bastioli, 2005). The hydrophobicity of LDPE is one of the reasons to its high resistance to the microorganism attack. Once its throw out that is produce unnecessary waste which will harm the sewage and further disturb the aquatic ecosystem. This situation will become worst when our environment become hazardous because of these problems.

To overcome all these problems, some steps have been undertaken. The first strategy involved production of plastics with high degree of degradability (Tokiwa, Y. et al., 2009). In recent years, polymer from with high degree of degradability is called 'bio-plastic' had successfully been used to produce plastic that is biodegradable under certain temperature and humidity conditions. Biodegradable polymer is a newly emerging field. A vast number of biodegradable polymers have been synthesized and some microorganism and enzymes capable of degrading them have been identified. In developing countries, environmental pollution by synthethic polymers have assumed dangerous proportions. As a result, attempts have been made to solve these problems by including biodegradability into polymers in everyday use through slight modifications of their structures. In right term, bio-plastics consist of either biodegradable plastics (i.e., plastics produced from fossil materials) or bio-based plastics (i.e., plastics synthesized from biomass or renewable resources) (Tolinski. M, 2012). For example, polyethylene (PE) and Nylon 11 (NY11) which produced from biomass or renewable resources are non-biodegradable. Acetyl cellulose (AcC) is either biodegradable or non-biodegradable, depending on the degree of acetylation. AcC's with a low acetylation can be degraded, while those with high substitution ratios are non-biodegradable (Bansal and Mona, 2011).

Biodegradation is a natural process where the organic chemicals in the environment are being converted to simpler compounds, mineralized and redistributed through elemental cycles such as carbon, nitrogen and sulphur cycles (Chandra & Rutsgi, 1997). In terms of biodegradable polymer, it can be divided into naturally occurring biodegradable polymers which is low cost, abundant availability, and can be added as filler in blends with other polymers. Starch is contain hydroxyl groups and readily biodegradable. Many efforts have been made to develop biodegradable polymers based on starch in order to overcome the problems caused by the petroleum-based polymers (Koenig & Huang, 1995; Avella et al., 2000).

Starch had been widely studied as an important natural polymer for many applications such as packaging, agricultural and biomedical applications due to its low cost, abundant availability and biodegradability (Prachayawarakorn et al., 2010). It can be mixed into the thermoplastics to increase the biodegradability and reduce the cost of the material. In 1970's, Griffin had conducted a research to study the biodegradability of the starch filled polyethylene. It was found that the starch was consumed by various microorganism when deposited in the environment. This will leave the polymer blends with a lot of holes that will ease the decomposition of materials into small particles. These small particles will increase the total surface area that will further allow the access of the oxygen and cause the oxidation process of the polyethylene becomes easier (Bikiaris & Panayiotou, 1998).

Durian (Durio Zibethinus) is a tropical fruit native to Southeast Asia. It is one of the most highly valued and desired fruits among Southest Asians and known as 'King of the fruits" due to its distinct flavour and unique taste. Durian is normally eaten fresh. Only one-third of durian is edible, whereas the seeds (20-25 %) and the shell are usually thrown away. Previous studies had shown that durian seed is very nutritious and has high fibre content (Amiz et. al., 2004a). Durian seed flour could be incorporated into various food products including cake, cookies, soup, tempura, etc. either as a substitute for wheat flour or as thickening agent (Amiza et. al., 2004b). Therefore, the focus of this research is to study about produce a biodegradable blends unmodified and modified starch with synthetic polymer which are LDPE at different filler loading. This research also investigates the effects on biodegradable with hybrid fillers.

Chemical modification of natural filler is the reaction between natural filler and chemical reagent, and it has the potential to improve the properties of natural filler. Most of modified starches are produced by chemical modification of the hydroxyl group attached to the starch molecules. Starch modifications, will greatly affect the characteristic of the final modified starch, consequently product quality. Starch modification achieved through derivation, such as etherification, esterification, cross-linking and grafting of starch. These modification alter starch gelatinization, pasting and retrogradation behavior (Yachuan et al., 2014). Modification of starch using carboxylic acid, such as acetic acid, acrylic acid, lactic acid and citric acid induced to acetylation process. According to Reddy and Yang (2009), citric acid also can act as crosslinker in starch film and improve the tensile strength of starch film approximately 150% higher as compared to non-crosslinking starch film.

1.2 Problem Statement

The limitation of petroleum based polymer and environmental issue promoted the polymer from renewable resources to have potential in the future market. The commodity plastics are made and synthesis from petroleum and also known as petroleum based plastics. LDPE was found to be the highest contributor to the number of plastic waste since it is one of the majorly used synthethic plastics. As it is petroleum based, it is hard to degrade and take a longer time to decompose. One thing that can be done to help and make it degrade is to blend it with filler especially natural filler such as Durian Seed Starch. By adding the starch into synthethic plastic, the composites will be partially or half biodegradable. In the biodegradable plastic composite, the starch or fiber will take place between the polymer molecules. The starch or fiber will be degrade thus break the bond between polymer and polymer.

The use of durian seed starch (DSS) as natural filler has not yet been widely used for commercialized. In 2012, a study has been done by Osman & Zakaria that incorporates the durian seed flour in the PP and HDPE composites (Osman & Zakaria, 2012). However, the uses of DSS as natural filler in the LDPE has not yet been studied. The incorporation of DSS alone might not give the best result in improving the characteristics and performance of its reinforced composites. However, better result might be obtained if the properties of the DSS are combined with the properties of well known and commercialized fillers to give a combined effect of both fillers when filled into a composites. Therefore, this research will further study the incorporation of DSS as a natural filler and hybrid filler of MMT and

Kaolin in the LDPE. Large difference in surface polarity between hydrophilic starch and hydrophobic thermoplastic matrix usually leads to poor interfacial adhesion and thus poor mechanical properties of final materials. To overcome this, the filler has to be modified in order to promote adhesion.

As mentioned ealier, DSS has been used as natural filler in LDPE matrix in order to produce LDPE composites. the incompatibility between DSS and LDPE plays a major problem in composites system due to different polarity between the hydrophilic DSS and hydropobic LDPE matrix. It brings adverse effect on the mechanical and thermal properties of the composites owing to weak interfacial adhesion and poor dispersion of DSS filler in LDPE matrix. In order to overcome this drawback, the hydrophlicity of DSS was reduced through chemical modification methods. The presence of amine and hydroxyl functional groups on chitosan is being a primary role in modifying the DSS surface using several modifying agents. This method is expected to yield positive result indicated by the enhancement of DSS-LDPE matrix interaction and improvement of mechanical and thermal properties of LDPE/DSS composites.

1.3 Research Objectives

The main objective of this study is to prepare a degradable composite containing durian seed starch (DSS) and low density polyethylene (LDPE) blends. This objective is divided into :

1. To investigate the characterization properties of filler regarding particle size, morphology and FTIR.
2. To study the effect of unmodified DSS content on mechanical, thermal properties, morphology, soil degradation and FTIR of LDPE/DSS.
3. To study the effect of different type chemical modification of DSS using Acetic Acid (AAc), Acrylic Acid (AA) and Lactic Acid (LA).
4. To compare the reinforcing efficiency between LDPE/DSS/MMT and LDPE/DSS/Kaolin Hybrid composites with different filler ratio.

1.4 Scope of Study

In order to achieve the objectives of this study, the LDPE/DSS and hybrid LDPE/DSS composites were compounded by using the internal mixer at temperature of 150 °C. prior to compounding, the DSS was going through modification by using 3 wt.% of Acetic Acic (AAc), Acylic Acid (AA) and Lactic Acid (LA). The filler loading used in this study were 0, 5, 10, 15 and 20 wt.%. For LDPE/DSS/MMT and LDPE/DSS/Kaolin hybrid filler, the ratio of 100/0, 94/5/1, 88/10/2, 82/15/3 and 76/20/4 was used. To further investigate the properties of the composites, characterization and testing were conducted on all composites series. The morphological analysis was studied through the use of scanning electron microscope (SEM), while the thermal analysis on the composites was determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Fourier transform infrared (FTIR) analysis was conducted to identify and study the chemical groups of he composites while the mechanical properties such as tensile strength, elastic modulus and elongation at break were determined using the tensile testing machine. Finally, the soil degradation test was conducted to investigate the biodegradability of all composites.

1.5 Outline of Thesis

The thesis has been divided into five (5) chapters and each chapter deals with an aspects of the overall problem of understanding the properties behavior of the DSS and hybrid filler MMT/Kaolin filled LDPE composites.

- Chapter 1 covers the introduction of thesis. It provides an overall introduction for the study including a brief introduction about research background, problem statements, objectives and scope of study, and outline of thesis.

- Chapter 2 provides a comprehensive review on natural filler namely starch in polymer matrices, along with some review of related works reported in the literature;
- Chapter 3 explains the experimental method used to prepare LDPE/DSS composites and chemical modification methods of DSS in order to increase the properties of composites. The types of testing and characterization used in this study were thoroughly discussed.
- Chapter 4 focuses the preliminary studies on filler characterization between unmodified and modified DSS; provides the characterization and properties on the effect of the filler content on properties of LDPE/DSS, LDPE/DSS/MMT and LDPE/DSS/Kaolin composites.
- Chapter 5 presents conclusions on the present work and suggestions for future works.

CHAPTER 2 : LITERATURE REVIEW

2.1 Polymer Composites

A composites is a material that consists of more than one component, in which at least one of the components remain in solid state during its manufacture (Weeton, 1987). Composites materials were developed because no single and homogenous structural material had all desired characteristics for a given application. The idea of composite materials is to improve mechanical characteristics such as stiffness, toughness and strength at ambient and high temperature that cannot be attained by individual constituents such as ceramics, metal alloys or polymers (Callister, 2000). The light weight and superior mechanical properties of polymer composites have made them good candidates for applications in wide areas of the modern industry that range from transportation, building to medicine and packaging (Seavey et. al., 2001).

A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Filler are employed the desired properties of the polymer or simply reduce the cost. Nowadays, the application of polymer composites as engineering materials has become state of the art. Polymer composites with improved mechanical, thermal, barrier and fire retardancy properties are widely used in very large quantities in variety of applications. However by the application of conventional filler such as talc, calcium carbonate, fibers, etc, its often requires to use a large amount of filler in the polymer matrix to have significant improvements in the composite properties which may result to some other undesired properties such as brittleness or loss of opacity (Zhang & Friedrich, 2003).

The final properties of reinforced polymers (composites) are influenced by the nature, properties and content of components, dimensions of components and micro structure of composite and interfacial interactions between matrix and dispersed phase. The efficiency of properties improvements depends strongly on the mechanical properties of the filler, the adhesion between matrix and filler and especially on the aspect ratio of the filler. The aspect ratio of the filler is very important and crucial for many properties in composite such as electrical (Al-Saleh & Sundararaj, 2010; Grosslord et al., 2008), mechanical (Zhang et al., 2007) and thermal (Meneghetti & Qutubuddin, 2006) properties. Polymer composites with high aspect ratio of nano-fillers such as platelet clays, carbon nanotubes and nanofibers are receiving considerable attention due to their unique multifunctional and highly enhanced properties. Combination of filler nanoscale dimension and high aspect ratio with its nanoscale dispersion within polymer matrix leads to the significant improvements in the polymer properties at very low filler volume fractions. As a result of lower filler using the macroscopic homogeneity and low density of primary polymer retains as well as it's opacity in the final nanocomposites are the new class of hybrid materials in this category (Mittal, 2009).

2.2 Classification of Polymer Composites

Polymer composites generally can be classified into four extensive classes based on polymer matrix, such as thermoplastic, thermoset, elastomer and TPE composites. The TPE belong to class of materials that have combination physical properties of thermoplastics and elastomers, in which exhibit properties typical of rubbery materials but can be processed liked plastics (Ismail, H. 2002). The thermoplastic composites are subdivided into commodity and advanced composites, distinguished by the type of materials that are used in construction and by the general market in which they can be found. The advanced composites can be distinguished from commodity composites because of their frequent use of more expensive matrix materials and higher-priced reinforcement such as carbon/graphite. Also they are always applied in more structure demanding locations that have a greater need for weight saving. Meanwhile, applications of the commodity composites is more common such as used in printed circuit boards, shower enclosures, pleasure boats etc. (Astrom, B. T. 1997).

2.3 Constituents of Polymer Composites

2.3.1 Matrix Phase

The matrix of the polymer composites providing uniform load distribution to the reinforcing constituents by holding the reinforcement/dispersed phase in place. The matrix generally is the thermoplastic, thermosets, elastomers and TPE. Primary consideration in the selection of the matrix is depends to the factors including compatibility with reinforcement, final properties of the end product, shape design of the product's component, fabrication or processing requirement and total cost of the production (Ismail, 2002). As regards to the selection factors of the matrix, it will enhance strength, modulus and toughness of the composites. Thus, the main functions and requirements of the matrix are including (Ismail, 2002).

(1) To bind the reinforcement together by virtue of its matrix interphase and reinforcement phase;

(2) To hold reinforcement in proper orientation or position, in order to carry loads, distributes and transfers them evenly to the reinforcement;

(3) To transfer stresses between the reinforcement;

(4) To provide a barrier against a crack propagation and an environmental degradation such as heat and moisture;

(5) To protect the surface of the reinforcement from mechanical degradation;

(6) To add toughness to the composites. Though reinforcement is very strong, it can be brittle. Thus, the matrix can absorb energy by deforming under stress;

(7) To provide a solid form to the composites this aids handling during and after fabrication. This is particularly necessary in discontinuously reinforced composites because the reinforcement is an insufficient length to provide a handle able form;

(8) To control electrical and chemical properties of the composites;

(9) To control transverse properties, interlaminar strength and elevated-temperature strength of the composites with continuous phase.

2.3.2 Dispersed Phase

Dispersed phase in solid material and used to be as an additional material in the matrix phase (M. Shah, A., 2005). They are usually is inert materials in various shape such as fiber, particulate, flake, filler or laminate and has been added to improve mechanical and physical properties of the composites mainly strength, toughness and stiffness. In plastic composites, usually refer as additive materials that increase general physical properties such as tensile strength, flexural modulus (Siriwardena, 2003). With an addition of the dispersed phase in polymer matrix, the noticeable effects are recognized such as add rigidity, stiffness and hardness, regulate thermal expansion and shrinkage, improve heat resistance, improve or regulate electrical characteristics, increase strength and reduce creep, modify rheological properties, aid processability, modify appearance and alter density (Leong, 2003).

According (Xanthos, 2005 (b)) studied, has proposed that the dispersed phase can be acted either as reinforcing filler or just as common filler. The common filler were considered as additive which due to their unfavorable geometrical features such as surface area or surface chemical composition) could not only moderately increase the modulus of the composite while strength (i.e., tensile and flexural) remained unchanged or even decreased. Their major contribution was in lowering the cost of materials by replacing the more expensive materials and induces specific properties. In contrary with the common filler, the term reinforcing filler has been generated to describe greater geometrical features of which have been suitable modified with the objective to improve the mechanical properties of the composites. Reinforcing fillers are characterized by relatively high aspect ratio (α), according to ratio of length to diameter for fibers and ratio of diameter to thickness for platelets or flakes. Nevertheless, for spheres a useful parameter for characterizing the effectiveness of the filler is the ration of surface area to volume that needs to be as high as possible for effective reinforcement.

In this research study, it is more appropriate to use the term "filler" to cover both reinforcing filler and common filler, as both filling matrices. The properties of filler approved can give high impact to the matrix-filler system, and thus determine the performance of the final products. Other factors that also contribute in reinforcing composites are particle size, particle surface area and surface activity. The smallest particle size of filler will offer greater properties of composites since it can highly transfer the stress applied from matrix to filler, and thus provide high strength and stiffness to the composite.

2.3.3 Filler-matrix Interface

The interface between filler and matrix is also crucial in terms of composite performance. The interface serves to transfer externally applied loads to the reinforcement via shear stresses over the interface. Controlling the 'strength' of the interface is imperative (Fowler, et al., 2006). Clearly, good bonding is essential if stresses are to be adequately transferred to the reinforcement and hence provide a true reinforcing function. Another important mechanical property is toughness, or the ability of an engineering material to resist the propagation of cracks. This occurs in composites by virtue of their heterogeneous structure (Fu, S. et al., 2008).

Owing to the general incompatibility between natural filler and most matrix polymers, methods of promoting adhesion are frequently needed. Several approaches have been explored, including chemical modification of the filler prior to composite manufacture and introducing compatibilising agents to the polymer/filler mix during processing (Tserki, et al., 2006).

Commonly, all composites materials comprise two different phases that are separated by a region which is called interface. Adhesive and cohesive forces on interface are very important in transferring the load from matrix phase to filler phase (Hull, D. & Clyne, T. W. 1996). The loading transfer depends on bonding strength on interface. A number of theories have briefly described the bonding phenomena on interface and most of them comprising of chemical and mechanical bonding.

2.4 Biodegradable of Polymers Composites

Littering and waste disposal with regard to environmental pollution has created urgency and the need to develop biodegradable materials that have comparable properties with current polymeric materials at equivalent or lower cost. Currently a number of biodegradable polymers are derived from both synthetic and natural sources. Polymers from renewable resources have attracted a lot attention in the past two decades. Mainly, due to the environmental concern and the realization that petroleum resources are diminishing (Vert et al., 2009). Renewable and sustainable biodegradable materials can reduce the use of petroleum reserves and also reduce dependence on foreign oil that has led to political instability in certain countries due to corruption (Garth and Kowal, 2001). Biodegradable polymers have offered scientist a possible from natural resources can be improved via blending and formation of composites, if their properties are not acceptable (Thanarathan, 2000). For instance, it is recognized that biodegradable polymers and composites plastics are a good choice for the packaging industry because packaging materials are widely used and disposed of after a short period of time (Yadaz et al., 2001). Therefore, due to their degradability the bio-plastics are more suited or the packaging applications than conventional plastics which persists for years after the disposal. The typical life cycle of biodegradable polymers is represented in Figure 2.1 (Yang et al., 2005).

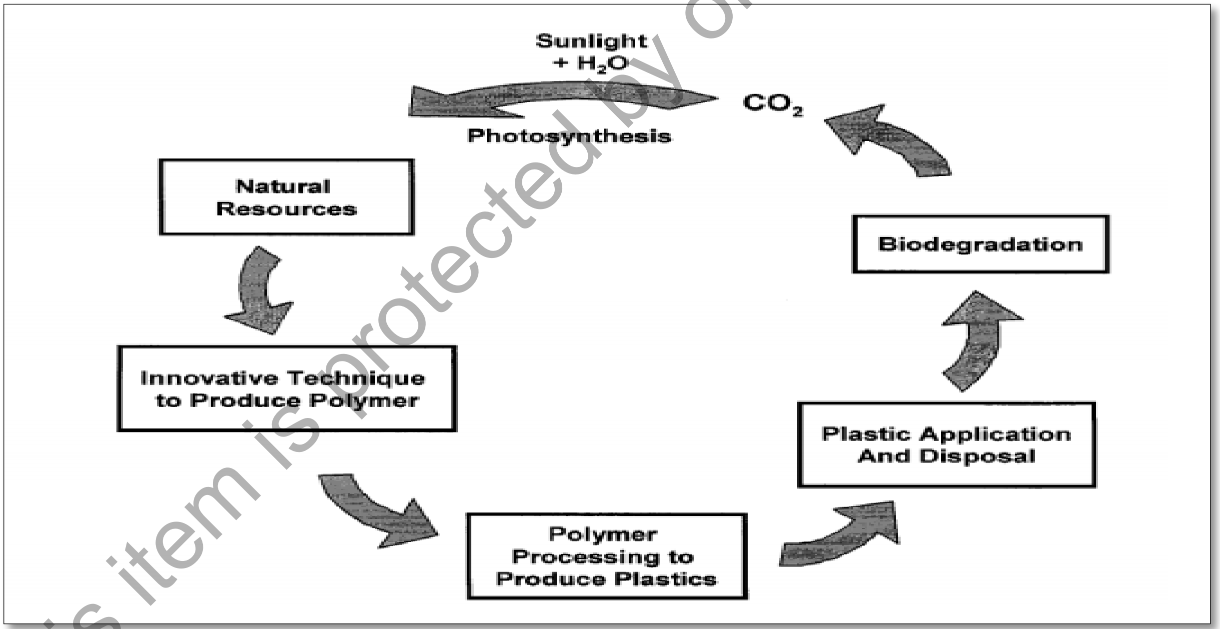

Figure 2.1 : Life cycle representation of biodegradable polymers (Yang et al., 2005).

2.5 Thermoplastic Starch

Thermoplastic starch (Shogren, Fanta & Doane, 1993) is a relativelty new material for application as a biodegradable plastic and is one of the main polymers studied today in this field. It is used alone or compounded, usually with polar synthethic polymers, in contents that usually exceed 50%. Starch is not true thermoplastic but in the presence of plasticizers (water, glycerin, sorbital, etc.) at high temperature (90 ^{o}C – 180 ^{o}C) and under shear, it readily melts and flows, allowing for its use as an injection, extrusion or blow molding material, similar to most conventional synthetic thermoplastic polymers. Thermoplastic starch has two main disadvantage compared to most plastics currently in use, i.e. it is mostly water-soluble and has poor mechanical properties. Its water resistance may be improved by mixing it with certain synthethic polymers (Bastioli, 1995), adding crosslinking agents such as Ca and Zr salts (Shogren, Lawton, Tiefenbacher & Chen, 1998) or adding lignin (Baumberg, Lapierre, Monties & Della Valle, 1998). Several synthethic polymer have been used to improve the mechanical properties of thermoplastic starch, such as ethylene-acrylic acid copolymer (EAA), ethylene-vinyl alcohol copolymer (EVOH) (Bastioli, 1995; Pierre, Favis, Ramsay, Ramsay & Verhoogt, 1997).

The starch have a crystalline structure will be disrupted at high temperatures in the presence of excess water or any other plasticizer able to form hydrogen bonding with starch hydroxyl groups. During this process starch undergoes an irreversible order-disorder process during which the crystalline structure of amylopectin and amylose chains in disrupted irreversibly. The process of starch decrystallization is called gelatinization which is associated with the loss of double helices together with the loss of the lamellar and long-range structure of starch. This requires sufficient chain mobility, which can be provided by heat and/or mechanical energy in the presence of a plasticizer. According Otey et al., (Otey, Mark, Mehltretter & Russess, 1974) demonstrated that gelatinization can be achieved through the processing of starch in presence of glycerol and water through conventional polymer processing equipment. According Averous (Averous, 2004) has schematically described this process, showing the different stages of extrusion (Figure 2.2). The crystalline starch structure disappears at temperatures higher than 70 °C – 90 °C in the presence of plasticizers such as water, glycerol, formamide, sorbitol and liquid ammonia (Carvalho, 2008). The harder it is for the plasticizer to get into the starch structure, which is affected by plasticizer size as well as type, the higher the temperature and/or mechanical energy must be for the starch chains to acquire the sufficient mobility to break down the crystal structure.

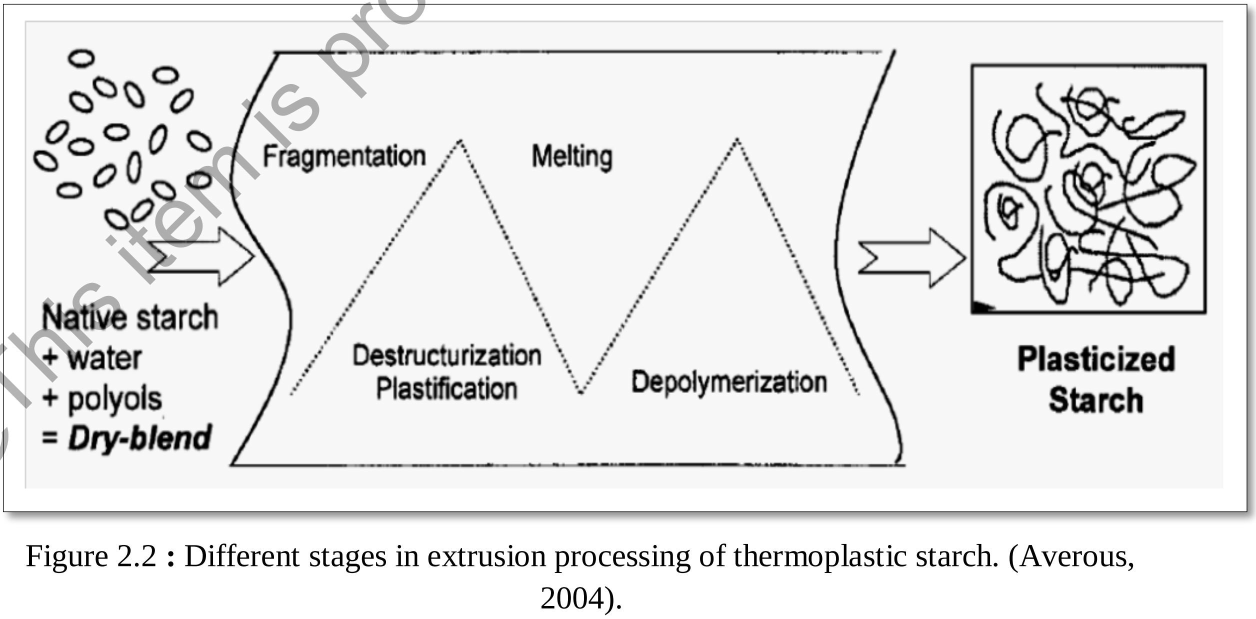

Figure 2.2 **:** Different stages in extrusion processing of thermoplastic starch. (Averous, 2004).

2.5.1 Classification of Thermoplastic Starch

Thermoplastic starch (TPS) is processed, like synthetic plastics, through extrusion and injection units. Unfortunately, TPS is a very hydrophilic product, and additional processing of starch to reduce the hydrophilic character of the starch chains is sometimes necessary. Research and development of biodegradable plastics were stimulated due to rising oil prices and further augmented by environmental concerns. The objective of intensive academic and industrial research was to develop plastics by using renewable, biodegradable resources that fulfill, market needs (Kassem et al., 2012). Pure starch is highly brittle, and has poor mechanical properties and stability; it is often reinforced with fibers or blended with synthethic polymers (Liu et al., 2009). Blending is important process for the modification of polymer properties. It is economical and usually does not needs special equipment and techniques. From a technological point of view, a compatible blend it attained when the preferred properties are improved as a result of mixing two or more polymers. TPS is blended primarily for two reasons (Murphy et al., 2000); 1) to improve water resistance and mechanical performance, 2) to use TPS as modifier to make polymer blends biodegradable and economical. Starch blends with polar polymers having hydroxyl groups, such as poly(vinyl alcohol) (PVA), copolymers of ethylene and partially hydrolyzed vinyl acetate (EVA) were prepared (Rodriguez et al., 2003). Due to the hydrophilic nature of these TPS blends, water used as the plasticizer.

Starch blends can be separated into two main categories according to (St. Pierre et al., 2007). The source and biodegradation properties of the polymer to be blended with starch. The processing technique for its preparation. As for the first category, the sources can be obtained directly from biodegradable biopolymers or can be synthethic polymers from either oil or renewable resources, not depending on their structure but biodegradable. As for the second category, starch blends are prepared by two main processing techniques, i.e. melting and solution/dispersion. In melt processing, plasticization of starch granules is done in an extruder or a batch mixer to prepare the starch blend. Alternatively, two extruders are used, first a single screw extruder is used to gelatinize starch (Follain N et al., 2006). In solution or dispersion processing, casting is frequently used to finish the product. Starch/poly (ethylene-co-acrylic acid) (EAA) cast films were the first commercial materials produced by solution or dispersion technique (Zhang JF et al., 2004).

2.5.2 Processing of Thermoplastic Starch

Thermoplastic starch is produced by mixing native starch with a plasticizer at a temperature above the starch gelatinization temperature, typically in the 70 ° C – 90 ° C range. This operation weakens the hydrogen-bonds present in the native starch leading to a fully amorphous free-flowing material. The resulting material is known as plasticized starch, destructured starch or thermoplastic starch (TPS). The properties and rheology of thermoplastic starch have been througly investigated (Aichholzer 1998; Vergnes 1987; Villar 1995; Willet 1995). As such, the TPS is not a suitable material for most common uses. It is very hydroscopic and its properties and dimensional stability are strongly affected by the humidity level since water is a plasticizer for TPS. Also in presence of humidity, the amorphous TPS tends to reform its hydrogen-bonds leading to recrystallization (also called retrogradation) and in turn to embrittlement of the material. This strong property dependence on plasticizer content can become an advantage however when the TPS is blended with another hydrophobic polymer. In this case, the hydrophobic polymer can protect the TPS from direct water contact and moisture uptake while the plasticizer level in the TPS can be used to tune the mechanical properties of the TPS. Therefore, the vast majority of work involving the use of starch as a material has focused on blending of TPS and other synthetic polymers (Averous 2004; Schwach 2004; Wang 2003). The synthetic material can be biodegradable to produce a fully compostable material or can be non-biodegradable to produce materials for longer-time applications. Examples of biodegradable blends include blends of TPS with polycaprolactone or polybutylene succinate which are two petrochemical based polymers. With the recent commercial introduction of poly(lactic acid) PLA, there has also been a high interest for PLA/TPS blends and these have been investigated in terms of their compatibility (Huneault 2007) and of their processing into injection molded product, biaxially oriented films (Capleau 2007) and low density foams (Mihai 2007).

The compounding process used for the preparation of TPS/polymer blends is relatively complex. It must nominally enable the precise metering of starch and plasticizers, the starch gelatinization and the mixing of the TPS with the second polymer phase to obtain finely dispersed or finely segregated blend morphology. Additionally, more elaborate functions may be performed. For example, venting or devolatilization may use to control volatiles level. Interface modification through in situ interfacial reaction may be used to compatibilize the blend or to modify the starch interface. Surprisingly, very little scientific publications have focused on the effect of the process on the final blend properties and little guidance can be found as to what could be the best practices in terms of TPS/polymer blend compounding technology. In order to prepare finely dispersed blends of thermoplastic starch and synthetic polymers, it is beneficial to prepare the blends using a sequence of operation carried out along a twin-screw extrusion process (Favis 2003; Favis 2005; Favis 2008; Rodriguez-Gonzalez 2003). In the process described in the Favis et al. patents (Favis 2003; Favis 2005; Favis 2008; Rodriguez-Gonzalez 2003), the basic ingredients for the making of thermoplastic starch, starch, water and glycerol, are first mixed in 50:25:25 proportions to form a suspension (also referenced as a slurry). This suspension is pumped into the extruder. Under the action of shear and heat, the starch and plasticizer (water and glycerol) are transformed into thermoplastic starch (TPS) through a well known transformation called “gelatinization”. Further along the extrusion process the extrusion process, the water is removed to get a water-free TPS that is solely plasticized by glycerol. Then, further along the process, a synthetic polymer is added and mixed with the TPS to form the TPS/polymer mixture that is the end result of the process. In the Favis et al. process, it is specified that the synthetic polymer must be added in molten form to prepare blends with an acceptable dispersion.

2.5.3 Application of Thermoplastic Starch

Thermoplastic starch is biodegradable plastic based on starch. The semi-crystalline starch granules must be broken by thermal and mechanical processing to obtain TPS (Cyras VP et al., 2008). The important role of a plasticizer, accompanied with heat and pressure, is to break up the crystalline structure of starch granules and form a continuous amorphous polymer (Chung. H et al., 2003). After TPS is produced, slight recrystallization can occur which improves the tensile strength but allows more ductility. Thermoplastic starch has been used widely in several applications such as packaging, adhesives, paper, bio-composites, tissue engineering and in food and pharmaceutical industries (Nyakanen V.P.S et al., 2014). Moreover, many studies on blending starch with synthethic polymers have been investigated (M. Kaseem et al., 2012). The idea was to decrease oil consumption and allow faster biodegradation (M.A. Carqueira et al., 2012). TPS can be blended with synthethic biodegradable polyester such as polycaprolactone (PCL), polyesteramide (PEA), (L. Averous et al., 2000) and poly-3-hydroxy butyrate-co-valerate (PHBV). These blends can improve the mechanical properties and improve hydrophobicity, comparing to pure TPS (J.Olivato et al., 2014).

2.6 Polyethylene

Polyethylene is atype of polymer that is classified as a thermoplastic, meaning that it can be melted to a liquid and remolded as it returns to a solid state. As the name implies, polyethylene is chemically synthesized from molecules that contain long chains of ethylene, a monomer that provides the ability to double bond with other carbon-based monomers to form polymers. Polyethylene is known by other, non-official names, such as polyethene in the United Kingdom. In addition, it is sometimes spelled as polyethylene or abbreviated to simply PE. The first laboratory creation of polyethylene in 1898 by accident