FABRICATION AND CHARACTERIZATION OF BIODEGRADABLE FILMS FROM SAWDUST

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DECLARATION

I declare that this thesis entitled "Fabrication and Characterization of Composite Biodegradable Films from Sawdust" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature	:………………………………
Name	: Nor Hafiza bt Hamidon
Date	: 20 APRIL 2009

DEDICATION

To my beloved Mum,

My family members that always love me,

My friends, my fellow colleague

My supervisor,

And all faculty members,

For all your care, support and believe in me.

Love,

Nor Hafiza Hamidon

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Bismillahirrahmanirrahim,

I am so thankful to Allah S.W.T for giving me patient and spirit throughout this project until the research is successfully complete. With the mercifulness from Allah therefore I can produces a lot of useful idea to this project.

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ABSTRACT

This report shows the performance of the composite biodegradable film using chitosan as a primary material with addition sawdust fiber and starch as polymer matrix. The main objective of this research is to fabricate the composite biodegradable film using chitosan with sawdust fiber (CS) and the composite biodegradable film using chitosan, starch and sawdust fiber (CSS). The films were prepared by wet casting of the aqueous solution containing chitosan as the main polymer, acetic acid 1% v/v as solvent, PEG 400 as plasticizer. Sawdust was used as fiber and starch as matrix polymer were added in the chitosan solutions. The solutions were poured on a glass plate and dry it in ambient temperature. The films morphology structure was observed using Atomic Force Microscopy (AFM). The results revealed that the CS film more smooth and good integrity structure. Chemical composition of the films was investigated using Fourier Transform Infrared (FTIR) and revealed the starch presence in CSS film. The thermal properties characterization using Thermal Gravimetric Analyzer (TGA) and Differential Scanning Calorimetric (DSC) showed that thermal properties for both films are not quite different in melting and degradation temperature.

ABSTRAK

Kajian ini menunjukkan pencapaian filem campuran yang mampu dibiodegradasi yang dibuat dengan *chitosan* sebagai bahan utama dengan tambahan hampas serbuk kayu sebagai gentian dan kanji sebagai polimer cetak. Tujuan utama kajian ini adalah untuk menghasilkan filem campuran menggunakan *chitosan* dengan serbuk kayu (CS) dan filem campuran menggunakan *chitosan*, kanji dan serbuk kayu (CSS). Filem ini diperbuat menggunakan kaedah acuan lembap larutan akueus daripada campuran *chitosan* sebagai polimer utama, asid asetik 1% v/v sebagai pelarut dan *PEG 400* sebagai bahan pengenyal. Serbuk kayu digunakan sebagai gentian dan kanji sebagai polimer cetak yang dicampurkan di dalam larutan chitosan. Larutan dituangkan ke atas plat kaca dan dikeringkan dengan suhu bilik. Struktur tatabentuk filem dikaji menggunakan *Atomic Force Microscopy (AFM)*. Hasilnya menunjukkan permukaan filem CS lebih lembut strukturnya dan kemas. Campuran bahan kimia bagi filem dikaji dengan menggunakan *Fourier Transform Infrared (FTIR)* dan daripada graf membukti kewujudan kanji di dalam filem CSS. Analisa terhadap haba pula menggunakan *Thermal Gravimetric Analyzer (TGA)* dan *Differential Scanning Calorimetric (DSC)*. Hasilnya kedua-dua filem mempunyai sifat kehabaan yang tidak banyak berbeza pada suhu pencairan dan suhu degradasi.

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LIST OF SYMBOLS

CS	Chitosan and Sawdust
CSS	Chitosan, Starch and Sawdust
PEG	Polyethylene Glycol
AFM	Atomic Force Microscopy
wt %	weight percent
Ra	means roughness
ρ	Density
m	Fluid viscosity
ρ_l	Liquid density
ΔH	Enthalpy changes, duty
ΔHl	Enthalpy for liquid
$\Delta H°f$	Standard heat of formation
$\Delta H°vap$	Standard heat of vaporization
ΔHv	Enthalpy for vapor
$\Delta Hvap$	Heat of vaporization
ΔP	Pressure differential or pressure drop
Cp	Vapor heat capacity
F	Molar flow rate
g	Gravity acceleration
H	Enthalpy
MW	Molecular weight
P	Pressure
Q	Duty or heat transferred per unit time
T	Temperature

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CHAPTER 1

INTRODUCTION

1.1   Project Background

Food packaging, an important discipline in the area of food technology, concerns preservation and protection of all types of foods and their raw materials, as well from oxidation and microbial spoilage. Petrochemical based plastics such as polyolefin, polyesters, polyamides, etc. have been increasingly used as packaging materials, because of their availability in large quantities at low cost and favorable functionality characteristics such as good tensile and tear strength, good barrier properties to O_2 and aroma compounds and heat sealability.

On the contrary they have a very low water vapor transmission rate and most importantly they are totally non-degradable, and therefore lead to environmental pollution, which pose serious ecological problems. Hence, their use any form or shape has to be restricted and may be even gradually abandoned to circumvent problems concerning waste disposal (Tharanathan and Saroja, 2001). Of late, there is a paradigm shift imposed by the growing environmental awareness by all to look for packaging films and processes, which are biodegradable and therefore compatible with the environment.

In a sense, biodegradability is not only a functional requirement but also an important environmental attribute. Thus, the concept of biodegradability enjoys both user-friendly and eco-friendly attributes, and raw materials are essentially derived

from either replinishable agricultural feedstock or marine food processing industry wastes, and therefore it capitalizes on natural resource conservation with an underpinning on environmentally friendly and safe atmosphere (R.N.Taranathan, 2003). An additional advantage of biodegradable packaging materials is that on biodegradation or disintegration and compositing they may act as fertilizer and soil conditioners, facilitating better yield of the crops.

Commonly it is the most important in the food industry to extend the storage time of food. Up to now, artificially synthesized additives of preservatives have been added to food directly or indirectly to improve the storage stability of food. However, such additives which are harmful to human bodies may exert a bad influence to health as well as peculiar flavor and fragrance of foods. Therefore, there is an urgent need for a method of extending food storage time without using a preservative.

In order to overcome the foregoing problems, research for developing antibacterial packaging film is being actively conducted. It is general that the antibacterial packaging film provides antibacterial property to the packaging material according to types of added antibacterial substances and preparations methods. Particularly, the antibacterial effect, maintenance and properties of the packaging material can vary depending on interaction between the used antibacterial substances and high molecules, which is the main component of the film construction.

Use plastics in cooking and food storage can carry health risks, especially when hormone-disrupting chemicals from some plastics leach into foods and beverages. Plastic manufacturing and incineration creates air and water pollution and exposes workers to toxic chemicals. Designing biodegradable packaging alternatives and ensuring that they end up in an appropriate disposal system can enhance the environmental quality of many products.

1.2 **Problem Statement**

Food packaging is concerned with the preservation and protection of all types of foods and their materials, particularly from oxidative and microbial spoilage and also to extend their shelf-life characteristics. The rational to do this research is to decrease the environmental pollution from non-biodegradable plastics. Increased use of synthetic packaging films has led to serious ecological problems due too their total non-biodegradability. Continuous awareness by one and all towards environmental pollution by the latter and as result the need for a safe, eco-friendly atmosphere has led to a paradigm shift on the use of biodegradable materials, especially from renewable agriculture feedstock and marine food processing industry wastes. A solution to this problem might be replacing the synthetic packaging plastics with active biodegradable plastics. So, the natural materials are using for developing the biodegradable film or packaging such as chitosan starch or sawdust. Also, the significant of this research is to decrease the use of synthesis additives and preventives for food stability and for developing antimicrobial packaging film.

1.2 **Objective**

a. To fabricate the sawdust composite biodegradable films with and without starch

b. To characterize the different composite biodegradable films using:
  i. Atomic Force Microscopy (AFM) for morphology characterization

  ii. Fourier Transform Infrared (FTIR) for chemical composition characterization.

  iii. Differential Scanning Calorimetric (DSC) and Thermal Gravimetric Analyzer (TGA) for thermal properties characterization.

1.4 Research Scope

The main scopes of this research are:

a. Fabrication two composite biodegradable films using chitosan with sawdust (CS) and chitosan, starch with sawdust (CSS)

b. Morphology or structure characterization using Atomic Force Microscopic (AFM),

c. Chemical composition characterization using Fourier Transform Infrared (FTIR),

d. Thermal properties characterization of the films using Thermal Gravimetric Analyzer (TGA) and Differential Scanning Calorimetric (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1   Composite

A composite material is a materials system composed of a suitably arranged mixture or combination of two or more micro- or macroconstituents with an interface separating them that differ in form and chemical composition and are essentially insoluble in each other. The engineering importance of a composite material is that two or more distinctly different materials combine to form a composite material that possesses properties that are superior, or important in some other manner, to the properties of the individual components (Smith *et al.,*2000)

Thus composites are those materials formed by aligning extremely strong and stiff constituents such as fibers and particulates in a binder called matrix. The materials in this class have exceptional mechanical properties. One of the components is that accommodate stress to incorporate component called reinforcing phase and provide a strong bond called matrix. Polymers, ceramic and metals have found application a matrix materials. The reinforcing phase is other component and is called reinforcement and can be fiber, particulate or laminar (Gupta, 2005). The composite properties depend on those of the individual components and on their interface compatibility. Many research works has been carried out to identify the parameters that govern mechanical behavior of particulate composites. Generally, it has been found that the reinforcement

effect increases with decreasing particle size and with increasing adhesion to the matrix (Marcovich *et. al,* 1998).

2.2   Matrix

In choosing to reinforce an engineering material the matrix are effectively selecting for a composite. This matrix is required to perform several functions, most of which are vital to the satisfactory performance of the composite. The matrix binds the fibers together, holding them aligned in the important stress direction. Loads are applied to the composite, are then transferred into the fibers, which constitute the principal load bearing component, through the matrix, enabling the matrix to withstand compression, flexural and shear force as well as tensile loads. The ability of composites reinforced with short or chopped fibers to support load of any kind is exclusively dependent on the presence of matrix as the load transfer medium and the efficiency of this transfer depends on the quality of the fiber-matrix bond.

The composite performance is influenced by the following matrix properties (Gupta, 2005).

a.   Elastic constants

b.   Yield and ultimate strength under tension, compression or shear

c.   Failure strain of ductility

d.   Fracture toughness

e.   Resistance to chemicals and moisture

f.   Thermal and oxidative stability

2.3   Biodegradable Composites and Packaging Film

The materials most used for food packaging are petrochemical-based polymers, due to their availability in large quantities at low cost and favorable functionality characteristics, such as, good tensile and tear strength, good barrier properties to oxygen and heat sealability (Tharanathan, 2003). However, these materials are totally non-biodegradable, leading to serious ecological problems. As a consequence, the consumer demand has shifted to eco-friendly biodegradable materials, especially from renewable agriculture by-products like chitosan, food processing industry wastes and low cost natural resources such as starch.

Although a total replacement of petroleum-based polymers by the biodegradable materials is just impossible, at least for some specific applications such as replacement seems obvious and useful. Nevertheless, such as a replacement by biodegradable materials, would allow us preserve or extend our expensive, dwindling petroleum resources. Essential prerequisites of a good packaging film (Kader, 1989) are:

a.   Allow for a slow but controlled respiration (reduces oxygen absorption) of the commodity

b.   Allow for a selective barrier to gases (Carbon Dioxide) and water vapor

c.   Creation of the modified atmosphere with respect to internal gas composition, thus regulating the ripening process and leading to shelf-life extension.

d.   Lessening the migration of lipids – of use in confectionary industry.

e.   Maintain structural integrity (delay loss of chlorophyll) and improve mechanical handling.

f.   Serve as a vehicle to incorporate food additives (flavor, colors antioxidants, and antimicrobial agent)

g.   Prevent (or reduce) microbial spoilage during extended storage.

All the above prerequisites can be met with by polymer composites, whose composition and formulation vary from commodity to commodity. Biopolymers from agricultural feed stocks and other resources have the ability upon blending and/ or processing to result in such packaging materials. Their functionality can be better expressed by using in combination with other ingredients such as plasticizers and additives. The potential uses for such biopolymeric packaging materials are:

a.   Use and throw, disposable packaging materials

b.   Routine consumer goods for day-to-day use, such as plates, cups, containers, egg boxes, etc.

c.   Disposable personal care napkins/ sanitary pads, diapers, etc

d.   Lamination coating

e.   Bags for agricultural mulching (nursery).

The most attractive feature of the biopolymer-based packaging films or composites is their total biodegradability. As a result they fit perfectly well in the ecosystem, and save our world from growing ecological pollution caused by non-biodegradable plastics, which are essentially petroleum based. A number of aerobic and anaerobic microorganisms have been identified for biodegradation. The carbon cycle involving the biopolymer degradation is shown in Figure 2.1
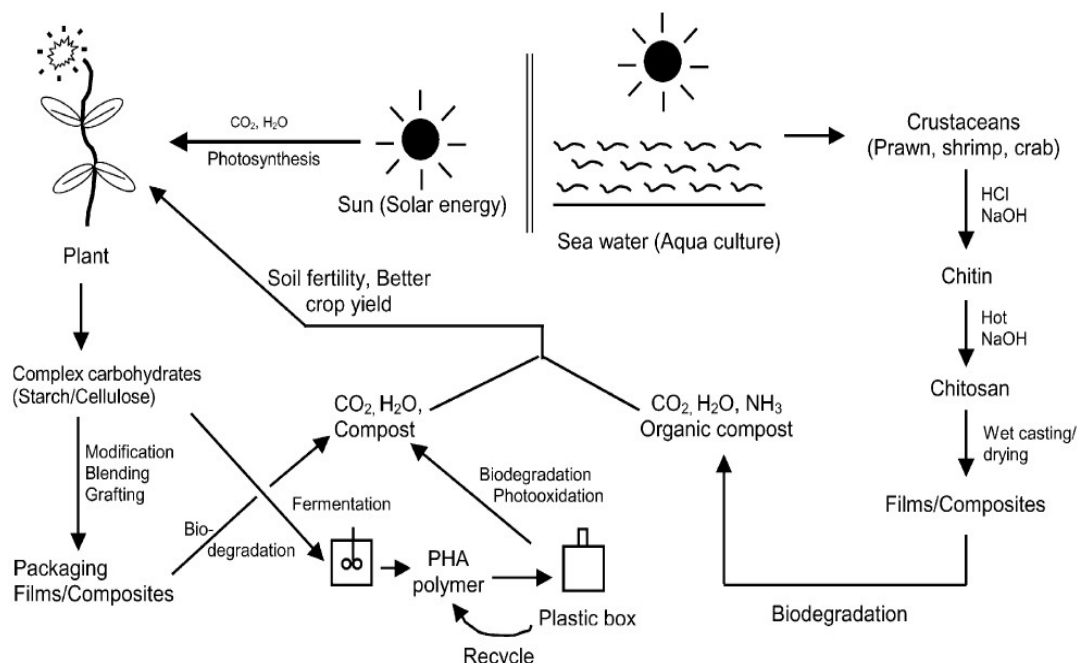
Figure 2.1: The carbon cycle of biodegradable polymers

2.4   Biodegradable Film Preparation

Two types of biomolecules, viz., hydrocolloids and lipids, are generally used in combination for the preparation of biodegradable packaging films or composites. Individually they lack structural integrity and characteristic functionality. For example, hydrocolloids, being hydrophilic are poor moisture barriers, a property compensated by adding lipids, which are very good moisture barriers. Composite films are in fact a mixture of these and other ingredients in varying proportions, which determine their barrier (to H2O, O2, CO2 and aroma compounds) and other mechanical properties.

Sometimes a composite film formulation can be tailored made to suit to the needs of a specific commodity or farm produce. For example, oranges having a thick peel are prone to anaerobic conditions, which lead to an early senescence and spoilage if the composite film is rich in lipids. Phase separation encountered during the preparation of composites is overcome by using emulsifying agents. Use of plasticizers such as glycerin, enthylene glycol, sorbitol, etc. in the film formulations or composites is

advantageous to impart pliability and flexibility, which improves handling (Garcia, Martino, & Zanitzky, 2000). Use of plasticizers reduces the brittleness of the film by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules.

The use of wax coating of fruits by dipping is one of the age-old methods that were in vogue in the early 12th century (Krochta, Baldwin, & Nisperos-Carriedo, 1994). This was practiced in China, essentially to retard water transpiration losses in lemon and oranges. Later fat coating of food products, specifically called ''larding'' was in vogue in England. Sausage casing used very commonly nowadays is nothing but a material derived from a protein source (gelatin). Usually a film thickness of ~2.5 mm is employed, and coating is done by several methods. Films are reformed thin membranous structures, which are used after being formed separately, whereas in coatings the thin film is formed directly on the commodity (R.N. Taranathan, 2003).

Dip method coating is the commonly used method for fruits, vegetables and meat products. In here the commodity is directly dipped into the composite coating formulations (in aqueous medium), removed and allowed to air dry, whereby a thin membranous film is formed over the commodity surface. Continuous dipping builds up decay organisms, soil and trash in the dipping solution, which needs to be, removed for better performance characteristics (R. N. Taranathan, 2003).

The coating can also be done by a foam application method. Emulsions are usually applied by this method. In here extensive tumbling action is necessary to break the foam for uniform distribution of the coating solution, over the commodity surface. Coating by spraying is the conventional method generally used in most of the cases. Due to high pressure (60–80 psi) less coating solution is required to give a better coverage. Programmable spray systems are available for automation during such operations (R.N. Taranathan, 2003).

Biodegradable packaging films are generally prepared by wet casting of the aqueous solution on a suitable base material and later drying. Choice of the base material is important to obtain films, which can be easily removed without any tearing and wrinkling. Infrared drying chambers are advantageous in that they hasten the drying process (Tharanathan, Srinivasa, and Ramesh, 2002). Optimum moisture content (~5–8%) is desirable in the dried film for its easy peel off from one edge of the base material.

2.5   Characterization of Biodegradable Film

There are several methods for characterize the biodegradable films which are using Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR), Differential Scanning Calorimeter (DSC) and Thermo Gravitation Analyzer (TGA).

2.5.1   Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is rather new method to characterize the surface of biodegradable film (Bining *et al.,* 1986). A sharp tip with a diameter smaller than 100 A is scanning across a surface with a constant force. London –van der Walls interactions will occur between the atoms in the tip and the surface and these forces are detected. This will result in a line scan or profile of the surfaces (Mulder, 1996). It has emerged as the technique of choice for conducting single molecule force spectroscopy, owing largely to the limited range of forces that can be applied by competing methodologies such as the use of optical tweezers or magnetic beads (Strick *et al.,* 2003). The level of information obtained from AFM images, however, depends critically on the size, shape, and terminal functionality of the probe tips used for imaging and whether the sample consists of isolated molecules or packed molecular arrays (Engel *et al.,* 1997)

2.5.1.1 Principle of Atomic Force Microscopy (AFM)

The AFM works in the same way as our fingers which touch and probe the environment when we cannot see it. By using a finger to "visualize" an object, our brain is able to deduce its topography while touching it. The resolution we can get by this method is determined by the radius of the fingertip. To achieve atomic scale resolution, a sharp stylus (radius ~1-2 nm) attached to a cantilever is used in the AFM to scan an object point by point and contouring it while a constant small force is applied to the stylus (Figure 2.2a). A fine stylus is mounted on a cantilever spring and scanned over the surface. The vertical deflection of the cantilever is detected by reflecting a laser beam onto a 2-segment photodiode. The photodiode signal is used to drive a servo system which controls the movement of the piezo xyz-translator. In this manner the applied force between the stylus and the sample can be kept constant within some tens of a piconewton. The imaging process can be performed in a liquid cell filled with buffer solution. This ensures that the biomolecules remain hydrated. At sufficiently small forces the corrugations of the scanning lines represent the surface topography of the sample. With the AFM the role of the brain is taken over by a computer, while scanning the stylus is accomplished by a piezoelectric tube (Figure2.2b). This simple technique provides a peep into the microscopic world, and it enables us to understand how the "smallest bricks" (i.e., the biomolecules) of biological systems might function. Figure 2.2 c is shown the atomic resolution of a mica surface recorded in aqueous solution. The distance between adjacent protrusions is 5.4 Å.

a

$\bar{F}$
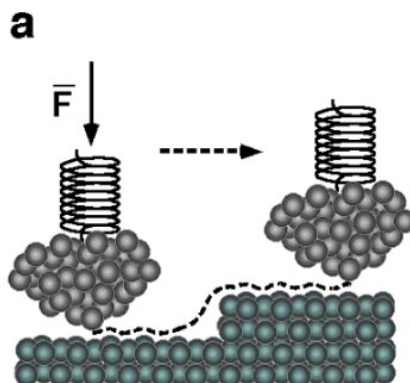
Figure 2.2 a: A cantilever spring and scanned over the surface.
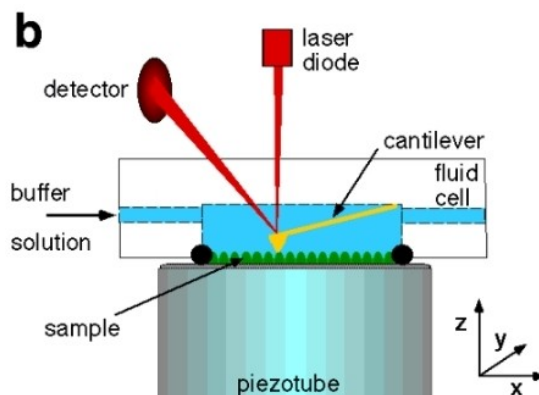
Figure 2.2 b: The vertical deflection of the cantilever
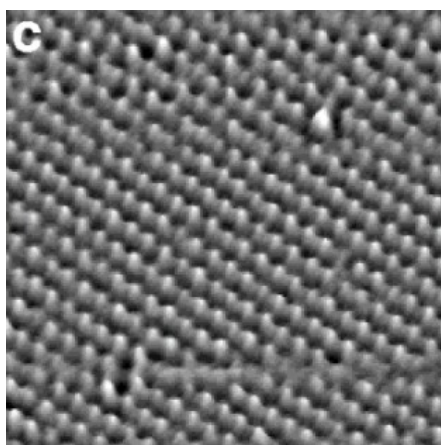
Figure 2.2c: Atomic resolution of a mica surface recorded in aqueous solution. The distance between adjacent protrusions is 5.4 Å.

2.5.2   Fourier Transform Infrared (FTIR)

The Fourier-transform infrared spectrometer gives an absorbance spectrum that can detect much higher absorbances than the UV-visible spectrometer. Here is a long-winded explanation of why, which might also help you understand the lecture portion of the class. The FTIR acquires an absorbance spectrum without using a monochromator. Infrared spectrometers used to have monochromators, but the spectra were usually noisy

because infrared detectors in are relatively insensitive. This is because thermal background noise is large in the infrared. The method of Fourier-transform was introduced to ease the disadvantage of the background noise.

The idea is that the instrument hits the detector with all wavelengths at once, so the signal will be well above the thermal background noise. This is what you might do if you wanted to weigh one sheet of paper using your bathroom scale. If you put a whole ream of paper on the scale at once, you would get a big signal, and you could then divide the total weight by the number of sheets to learn the weight of one sheet. This is called the *multiplex advantage*. The FTIR has a more complicated calculation to do, and it sorts out the spectrum by using an interferometer, where the interference of each wavelength is sensed to determine the intensity at each wavelength. The lamp power is now very bright compared to the detector noise because all wavelengths are striking the detector simultaneously. Consequently, much higher absorbances can be measured in FTIR than in UV-Vis. We saw for the UV-visible spectrometer that the peaks flattened out around 3.0 to 3.5 absorbance units. For the FTIR, the peaks flatten out around 6 absorbance units. In this lab, the polymer samples will sometimes result in these very large absorbance.

Many polymers are made by the polymerization reaction of a vinyl functionality, $R = -CH=CH_2$, shown in Fig. 5-1, to give very long polymer chains. The identity of R affects the chemical and mechanical properties of the polymer; there is a wide range of polymers. Figure 2.3 shows several examples, all of which are commonly used in the food-packaging industry. Polyethylene is used for sandwich bags, polypropylene is used for soda bottles, polystyrene is used for coffee cups, and polyvinylchloride (PVC) is used for food wraps and piping. Teflon polytetrafluoroethylene is a common material for making nonstick pans, as you know.

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R = H   polyethylene
R = CH$_3$ polypropylene
R = C$_6$H$_6$ polystyrene
R = Cl   polyvinylchloride

Sometimes multiple groups are used, e.g. F:

Tetrafluoroethylene yields Teflon®.

Figure 5-1. Basic structure of polymers.
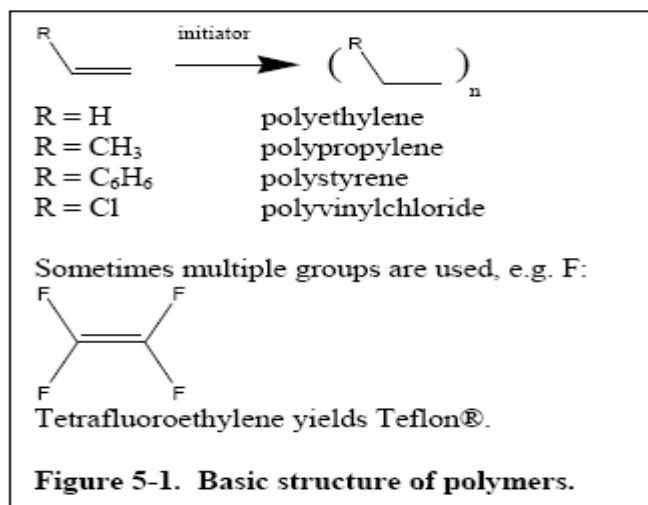
Figure 2.3: Basic structure of polymers

Polymers can readily be distinguished from one another using FTIR. You can imagine that it might be difficult to stuff a sandwich bag into an NMR tube; hence NMR is not usually the method of choice for studying polymer films. Infrared and Raman spectroscopy are always included in the polymer chemist's toolbox. The stretching frequency of the C-R bond is characteristic of the polymer. If -R is more than one atom (i.e. if the polymer has a "side chain"), -R might have its own characteristic spectrum.

2.5.3   Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of the sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should well-defined heat capacity over the range of temperatures to be scanned.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity. The technique was developed by E.S Watson and M.J. O'Neill in 1960, and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. DSC is used widely for examining polymers to check their composition. Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show up possible polymer degradation by the lowering of the expected melting point, T_m, for example. T_m depends on the molecular weight of the polymer, so lower grades will have lower melting points than expected (Rizan, 2004).

A small portion of the sample is placed in an aluminum pan and heated and or or cooled in a controlled manner. A reference material (usually an empty aluminum pan) simultaneously undergoes the same programmed time/temperature routine. Calorimetric measurements are made during the heating or cooling cycle.

Figure 2.4: DSC TAQ-500 in Analytical Lab, FKKSA Laboratory, UMP

In 1990, W. J. Sichina has reviewed used of HSDSC for characterization of starches. For the successful characterization of starches, it is important to have high performance DSC instrument, as the critical transitions associated with starches are very weak and can be difficult to detect. In 1996, Edward Kolbe *et al* has participated also in a thermal analysis study to determine onset and peak transition temperatures and enthalpy, for both starch gelatinization and tristearin melting and crystallization using 3 types of DSC.

2.5.4   Thermo Gravimetric Analysis (TGA)

Thermal methods investigate changes that occur upon heating a sample. Thermo gravimetric measures changes in the mass of a sample that occur when it is heated. These changes relate to the reactions during decomposition, the loss of volatile material and the reactions with the surrounding atmosphere. Thermo gravimetric analysis (TGA) continuously measures a weight of samples as a function of temperature and time.

The sample is place in a small pan or crucible connected to the microbalance and heated in a control manner and or or held isothermally for a specified time. The atmosphere around the sample may consist of an inert gas, such as nitrogen, or reactive gas, such as air and oxygen. The heated program may started in an inert atmosphere and then be switched to air at a certain point to complete the analysis. Weight changes observed at specific temperature correlates to vitalization of sample components, decompositions, oxidation or reduction reactions or other reactions or changes. Temperature and mass data are collected and processed by computer dedicated to the system.

Figure 2.5: TGA TAQ-500 in Analytical Lab, FKKSA Laboratory, UMP

The TGA data gives information about such properties as; thermal stability, moisture or solvent content, additive or filler content, oxidation and decomposition temperatures and rate. Thermal events such as melting, glass transition and other changes are not detected because there are no changes in the sample mass associated with this events. Any physical and chemical change involving mass may be studied.

2.6   History of Chitosan

The origin of chitosan can be traced back to 1811 when "chitin" from which it is derived, was first discovered by Braconnot, a then professor of the natural history in France. According to some researches, while Braconnot was conducting research on mushrooms, he isolated what was later to be called chitin (Braconnot, 1811). Twenty years later, there was a man who wrote an article on insects in which he noted that similar substance was present in the structure of insects as well as the structure of plants (Odier, 1823). He then called this astounding substance as chitin. Basically, the name chitin is derived from Greek, meaning 'tunic' or 'envelop'. The concept was further

known in 1834 when Lassaigne demonstrated the presence of nitrogen in chitin. Following the discovery of chitin, the name 'chitosan' emerged in the scene. It was first discovered by Rouget while experimenting with chitin (Rouget, 1859). Rouget observed that the compound of chitin could be manipulated through chemical and temperature treatments for it to become soluble. Then, it was in 1878 when Ledderhose identified chitin to be made of glucosamine and acetic acid. It was not actually until 1894 that Hoppe-Seyler named the tailored chitin, chitosan.

During the early 20th century, several researches took chitosan as their subject of study. They then involved sources of chitin, including crab shells and fungi. It was the work of Rammelberg in the 1930s that led to the confirmation on the identity of chitosan from these sources. It was also noted that by hydrolyzing chitin in several ways, it was determined by experts that chitin is a polysaccharide of glucosamine. They can take on a positive charge which gives chitosan its amazing properties. Research on the uses of chitin and chitosan flourished in the 1930s and early 1940s but the rise of synthetic fibers, like the rise of synthetic medicines, overshadowed the interest in natural products.

During the 1950s, the use of x-ray analysis had advanced about the study of the incidence of chitin or chitosan in fungi. However, it is only the most advanced technologies that proved the most reliable in accepting the existence of chitin as well as cellulose in the cell walls. The first book on chitosan was published 140 years after the initial observation of Braconnot, and that was in 1951. During the early 1960s, chitosan was examined for its ability to bind with the red blood cells. That time also, the substance was considered as a hemostatic agent. Then, for the past three decades, chitosan has been used at water purification plants for detoxifying water. It is spread over the surface where it absorbs greases, oils, and other potential toxins. Interest in natural products, including chitin and chitosan, gained resurgence in the 1970s and has continued expend ever since (Hennen, 1996). Nowadays, Chitosan it is known as a dietary supplement that is good for weight loss. In fact, it has been marketed for such purpose for about 20 years in Japan as well as in Europe.

2.6.1   Overview of Chitosan

Chitin (poly-N-acetyl-D-glucosamine, 2-acetamido-2-deoxy-1, 2-ß-D-glucan) is one of the three most abundant polysaccharides in nature which is byproduct of the crab and shrimp processing industries (Paulk *et al.,* 2002). It ranks second to cellulose as the most plentiful organic compound on earth.

Chitosan, known as soluble chitin, is a natural product obtained from deacetylated chitin. Chitosan is a β-1, 4-linked polymer of glucosamine (2-amino-2-deoxy- β-D-glucose) and lesser amounts of N-acetylglucosamine. According Se'bastian *et al.,* (2006), Chitosan is non-toxic, biodegradable and biocompatible polymer. Chitosan is soluble in 1% acetic acid (Peter, 1995) and most commercially available Chitosan preparations are more than 85% deacylated, and have molecular weights between 100 kDa and 1000 kDa.
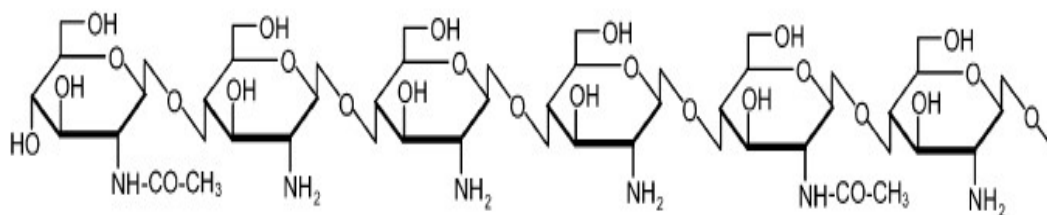
Figure 2.6: Chemical structure of Chitosan.

They are usually complexes with acids, such as acetic or lactic acids. Chitosan widely existing in the nature and has an antibacterial effect, heavy metal adsorption effect, anti-oxidation effect (Ozmeric *et al*., 2000) and film formability (Bordenave *et al*., 2007), (Bourtoom and Chinnan, 2008), (Gaellstedt *et al*., 2005), (Kumar, 2000), (Mucha and Miskiewicz, 2000), (Nada *et al.,* 2006) and (Ziani *et al.,* 2008). Also, it is a functional substance showing various functions that a food packaging film needs, such as stabilization of boold pressure, enhancement of immunity, ability and anti tumor effect. Free standing films have been prepared from Chitosan and its derivatives, and their mechanical, barrier and biodegradation characteristic studied (Kittur, Kumar, and

Tharanathan, 1998). Cross-linked Chitosan films offer greater strength and resistance for handling. By being antifungal and antimicrobial, Chitosan based films and coating formulations have additional value addition (Tharanathan and Kittur, in press). Chitosan based composite coating formulations (Kittur, Saroja, Habibunnisa, & Tharanathan, 2001) as well as films (Srivinasa *et al.,* 2002) have been shown to prolong the self-life of banana, mango and capsicum.

2.6.2   Application of Chitosan

The growing environmental awareness experienced in recent decades has promoted a great theoretical and industrial interest in the use of chitosan-based in biodegradable film field. The present invention relates to a method for preparing a food packaging film containing chitosan, and more particularly, it relates to a method for preparing a food packaging film using a premix containing chitosan powder, in which the chitosan powder particles are evenly dispersed and distributed in the food packaging film so that they can be slowly released to prevent deterioration of the food by microorganisms upon a long term storage, while suppressing oxidation and maintaining peculiar taste and color of the food for fresh storage. Several studies have been carried out in chitosan composites biodegradable film and several methods for improvement in chitosan composites have been developed.

Sebastian *et al.,*(2006) studied about biodegradable films made from chitosan and poly(lactic acid) with antifungal properties against mycotoxinogen strains. Composite films from chitosan and poly (lactic acid) (PLA) were prepared by solution mixing and a film casting procedure. The main objectives of this study were the elaboration and the characterization of chitosan/PLA based bio-packaging for potential food applications and the study of antifungal activity of coatings and films on three mycotoxinogen fungal strains, Fusarium proliferatum, Fusarium moniliforme and Aspergillus ochraceus. The first part of the study was related to the impact of the

Polyethylene glygol content, allowing an easy film recovery without considerably decreasing the moisture barrier properties of materials: 16.6% of plasticizer was selected. Difficulties were however encountered to produce miscible PLA and chitosan film forming solution, leading to heterogeneous films with high water sensitivity. Although composite films offer a great advantage in preventing the surface growth of mycotoxinogen strains because of their antifungal activity, the physico-chemical properties of such heterogeneous films, dramatically limit their further usage as packaging materials.

Tharanathan *et al*., (2002) also studied about the storage of mango packed using biodegradable chitosan film. The effect on the quality of mango fruits (*Mangifera indica*) during modified atmosphere packaging was investigated. The fruits were kept in carton boxes whose top surface was covered with either chitosan film or with low-density polyethylene (positive control) or kept as such (control), and stored at room temperature (27 ± 1°C at 65% RH). The CO_2 and O_2 levels measured on day 3 were 23-26% and 3-6%, and at the end of the storage period they were 19 to 21% and 5 to 6%, respectively. Various quality parameters such as colour, chlorophyll, acidity, vitamin C, carotenoid and sugar contents were studied. The fruits stored as such had a shelf life of 9 ± 1 days, whereas those stored in low-density polyethylene showed off-flavour due to fermentation and fungal growth on the stalk and around the fruits, and were partially spoiled. On the other hand, fruits stored in chitosan-covered boxes showed an extension of shelf life up to 18 days and without any microbial growth and off-flavour. Being biodegradable and ecofriendly, chitosan films are useful as an alternative to synthetic packaging films in the storage of freshly harvested mangoes.

2.7   Overview of Starch

Most foods are multi-component, multi-phase systems that contain complex mixtures of water, polysaccharides, proteins, lipids and numerous minor constituents.

Starch is present as a macro-constituent in many foods and its properties and interactions with other constituents, particularly water and lipids are of interest to the food industry and for human nutrition. Starch contributes 50 to 70 % of the energy in the human diet, providing a direct source of glucose, which is an essential substrate in brain and red blood cells for generating metabolic energy (Copeland *et al.*, 2009).

Starch is the main storage carbohydrate of plants. It is deposited as insoluble, semi-crystalline granules in storage tissues (grains, tubers, roots) and it also occurs to a lesser extent in most vegetative tissue of plants. It consists of two components: amylose, in which the glucose units are 1,4-α-D-linked together in straight chains, and amylopectin (colored by elemental iodine), in which the glucose chains are highly branched (Flieger *et al.,* 2002). Although a minor component by weight, lipids can have a significant role in determining the properties of starch. The lipid content and composition of starch granules varies among plant species. Lipids associated with isolated cereal starch granules occur on the surface as well as inside the granule. The lipid content of native starches is highly correlated with amylase content; the higher the amylase content the more lipids are present.

Research on biodegradable plastics based on starch began in the 1970s and continues today at various labs all over the world. Technologies have been developed for continuous production of extrusion blown films and injection-molded articles containing 50% or more of starch. Water sensitivity of such films has been reduced by lamination with polyvinyl chloride (PVC) (Shorgren, Fanta, and Doane, 1993). Combination of urea with certain polyols provides better plasticization of starch with good quality film (Doane, 1992). Utilization of the starch portion by the fungi exposes the plastic polymer for enhanced biodegradability by microbial and oxidative degradation.

Starch is another raw material in abundance, especially from rice powder, having thermoplastic properties upon disruption of its molecular structure (Tharanathan, 1995,

Tharanathan and Saroja, 2001). Preponderance of amylose gives stronger, more flexible films. Branched structure of amylopectin generally leads to films with poor mechanical properties (decreased tensile strength and elongation. Melted or destructurized starch, obtained by disruption of the granular architecture resulting in loss of crystallinity, has emerged as a new type of the thermoplastic material for commercial development. To increase the compatibility of hydrophilic starch with the hydrophobic plastic matrix, starch granules have nee surfaced treated, for example with silanes (Doane, 1992). Pro-oxidants can sometimes be added to enhance oxidative degradation of the synthetic polymer. Hydroxypropyl starch composites are used for the preservation of candies, raisins, nuts and dates from oxidative rancidity (Arvanitoyannis, Nakayama, and Aiba, 1998).
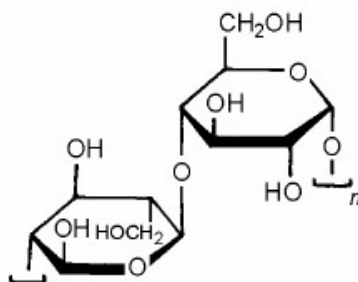
Figure 2.7 Chemical structure of Starch

Starch-based plastic foams formed by blending starch with polylactic acid are used as loose-fill cushioning materials to protect against shock and vibration during transportation (Fang and Hanna, 2000). Laminated films from pectin and chitosan together with either glycerol or lactic acid as a plasticizer have been prepared (Fishman, Friedman, and Huang, 1994). Starch derived product; glucose can be fermented to lactic acid, which can be polymerized to polylactic acid polymers and copolymers. Their use as biodegradable plastics is of considerable interest and demand (Narayan, 1993). These polymers either alone or in combination with synthetic plastics or starch (Ke and Sun, 2000) produce excellent packaging films.

2.7.1 Rice Starch

Starches have been widely used as thickeners for the food industry for many years. The primary sources of food starches are corn, wheat, potato and tapioca. Rice starches are the little known secret of the starch world, comprising a very small percentage of the total starch usage. Don't be fooled by the fact that rice starches are not as common as the other starch sources. They have many unique attributes that make them some of the most interesting starches in the food industry.

Rice is the most widely consumed basic foodstuff in the world. Each year over 500 million tons of rice is harvested, providing sustenance to many countries and people throughout the world. The keys to the unique properties of rice starches are found in its many varieties. Due to different climates, soil characteristics and cultures, over 240,000 registered varieties of rice exist in the world. This variety leads to a wide range of rice starches with many different characteristics including: different starting gelatinization temperatures, textures, processing stabilities and viscosities. This means that a natural "native" rice starch may provide all the stability that a food processor will need without having to resort to chemical modifications.

2.7.2 Rice Starch Characteristics

2.7.2.1 Granule Size and Color

Rice starch has by far the smallest particle size of all the commercial starches. The average rice starch granule is between 2-8 microns. A smaller granule means a much higher concentration of particles in a specific area and a much greater specific surface. This quality makes it possible for rice starch to absorb more products on their surface, such as flavors and emulsifiers. Rice starch is also known to have the whitest color of all the starches. The very fine white particle produces a smooth, glossy finish when used as a coating for tablets and confections.

2.7.2.2 Nutritional Qualities

One important feature of rice starch is its easy digestibility. The relevant literature quotes a digestibility rate of between 98 and 100%, which means that rice starch is one of the most easily digestible starches of all. This digestibility, together with the fact that it is totally hypoallergenic, is one of the main reasons why rice is used so widely in baby food and other special dietary foods.

2.7.2.3 Flavor Release

Rice starches are known for their very clean taste profile, which will not interfere with the final flavor of a product. They also exhibit quick melt characteristics, which allow flavors to come through much cleaner and quicker on the palate.

2.7.2.4 Gel Characteristics

Rice starches are known for their soft gel and creamy mouth feels. They have been widely used as fat replacers in a wide range of food products. Waxy rice starches can be used at low levels in foods to create the sensation of a richer and higher fat product.

2.8 Natural Fiber

The use of natural fibers as additives for composite biodegradable films has been rapidly expanding. A 50% growth in the use of natural fibers in the plastics industry is forecast for 2000-2005. Natural fibers generally refer to lignocellulosic materials derived from sawdust or agricultural materials such as kenaf, jute, hemp, flax, or other

natural resources. Natural fibers are available in many different forms and produce different properties when added to thermoplastics. Natural fibers may be used in the form of particles, fiber bundles, or single fibers, and may act as a filler or reinforcement for plastics (Stark *et al.*, 2003). The use of natural fibers as reinforcements in polymer composites has been widely studied. Their major problems are degradation by moisture, poor surface adhesion to hydrophobic polymers, and susceptibility to fungal and insect attack, but they offer a number of advantage, such as low density, low cost, better composite damage tolerance and high specific strength and stiffness (property divided per weight) (Tan, 1997).

2.8.1   Properties of Natural Fiber

Franco *et al.*, (2005) have studied the fiber-matrix adhesion in natural fiber composites. Depending on their origin, natural fibers can be grouped into bast, leaf and seed or fruit fibers. Cellulose is the main component of natural fibers, and the elementary unit of a cellulose macromolecule is anhydro-D-glucose, which contains three hydroxyl (OH) groups. These hydroxyl groups form hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecules (intermolecular). Therefore all natural fibers are hydrophilic in nature. The cellulose of natural fibers contains different natural substances such as lignin and waxes. The fibers are made up of cellulose microfibrils bonded together by lignin. The physical properties of natural fibers are basically influenced by the chemical structure such as cellulose content, degree of polymerization, orientation and crystallinity. Sawdust fibers are more frequently used since they are obtained in the preparation of pulps for the paper industry.

2.8.2   Sawdust

The use of various renewable organic fillers, such as sawdust fiber as filler/reinforcing agent in thermoplastic polymers, has received considerable attention in recent years. Surface treatment using coupling and wetting agents is the key factor in the use of these fillers in thermoplastic matrices (Cheremisinoff, 1992). Although the used of sawdust-based fibers is not as popular as the use of mineral or inorganic fillers, sawdust derived fillers have several advantages over traditional fillers and reinforcing materials: low density, flexibility during the processing with no harm to the equipment, acceptable specific strength properties and low cost per volume basis (Ichazo *et al.,* 2001). Sawdust fiber, although more difficult to process than sawdust flour, it can lead to superior composite properties. Sawdust fiber is available from both virgin and recycled sources. Recycled sources include pallets, demolition lumber, and old newsprint. Sawdust from small-diameter trees and under-utilized species can also be used (Forest Product Laboratory).

Sawdust is composed of fine particles of woods. This material is produces from cutting with a saw, hence its name. Sawdust were initially used for reducing and disposing of large amounts of natural fiber waste materials in polymers, and offer low cost and low density products. Xu *et al.,* (2008) stated that improvement of mechanical properties for structural engineering applications can be obtained if the Sawdust fibers are properly blended with the polymers. Also, sawdust acts as barrier layer to retard moisture intrusion and biological attack (Joshi *et al.;* 2004).

Sawdust plastic composites (WPC) have attracted a number of researchers and manufacturing engineers because of the good mechanical properties, better dimension stability, and environmentally friendly products, as compared with synthetic fibers/plastic composites. Many applications for WPC products include decking, window and door profiles, automobile paneling, panel inserts and flower pots which were classified as decorative materials.

Godavarti (2005) also studied the thermoplastic sawdust fiber composites. Sawdust fiber has been blended with plastics to improve performance virtually since the invention of polymers. Beginning with bakelite in the early 1900s, engineers and scientists have continued to work to improve the various attributes of both thermosets and thermoplastics through the addition of sawdust fiber. The unique properties of cellulose in combination with its wide availability, renewable nature, and adaptability to chemical treatments, favorable viscoelastic behavior, and its remarkable anisotropic properties with orthotrophic ratios of 50 are fast making it a material of choice, especially in technologies with significant environmental impacts. Its fibrous nature makes it an efficient load-carrying structure and the fiber is the smallest structural element used commercially.

2.8.2.1 Structure, Composition & Properties

The chemical makeup of sawdust is complex. Sawdust is made up of cellulose, hemicellulose, and lignin and is infiltrated with many other compounds. Sawdust fibers produced by thermomechanical means usually display lignin-rich surfaces while fibers produced by chemical means display carbohydrate-rich surfaces. The surface tension of chemically produced fibers is often higher than the mechanically produced fibers. The type and amount of the other compounds are often distinctive with certain species of tree and can have a pronounced effect on properties. The four major constituents of Sawdust include (Hill, 2006, William, 2005)

a.   Cellulose

Function as primary structural component within the Sawdust fiber cell walls. In thermoplastic sawdust fiber composites, cellulose is primarily for reinforcement. It is the most important component for its effect on the properties of sawdust.

b.   Hemicellulose

Primarily serves as connecting agent that links or bonds the microfibrils providing additional structural reinforcement to the sawdust fiber cell wall. Hemicellulose, composed of shorter molecules than cellulose, makes up a large part of sawdust. It is also important for some properties of sawdust.

c.   Lignin

   i.   An amorphous polymeric material, acts as cement in bonding the cellulose filaments providing stiffness to sawdust.

   ii.   Lignin can be thought of as the glue that holds the sawdust (cellulose and hemicellulose) together. Lignin is important because it gives rigidity to the cells so that a tree can grow large and tall.

d.   Extractives

   i.   Extractives are often low-molecular-weight oleophilic compounds. It influences the surface chemistry of sawdust and thereby affects the wet ability and chemical interaction of sawdust particles and fibers with synthetic thermoplastics.

   ii.   Without extractives, sawdust would have to be identified solely by its anatomical structure. Extractives are made up of an extremely wide range of organic compounds. These chemical compounds are not part of the sawdust but accumulate there.

   iii.   The amounts and types of extractives help to determine the sawdust's permeability to liquids and influence other sawdust properties such as density, hardness, and compressive strength. Extractives give certain sawdusts their resistance to insect or fungi attack.
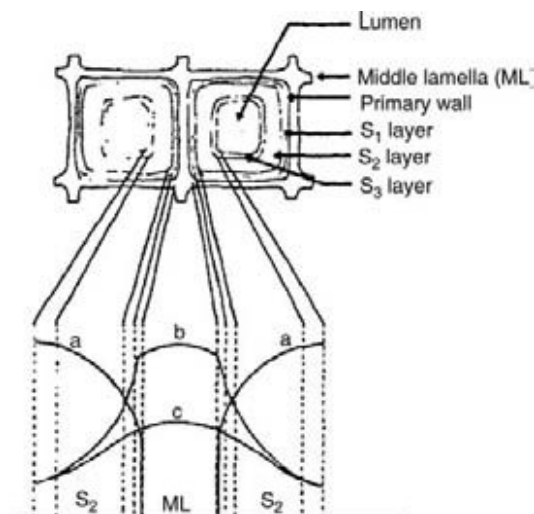
Figure 2.8: Diagram showing the relative amounts of cellulose, hemicellulose, and lignin a cross section of two Sawdust cells: a) cellulose; b) lignin; c) hemicellulose.

2.8.2.2 The Need for Sawdust Modification

Due to environmental concerns regarding the use of certain classes of preservatives, there has recently been a renewed interest in sawdust modification. Sawdust modification represents a process that is used to improve the material properties of sawdust, but produces a material that be disposed of at the end of a product life cycle without presenting an environmental hazard any greater than that associated with the disposal of unmodified sawdust. Although sawdust modification has been subject of a great deal of study at an academic level for over 50 years, it is only comparatively recently that there has been significant commercial development. Sawdust is a natural material, and as such it exhibits great variability in its properties. Sawdust modification is a means of altering the material to overcome or ameliorate one or more of its disadvantages. The term 'sawdust modification' applies to the application to a process that alters the properties of the material such that during the lifetime of a product no loss of the enhanced performance of the sawdust should occur (Hill, 2006).

2.8.2.3 Sawdust and Plastic Composites

The growing environmental awareness experienced in recent decades has promoted a great theoretical and industrial interest in the use of natural fibers as reinforcing material in polymer composites. Several studies have been carried out in sawdust/plastic composites and several methods for improvement in sawdust/plastic composites have been developed.

Escobar W. G., (2008) has studied the influence of sawdust species on properties of sawdust/High Density Polyethylene (HDPE) composites. According to his research; the morphology of sawdust species affecting sawdust-plastic interaction, in mechanical interlocking, the main objective is to quantify the anatomical features that could relate to the interaction between a molten thermoplastic and the sawdust cell structure. Using vacuum bagging process and Scanning Electron Microscopy (SEM), the study was carried out in the mechanical interlocking mechanism between sawdust species from small diameter logs and high density polyethylene (HDPE) without coupling agents or additives. Both the vacuum process and the pressure at high temperature increased flow of the HDPE, mainly through the radial face (tangential direction) in small soft sawdust samples. The vacuum bagging cycle used here, combined with the morphology analysis with SEM, provided a good comparison of the physical interaction of a thermoplastic with different sawdust species.

Jacoby *et al.,* (2001) have investigated a comparison of sawdust-filled high crystallinity polypropylene with other sawdust-filled polyolefins. Over the past decade, sawdust-filled polyolefins have become accepted as a replacement for lumber in high value outdoor applications such as decks. Most of the products offered have used polyethylene as the polymer matrix, with sawdust flour as the typical filler. It is well known that polypropylene offers certain benefits over polyethylene in terms of higher stiffness, strength, heat deflection temperature (HDT), and high-temperature creep performance. The physical property data for sawdust flour levels ranging from 20 to 60 percent in both polypropylene and high-density polyethylene matrices. The PP resins

studied included standard homopolymer, high-crystallinity homopolymer (ACCPRO), and impact copolymer. The effect of different levels of a maleated polyolefin coupling agent will also be examined. The ACCPRO-based composites showed a significant improvement in stiffness, strength, and HDT over that of the standard homopolymer PP, with no loss of impact. All of the filled PP materials were substantially stiffer and stronger than the filled HDPE, especially at elevated temperatures. The homopolymer and ACCPRO materials also had much better creep resistance compared to the HDPE at both ambient and elevated temperatures. The water absorption characteristics absorbed less moisture than that of the comparable HDPE based materials, and the loss of strength and stiffness with water pickup was also less pronounced for the sawdust-filled PP. These results indicate that sawdust-filled PP, and especially high-crystallinity-filled PP, will provide better mechanical performance in structural applications such as outdoor decks as compared to that of sawdust-filled HDPE.

Sears *et al.,* (2001) have studied the reinforcement of engineering thermoplastics with high purity sawdust cellulose fibers. High-purity sawdust cellulose fibers ($\geq$95% α-cellulose content) can provide good reinforcement properties for engineering plastics melting above 200°C, such as nylon 6, to yield mechanical properties that are intermediate between glass fiber and mineral materials such as wollastonite. Composite discoloration and decomposition are minimized using such high-purity sawdust pulp fibers. At the levels employed (30-33% by weight), processing temperatures in both compounding and injection molding can be substantially lowered. Of six sawdust pulps studied, two with α-cellulose contents greater than 97 percent gave the best overall results with one appearing superior (a hard sawdust craft pulp). In this study, pulp fibers were granulated with a rotary knife cutter prior to compounding them with nylon 6; this step reduced fiber length. It was later found that pelletizing the fibers helps preserve original fiber length, improves processing, and leads to better mechanical properties (at times exceeding those for glass fibers). Mercerization of the hard sawdust craft fibers results in additional processing and mechanical property improvements. These studies with nylon 6 will be presented and discussed, along with some limited results obtained using certain process additives as well as other engineering plastics.

Wolcott *et al.,* (2001) have studied coupling agent/lubricant interactions in commercial sawdust fiber-plastic composite formulations. Maleated polyolefin copolymers have been widely studied for their ability to enhance the interaction between sawdust and polyolefin matrix polymers. In most studies, the copolymer is applied to the sawdust prior to extrusion. However, in commercial operations a simple mixture of material components may be used where the copolymer might only comprise a small percentage of the total formulation. To emulate commercial practice, copolymers are blended with other components at relatively low levels (< 3%). The crystallization rates of the sawdust fiber plastic interface are thermally characterized using DSC. The existence of transcrystalline morphologies in the interface region is determined using polarized light microscopy. Mechanical and physical properties of formulations incorporating copolymers are determined from characterization of extruded sections. Maleated copolymers significantly improve the mechanical performance of extruded sawdust fiberplastic composites. The composite moisture absorption and wet-strength are also enhanced, presumably by reducing interfacial gaps and defects. Some commercial lubricants interfere with the action of the commercial coupling agents, although the extent of disruption is highly dependent on lubricant type.

2.9   Application and Historical Development in Sawdust-Plastic Composites

Plastic/sawdust fiber composite products are currently used in the building industry for sliding, window and door frame, and decks as a replacement for conventional pressure-treated sawdust lumbers. A few of the historical developments in the U.S. sawdust-plastic composites industry are mentioned here (Clemons, 2000).

In 1983, American wood stock (Sheboygan, Wisconsin) began producing automotive interior substrates using Italian extrusion technology. Polypropylene with approximately 50% sawdust flour was compounded in-line and extruded into a flat sheet

that was then formed into various shapes for interior automotive applications. This was one of the first large applications of sawdust-plastics technology in the United States.

In the early 1990s, Advanced Environmental Recycling Technologies (AERT, Junction, and Texas) and a division of Mobil Chemical Company (Winchester, Virginia) began producing solid sawdust-plastic composites consisting of approximately 50% sawdust fiber in polyethylene. These composites were used as deck boards, landscape timbers, picnic tables, and industrial flooring. Today the decking market is the largest and fastest growing sawdust fiber-thermoplastic composite market. Similar composites were milled into window and door component profiles.

In 1996, a few U.S. companies that specialize in sawdust or natural fiber-plastic composites began producing a palletized feedstock for the sawdust-plastic composites industry. These companies provide compounded pellets for many processors who do not do their own compounding.

2.10   Polyethylene Glycol (PEG)

The general formula of polyethylene glycol (PEG) is $H(OCH_2CH_2)_nOH$, where n is the number of ethylene oxide groups. PEG of different molar masses can be obtained by varying n. In addition, wide availability, non-volatility, non-toxicity, biodegradability, and low price of PEG make it promising green solvent for different processes (Minqiang $et\ al.,$ 2007). In biodegradable film, adding plasticizers, such as polyethylene glycol (PEG), instead of chemical modification of polymer was proposed to increase the hydrophilic property of the films (Ani $et\ al.,$ 2006).

PEG 400 is harmless towards skin; easily soluble in water and faintly sweet in taste. This makes it an attractive ingredient in cosmetics such as creams; jellies and lotions. PEG-400 is added to lotions intended to have a mild relaxing effect on skin. It

is easily absorbed by the skin acting as solution promoter for the therapeutic agents which can be added to the lotion. It imparts smoothness to skin but does not have a strong dehydrating effect as glycerin. PEG 400 is a superior and thermally stable heating medium than the conventional mediums, due to its higher molecular weight; higher boiling point and specific heat. It is therefore preferred in hot bath applications. Other uses of PEG 400 are as lubricant in tire manufacturing; plasticizer for sponges and synthetic leather; paper softener; anti curl agent; flux for soldering; intermediate in resin manufacturing. PEG 400 also fined uses in toothpaste to remove dirt on the teeth and in cosmetics soaps as a wetting agent preventing the soap from cracking.

2.11   Acetic Acid

The acid most commonly associated with vinegar. Acetic acid is the chemical compound responsible for the characteristic odor and sour taste of vinegar. Typically, vinegar is about 4 to 8% acetic acid. As the defining ingredient of vinegar, acetic acid has been produced and used by humans since before the dawn of recorded history. In fact, its name comes from the Latin for vinegar, *acetum*. Vinegar is formed from dilute solutions of alcohol, such as wine, by the action of certain bacteria in the presence of oxygen. These bacteria require oxygen, and the overall chemical change is the reaction of ethanol with oxygen to form acetic acid and water. Acetic acid is a two-carbon carboxylic acid. Its formula is: CH_3COOH. It is the most commercially important organic acid and is used in the manufacture of a broad range of chemical products, such as plastics and insecticides.

$$CH_3CH_2OH + O_2 \longrightarrow CH_3\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}OH + H_2O$$

Figure 2.9: Stoichiometric the production of acetic acid from vinegar.

Pure acetic acid was first isolated about 1700 by the distillation of vinegar. When pure, acetic acid is a clear,colorless liquid with a sharp, irritating odor of vinegar. In poorly heated laboratories, the acid was oftentimes found frozen inside its container because its freezing point is only slightly below room temperature at 16.7°C. The term glacial (ice-like) came to be applied to the pure acid in either its solid or liquid state. Glacial acetic acid boils at 118°C, and has a density of 1.049 g / mL at 25°C. It is flammable with a flash point of 39°C. Through hydrogen bonding interactions, acetic acid is miscible (mixable) in all proportions with water, ethyl alcohol, and diethyl ether. Pure or concentrated solutions of acetic acid are very corrosive and can cause painful burns. Aqueous solutions of acetic acid freeze at temperatures below the freezing point of water.

Acetic acid is an important industrial chemical. About 3.2×109 kilograms of acetic acid were produced in the United States in 1999. The primary use of this chemical is in the manufacture of assorted acetate esters. These are substances formed by reacting acetic acid with a substance containing a hydroxyl (–OH) group. Cellulose, found in cotton and wood, is a polymeric material containing multiple hydroxyl groups. It reacts with acetic acid to yield cellulose acetate, which is used to make films and textiles. Some photographic films are made of cellulose acetate, and rayon is made from cellulose acetate fibers. Vinyl acetate, another ester of acetic acid, polymerizes to form poly(vinyl acetate), which is used in water-based latex paints and in glues for paper and wood. Acetic acid is also used as a fungicide and as a solvent for many organic compounds.

Acetic acid is also used in the preparation of pharmaceuticals. Aspirin (acetylsalicylic acid) is formed by the reaction between acetic acid and salicylic acid. As with acetic acid, the primary use of acetic anhydride is used in the manufacture of cellulose acetate for films and plastic goods; about 75 percent of the acetic anhydride produced annually in the United States is used for this purpose. Approximately 1.5 percent of the annual acetic anhydride production is used in the synthesis of aspirin. Other uses include the manufacture of industrial chemicals, pharmaceuticals, perfumes,

plastics, synthetic fibers, explosives, and weed killers. Because acetic anhydride reacts with water, it is sometimes used as a dehydrating agent in reaction mixtures where removal of water is necessary.

CHAPTER 3

METHODOLOGY

3.1 Raw Materials and Equipment

The raw materials that used in this experiment are chitosan powder and sawdust.

3.1.1 Chitosan

Commercial low molecular weight chitosan purchased from Aldrich Chemistry in fine powder form. The chitosan have been used in this experiment because it is a natural materials are using for developing the biodegradable film that has antimicrobial effect, non-toxic, and film formability characteristic.

Figure 3.1: Chitosan

3.1.2   Sawdust

Sawdust used as fiber in the composite biodegradable film.   Sawdust obtained from Kilang Playwood Sdn Bhd, Kuantan, Pahang.   Sawdust is form in fine and curse particles and the average particle size is 100 μm

Figure 3.2: Sawdust

3.1.3   Isolation of Fiber

Solvents used for fiber isolation are Sodium Hydroxide (NaOH) and Hydrochloric Acid (HCl) where was supplied by R & M Chemicals Malaysia.   For pre-treatment methods used 17.5 % w/w NaOH solution and 2 % w/w for alkali treatment. The molar concentration of HCl for acid hydrolysis is 1 M.

3.2   Matrix Polymer

Starch (rice powder) used as matrix polymer in preparation of composite biodegradable films solution. Rice powder was purchased at local store. The powder is in fine powder.

3.3   Plasticizers

Polyethylene glycols (PEG) with molecular weight of 400 supplied by R & M Chemical Malaysia Sdn Bhd in constant concentration used as plasticizer.   The plasticizers amount applied 3.3 ml for every composite biodegradable film.
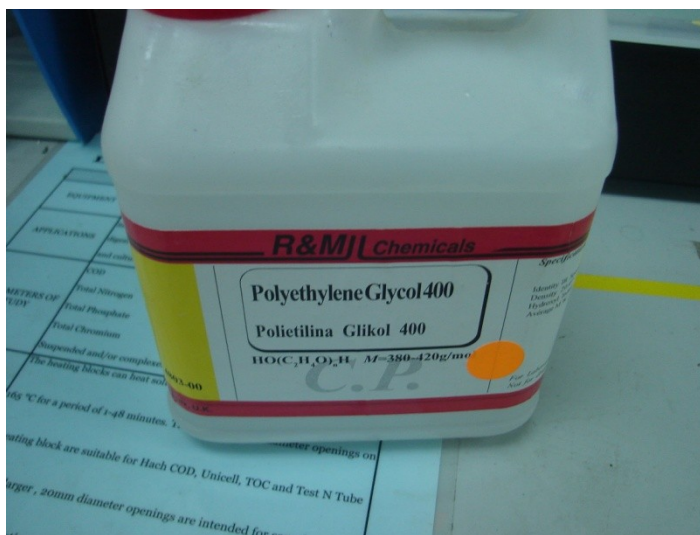

Figure 3.3: Polyethylene Glycol 400

3.4   Films preparation

There are two solutions were prepared. One solution is a mixture of chitosan with sawdust (CS) and other one is a mixture of chitosan, starch with sawdust (CSS). Table 3.1 is show the detail about the amount of substance for both of solutions.

Table 3.1: The amount of substances for preparing the solution

Materials	Solution CS(Chitosan + Sawdust)	Solution CSS (Chitosan + Sawdust + Starch)
Chitosan	2 g	2 g
Starch	-	2 g
Sawdust Fiber	2 g	2 g
Acetic Acid 1% v/v	100 ml	100 ml
PEG 400	3.3 ml	3.3 ml

3.4.1   Isolation of Fiber

Cellulose fibers were extracted from sawdust by chemical treatment, resulting to purified cellulose. An alkaline treatment was applied on sawdust. The sawdust was soaked in a concentrated 17.5% w/w sodium hydroxide (NaOH) solution and then after 2 hours it was washed with distilled water. The pre-treated pulp was hydrolyzed by 1 M of hydrochloric acid (HCl) at $80 \pm 5°C$ for 2 hours and then washed with distilled water repeatedly. The pulp was treated once more with the 2% w/w of NaOH solution at $80 \pm 5°C$ for 2 hours. The alkali treated pulp was washed several times with distilled water until the pH of the fiber suspension became neutral before being dried at room temperature.

Figure 3.4: Isolation of sawdust fiber

3.4.2 Gelatinization of Rice Powder

2 g rice powder and 100 ml distilled water was brought to gelatinization by heating until sample achieved 82 – 90 °C using hot plate and magnetic stirrer EMS-HP 7000 and became gelatin.
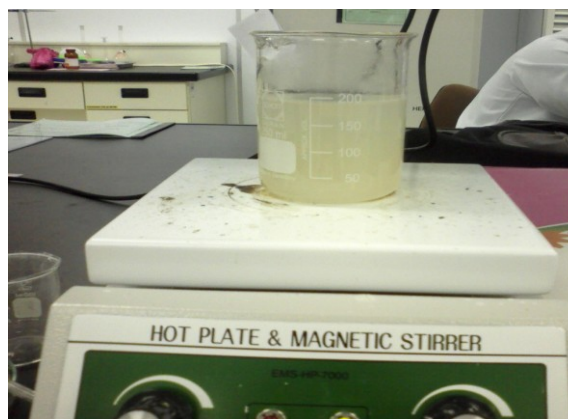

Figure 3.5: Gelatinization of rice powder

3.4.3 Mixing Process

The mixing of the composites was carried out by using Jar Tester PHIPPS & BIRDS mixer at 300 rpm. Two beakers 500 ml of 2 g Chitosan powder was dissolved with 100 ml acetic acid 1 % v/v and stirred until become solutions. Then, both solutions were added with 2 g sawdust fiber and 3.3 ml PEG 400. Then, one solution was added with starch gelatin. Both solutions were continuous stirring about 7 hours. Figure 3.2 showed the mixing process of the solutions

Figure 3.6: Mixing Process

3.4.4 Film formation

Followed by, both solutions prepared were sufficiently mixed and degassed under reduced pressure about 24 hours. Afterwards, the mixed solutions was poured onto a glass plate and waited at ambient temperature until 1 day and it was completely dried. After films formation, them carefully removed by peeling from the glass plate.
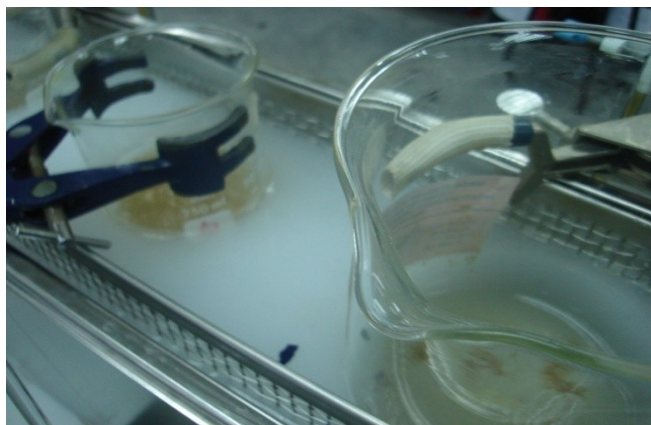
Figure 3.7: Degassed under pressure

Figure 3.8: Film formation

3.5 Films Characterization

Films were characterized in term of atomic force microscopy (AFM), fourier transformi (FTIR), differential scanning calorimeter (DSC), and thermo gravimetric analysis (TGA).

3.5.1 Atomic Force Microscopy (AFM)

The surface morphology (2D and 3D topographic images) and roughness analysis of mean roughness (Ra), the root mean square of data (Rz) and the mean difference in the height between the five highest peaks and the five lowest valleys (Ry) for Chitosan with sawdust (CS) film and Chitosan, starch with sawdust (CSS) film with PEG 400 as plasticizer in scan area of 2 µm x 2 µm and 0.5µm x 0.5 µm were characterized using an atomic force microscope model Shimadzu SPM-9500J2 (Norashikin *et al.,* 2007).

3.5.2 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The FTIR generates an infrared spectral scan of samples that absorb infrared light. FTIR spectra were recorded between 400 and 4000 cm^{-1} with a piece of film 2 cm in diameter. Spectral outputs were recorded in absorbance as a function of wave number.

Figure 3.9: Fourier Transform Infrared analysis

3.5.3 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis was performed to study the degradation characteristic of the fibers after each step of preparation the composite biodegradable film. Thermal stability of each sample was determined using TGA Q500 series Thermo gravimetric analyzer (TA Instruments) with a heating rate of 10 °C/min in a nitrogen environment. It has a weighing capacity 1.0 g, and final temperature 600°C.

3.5.4 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry (DSC) identifies the melting temperature of the composites biodegradable films. The thermal properties of the film samples with a weight about 10 mg to 20 mg were performed by a DSC Q1000 series (TA Instrument) under nitrogen atmosphere, with a flow capacity of 25 ml/min from 20 to 300 °C at a heating rate of 10 °C/min.

Figure 3.10: Differential Scanning Analyser

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Atomic Force Microscopy (AFM)

Figure 5.1 (a) and (b) shows the 2D and 3D AFM images of chitosan with sawdust (CS) film with a scan area of 2 µm x 2 µm.and 0.5 µm x 0.5 µm.
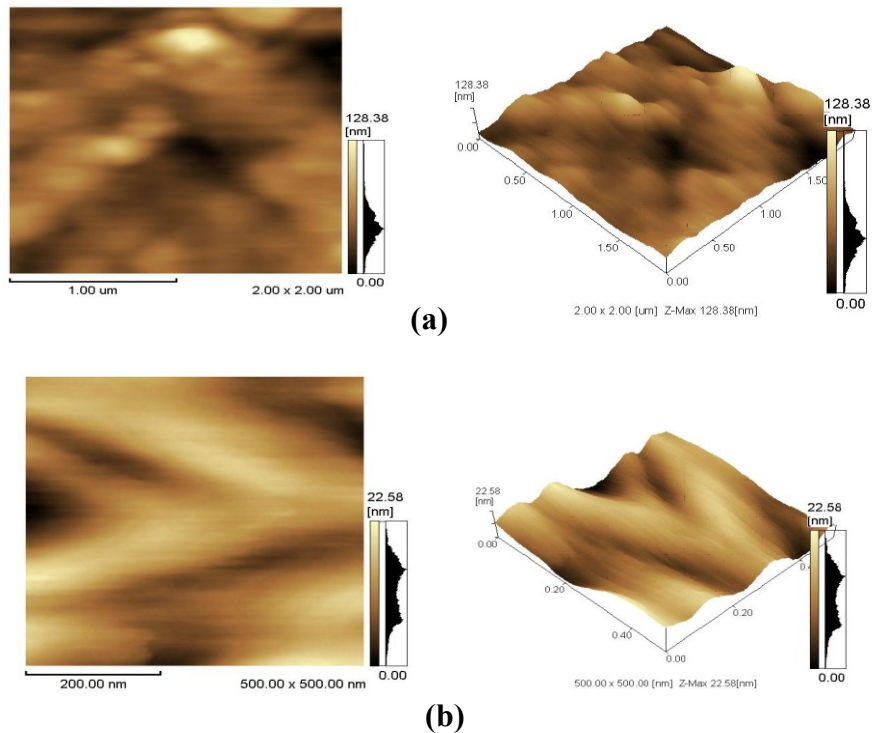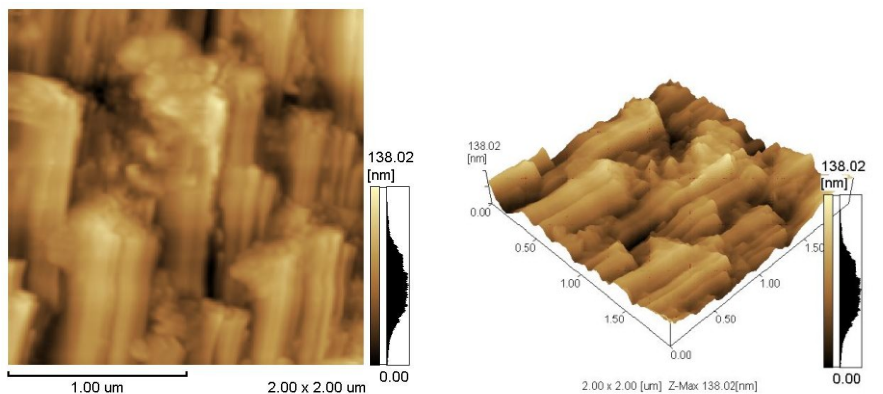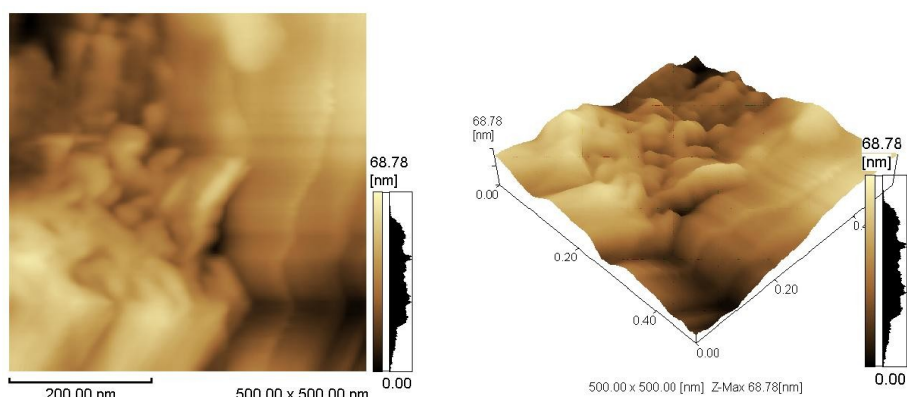

(a)

(b)

Figure 4.1:   Series of AFM topographic images of chitosan, with sawdust (CS) composite biodegradable films (a) 2 µm x 2µm (b) 0.5 µm x 0.5 µm scan area

Figure 5.2 (a) and (b) shows the 2D and 3D AFM images of chitosan, starch and sawdust (CSS) film with a scan area of 2 µm x 2 µm.and 0.5 µm x 0.5 µm.

(a)

(b)

Figure 4.2: Series of AFM topographic images of chitosan, starch with sawdust (CSS) composite biodegradable films (a) 2 µm x 2µm (b) 0.5 µm x 0.5 µm scan area

The result clearly show that the morphology of the surface changes with different presence of starch in both composite degradable film with sawdust. On comparing from Figure 4.1 (a) and (b), they are observed that the nodules are merged closely together, while from Figure 4.2 (a) and (b), they are observed that the nodules are also merged close together but not in uniform state. The Figure 4.1 (a) and (b) shows the surface of

CS films is smoothing, homogenous and with good structural integrity. It was flat and compact with very sparsely distributed small particles with low phase separation. The blend films of CSS in Figure 4.2 (a) and (b) exhibits such patterns because presence of amylose molecules that the continuous region (matrix) correspond to a network structure consisting mostly of amylose and chitosan. This will lead to the smooth surface results for composite biodegradable film without starch and rough surface for composite biodegradable film with starch.

Table 4.1: Roughness parameter of CS and CSS composite biodegradable films.

| Sample	Ra (nm)	Ry (nm)	Rz (nm)	Rms (nm)
Chitosan + Sawdust	12.654	126.517	70.925	16.998
Chitosan + Starch + Sawdust	17.020	131.044	82.252	20.796

The roughness analysis of mean roughness (Ra), the root mean square of data (Rz) and the mean difference in the height between the five highest peaks and the five lowest valleys (Ry) are presented in Table 4.1. The roughness parameter of these films increased with addition of starch as polymer matrix. For CS film, the Ra is 12.654 nm and for CSS film, the Ra is 17.020 nm. This low molecular weight and without starch probably formed very tight nodules creating a very smooth surface indicated by the low roughness parameter value. The results indicated that the CSS film have rough surface because of the interaction properties between starch and chitosan because of amylose and chitosan that explains the low miscibility between the two compounds.

4.2   Fourier Transform Infrared (FTIR)

Figure 4.3 below show the Fourier Transform Infrared spectrum of the both composite biodegradable films from sawdust. The FTIR spectral of CS film and CSS film is shown in Figure 4.3(a) and (b)
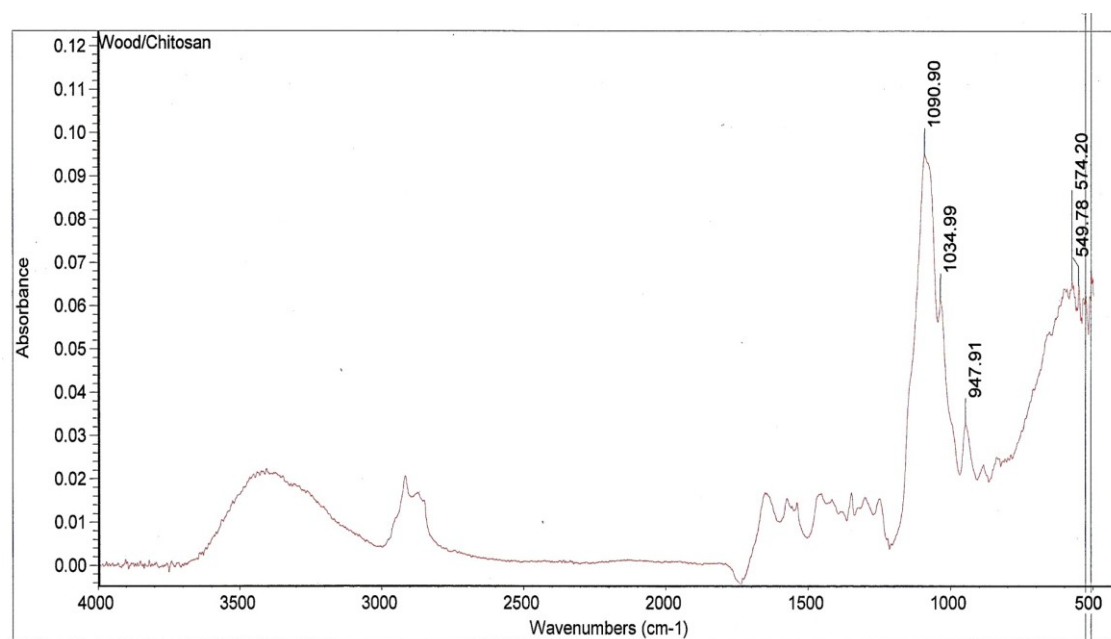
(a)
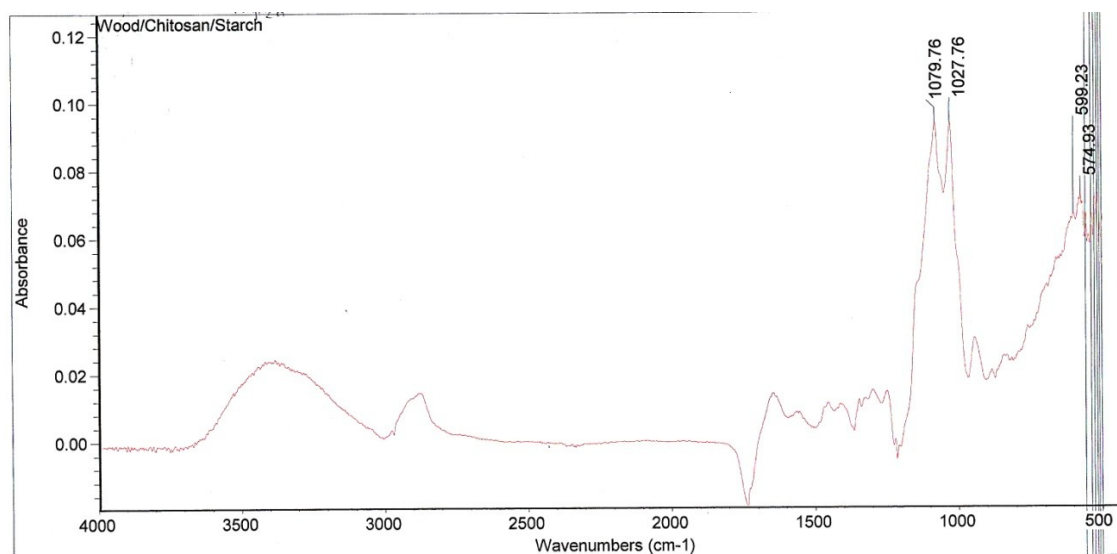
(b)

Figure 4.3: FTIR spectra of (a) CS film, and (b) CSS film

The CS film spectrum was very similar to that in the study of Nunthanid, Puttipipatkhachorn, Yamamoto and Peck (2001). The broad band area 3500 and 3000 cm^{-1} was the O-H stretching, while the band around 1650 and 1500 cm^{-1} was the N-H bending and C=O stretching presence amide II and amide I respectively. The peaks at 1090.90 cm^{-1} and 1079.76 cm^{-1} suggested the presence of an ether group in the film and 599 to 574 cm^{-1} indicative of aromatic ring. When two components are mixed, the physical blends versus chemical interactions are affected by changes in the characteristic spectra peaks (Guan *et al.,* 1998; Yin, Yao, Cheng & Ma, 1999). In the spectrum of CSS biodegradable blend film, the amino group peak of chitosan shifted because there have interactions were presence between the hydroxyl group of starch and the amino group of chitosan (Meenakshi *et al.,* 2002; Xu *et al.*, 2005). The absorption at 1027.76 cm^{-1} is detected at Figure 4.3 (b) but not appear at Figure 4.3 (a). This peak is responsible for aliphatic amines, C-N. Thus, suggests that cross linking between amino group of chitosan and amylose as cross-linkable monomer at their active sites occurred.

4.3   Differential Scanning Calorimetric (DSC)

The DSC thermogram of the CS film is shown in Figure 4.4 (a) and CSS film in Figure 4.4 (b). Thermogram at Figure 4.4 (a) of CS film showed an initial broad peak at 64.5°C due to removal of absorbed moisture or nonstructural water. The temperature range from 30 °C up to 300 °C was selected for two reasons:

a.   To avoid endothermic signals related to the melting of frozen water around 0°C.

b.   To limit possible sample degradation.

The observed endotherms are related to the evaporation of water present in the samples (Bershtein & Egorov, 1994) that occur over a large temperature interval (about 100 °C of chitosan and 150 °C for starch). The melting for CS film and CSS film are close to each other which 106.73 °C and 107.90 °C respectively. For higher

temperatures, in the case of CS and CSS films is accompanied by a sharp exothermic curve above 270 °C due to a degradation of the samples. A similar, linear relationship is obtained for both the polysaccharides films.
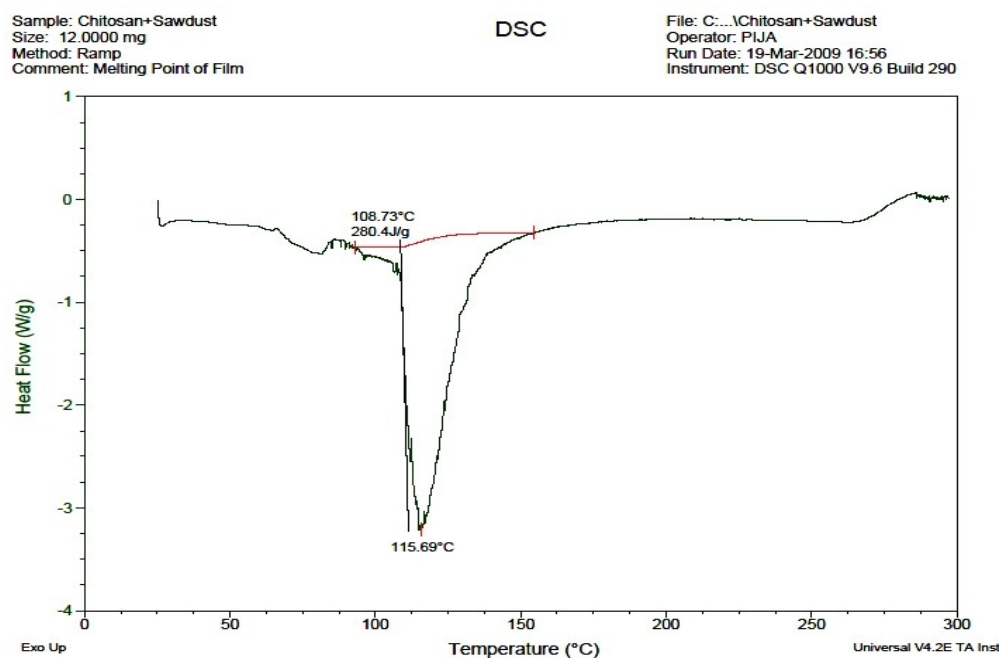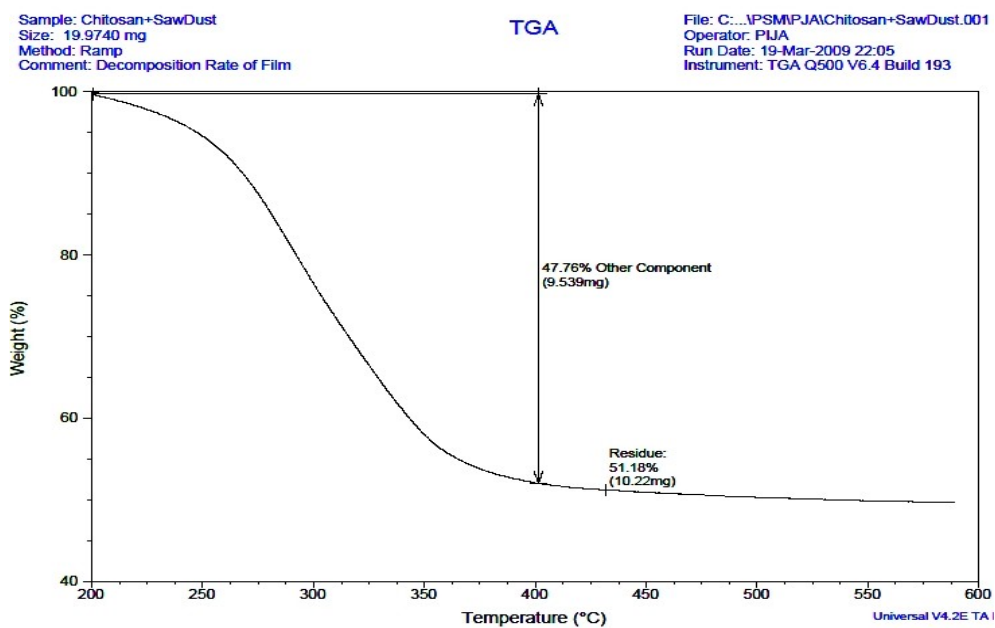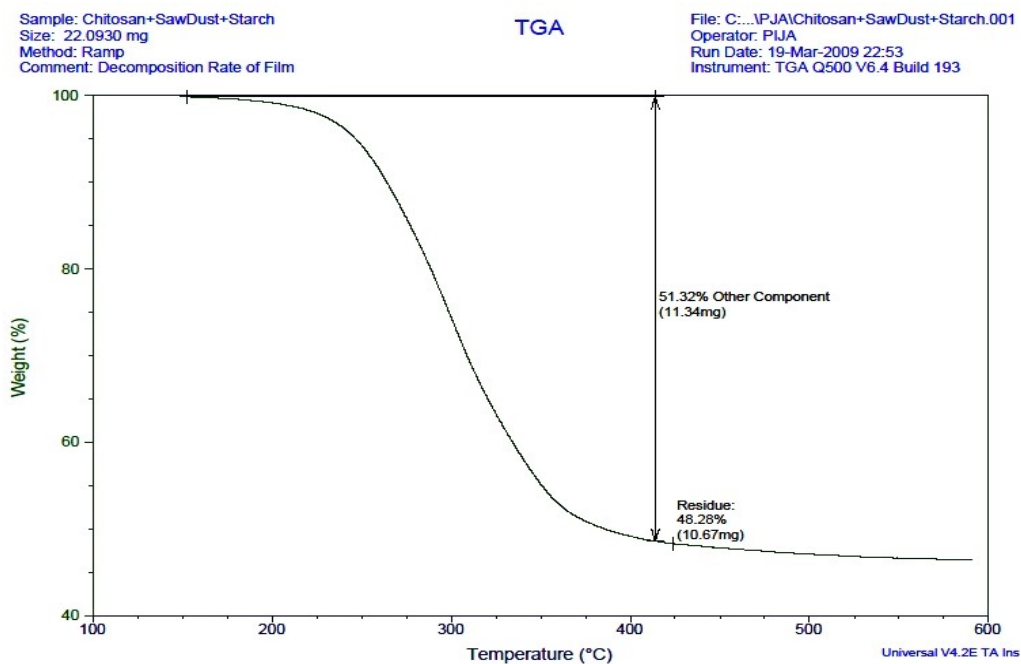

(a)
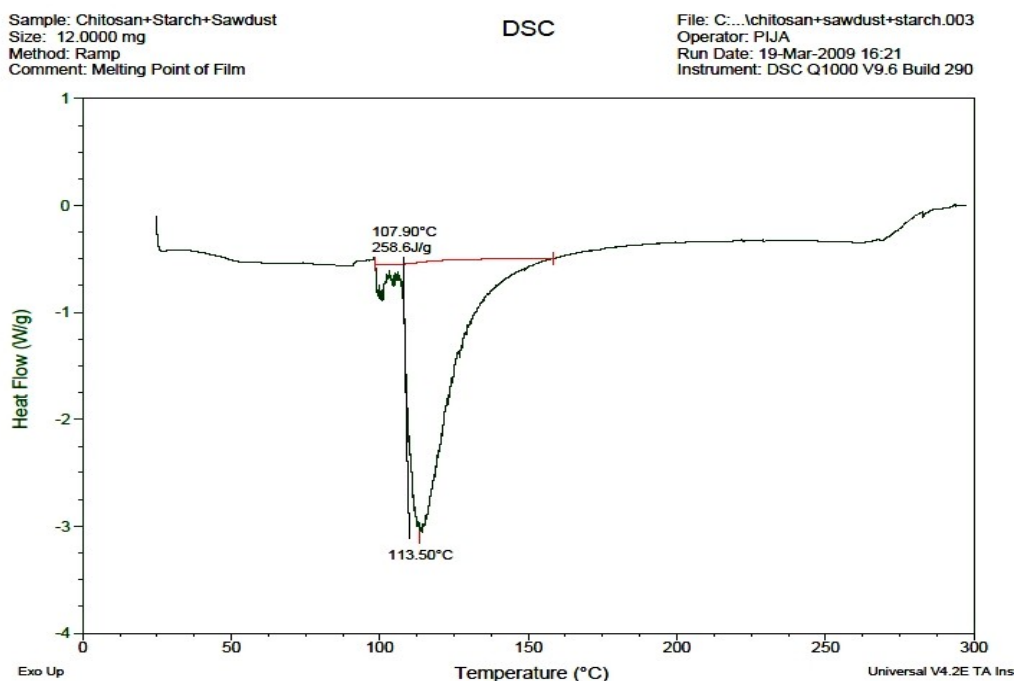
(b)

Figure 4.4: DSC thermograms for (a) CS film and (b) CSS film

4.4 Thermo Gravimetric Analyzer (TGA)

(a)

(b)

Figure 4.5: TGA curves for CS film (a) and CSS film (b)

Figure 4.5 shows the TGA thermogram of CS film and CSS film composites. Decomposition temperature was obtained from TGA curve below. The first weight loss of 1-5 % observed up to 100 °C is due to loss of water from polymer composites (Chan *et al.,* 1989; Yue, Epstein, Zhong, 1991). Chitosan shows a discrete weight loss at 286 °C, attributable to the degradation of chitosan chains (Thanpitcha *et al.,* 2006). Also, there was found that the starch start to degrade at around 275 °C. The addition of starch contributed to the most amount of weight loss. Thus, the amount of residue left behind decrease also with the addition of starch. The degradation temperatures for both films are close to each other and smaller than that of each component. These results are on agreement with Averos and Boquillon's, (2004) work where they showed that the degradation temperature variation between starch and the composite filled with lignocellulosic fibers are rather low. Starch film well known their ability to bind with water molecules therefore, a tolerable amount of water contains inside a starch – based film should able to observed. CS film exhibits the highest thermal stability, where has high residue percent compared than CSS film, 51.58%.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1   Conclusion

In this work, cellulose fibers were extracted from sawdust by chemical treatments in isolation fiber methods. Morphology, chemical composition and thermal properties of the composite biodegradable films were characterized to investigate their usability in biocomposite applications. Experimental results showed that the roughness of the film surface will increase with addition the starch as polymer matrix. FTIR measurements of the composites film revealed that presence starch in the composite films when N-H spectrum peak was detected at 1027.76 cm^{-1}. For the thermal properties, the melting and degradation temperature very close for each other of both of CS and CSS films and proved the Averos and Boquillon's, (2004) statement where they showed that the degradation temperature variation between starch and composite filled with lignocellulosic fibers are rather low. But, the CS films exhibits the high thermal stability compare than CSS film where has high percent of residue

5.2   Recommendations

To enhance the results of the composite biodegradable films, there are several recommendations listed here.   First, for the characterization of composite biodegradable films, the mechanical properties must be test to ensure the increasing when they content of the sawdust fiber. With this, more data can be obtained and more comparisons can be done. If there are more comparisons have been done, its can strengthen the results and justification.

Second, in order to see clear view of morphology the composite biodegradable films, Scanning Electron Micrographs (SEM) is the suggestion method.   SEM will show clearly the fibers formed structural network between chitosan and starch.

Third, polylactic acid (PLA) is the suggestion plasticizer replaces the polyethylene glycol or as additive to the films. It is because, production of PLA from the lactic acid monomer (Lunt, 1998) from corn or sugar beet as a feedstock for fermentation while show that PLA is from a natural resource that easily degrades.

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