PREPARATION OF ADHESIVE USING SOY PROTEIN AND LIGNIN

ALICIA NG YIT HUI

BACHELOR OF CHEMICAL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

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PREPARATION OF ADHESIVE USING SOY PROTEIN AND LIGNIN

ALICIA NG YIT HUI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality.for the award of the degree of Bachelor Chemical Engineering.

Signature   :
Name of main supervisor   : DR. ARUN GUPTA
Position   : SENIOR LECTURER
Date   : 3 JANUARY 2014

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. This thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ID Number   : KA10177
Date   : 3 JANUARY 2014

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ABSTRACT

Abundant, renewable and inexpensive soybean can be a good alternative to natural adhesive. Soy flour was modified by repeated digestion of soy flour by sodium hydroxide and hydrochloric acid. 5%, 10% and 20% modified soy flour (MSF) was then prepared. Medium density fibreboard (MDF) of 810 kg/m^3 was made using wood fibre and thickness swelling properties and mechanical properties were analyzed to determine the performance of the board. In the second part, the MSF concentration with the best mechanical result was used to prepare MSF with enzymatic hydrolase lignin (EHL) of that particular concentration. Laccase enzyme was added to 5% lignin to produce EHL. Thickness swelling and mechanical properties were analyzed to determine the performance of the board. FTIR and DSC analysis were performed to understand the structure and properties of all the different types of adhesive. Thickness swelling test exhibit that 5% MSF showed the least thickness swelling. However it did not meet the requirement of ASTM. 10% MSF with EHL did not show a better result either as it increased to more than 100%. For mechanical testing, internal bonding for 10% MSF showed the best result and it almost reached the ASTM standard. 10% MSF with EHL also showed similar result as the 10% modified soy flour. As for modulus of rupture, 10% MSF also had better results. However, both 10% MSF and MSF with lignin had results that were passing the ASTM standard.

ABSTRAK

Kacang soya yang banyak, boleh diperbaharui dan murah boleh menjadi alternatif yang baik untuk pelekat semula jadi. Tepung soya telah diubahsuai dengan berulang tepung soya penghadaman oleh natrium hidroksida dan asid hidroklorik. 5%, 10% dan 20% tepung soya yang diubahsuai (MSF) disediakan kemudian. Papan gentian ketumpatan sederhana 810 kg/m^3 dibuat menggunakan serat kayu dan harta Dalam bahagian kedua, tumpuan MSF dengan keputusan mekanikal yang terbaik telah digunakan untuk menyediakan MSF dengan lignin hydrolase enzim (EHL) tumpuan yang tertentu bengkak ketebalan dan sifat mekanik telah dianalisis untuk menentukan prestasi papan. Laccase enzim ditambah kepada 5% lignin untuk menghasilkan EHL. Bengkak ketebalan dan sifat mekanik telah dianalisis untuk menentukan prestasi lembaga. Analisis FTIR dan DSC telah dijalankan untuk memahami struktur dan sifat-sifat semua jenis pelekat. 5% MSF menunjukkan bengkak ketebalan yang paling kurang. Walau bagaimanapun ia tidak memenuhi keperluan ASTM. 10% MSF dengan EHL juga tidak menunjukkan keputusan yang baik kerana ia meningkat kepada lebih daripada 100%. Untuk ujian mekanikal, ikatan dalaman 10% MSF menunjukkan hasil yang terbaik dan ia hampir mencapai standard ASTM. 10% MSF dengan EHL juga menunjukkan hasil yang sama seperti 10% MSF. Bagi modulus pecah, 10% MSF juga mempunyai keputusan yang lebih baik. Walau bagaimanapun, kedua-dua 10% MSF dan MSF dengan lignin mempunyai keputusan yang memenuhi standard ASTM.

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LIST OF SYMBOLS AND UNIT

°C	celcius
cm	centimetre
g	gram
kDa	kilo Dalton
kg	kilogram
MPa	megapascal
mg	milligram
min	minute
ml	millilitre
mm	millimetre
h	hour
m.w	molecular weight
M	molarity
N	normality
rpm	revolution per minute
U	unit

LIST OF ABBREVIATIONS

3D   Three dimensional

7S   β-conglycinin

11S   Glycinin

AMSP   alkali-modified soy protein

ASTM   American Society for Testing and Materials

DSC   Differential Scanning Calorimetry

EHL   enzyme hydrolase lignin

ESL   extruded sorghum lignin

FTIR   Fourier Transform Infrared

GH   Guanidine Hydrochloride

HCl   Hydrochloric acid

IB   Internal Bonding

LVL   Laminated venner lumber

MDF   Medium Density Fibreboard

MOE   Modulus of Elasticity

MOR   Modulus of Rupture

MSF   Modified soy protein

N   Normality

NaOH   Sodium hydroxide

OSA   2-octen-1-ylsuccinic anhydride

OSB   Oriented Strandboard

PAE   polyamidoamine-epichlorohydrin

PF   Phenol-Formaldehyde

SDS   Sodium Dodecyl Sulfate

SDBS   Sodium Dodecylbenzene Sulfate

SL   Sorghum lignin

SPI   Soy Protein Isolate

TMSP   Trypsin Modified Soy Protein

UF   Urea-Formaldehyde

U-SPI   Urea Soy Protein Isolate

CHAPTER 1

INTRODUCTION

1.1　Motivation

Over the past 75 years, the source for wood adhesives has dramatically changed. For centuries, natural adhesives have been used to make products. Since the early days, adhesive was used to glue wood veneer to furniture. Nowadays, they are used in application such as assembling furniture and in roof beams. Back in the days, soy protein based adhesive was widely used where the protein was mainly taken from animals and plants (Mcgraw-Hill Yearbook of Science & Technology, 2010).

However, due to the easiness to convert into well-defined, uniform and specifically designed polymers, fossil fuels have made a prominent role in replacing soy protein adhesive. Adhesive was shift to petroleum-based adhesives as they have better glueing strength, water, heat, moisture and decay resistance, making it a better choice as adhesive in the wood market. Another factor that contribute to this shift was because of the decreased in petrochemicals cost (Mcgraw-Hill Yearbook of Science & Technology, 2010).

Moving forward 75 years later, its use has been touted as not environmental friendly and resulted in unfavourable environmental issues in addition to poor waste management, harmful effects on human's health and the hiked in prices and the desire to turn to greener and more environmental friendly products have led people to revert back to adhesive made from soy protein-based ones. In the desire to produce and come out with a more environmental friendly adhesives, researches need to come out with better and suitable technologies. Moreover, the increase need for low-cost adhesives with enough supply and durability were also the factors that contribute to the effort to replace petrochemically based adhesives.

For soy protein, it is vital to understand the structure and the key components that lead to good adhesive properties. Proteins are different from other adhesives in terms of their structure and property relationships. Protein is modified to improve the structure of native

soybean proteins which are a highly ordered global structure with the hydrophilic groups being exposed on the outside while the hydrophobic groups are buried on the inside. Hydrogen bonds which prevent the reactive group from interacting with the wood substrate can be broken by making modifications to its functional properties at the secondary, tertiary and quarternary levels by changing its molecular structure by physical, chemical means or by enzymatic reaction. These modifications will cause the internal hydrogen bonds to break resulting in the unfolding of the protein molecules thus making the reactive structure to react with cellulosic materials and increase its adhesion properties (Mo et al., 2004). Zhong et al. (2003), Huang and Sun (2000), Hettiarachchy et al. (1995) and Sun and Bian (1999) are some of the researches that have studied the properties of soy protein by modifiying it by adding alkali, trypsin, sodium dodecyl sulfate, guanidine hydrochloride and sodium dodecylbenzene sulfonate.

Lignins on the other hand are mainly recovered as byproducts from wood pulping operations where around 75 million tons are annually produced worldwide. (Petrie, 2012). They are the components that hold the plant fibres together. This particular property has roused interest for lignin to be used as a good wood adhesive which are non-toxic and more environmental friendly. Lignin being a renewable, non-toxic, easily available and low cost material has seen in recent years being used in the development of thermosetting resins used as wood adhesive. They are used to substitute part of phenol-formaldehyde or urea-formaldehyde resins. Olivares et al. (1988) used lignin as a copolymer in lignin-phenol-formaldehyde resin binders while Mancera et al. (2011) have used lignin as an adhesive to manufacture Vitis vinifera fibreboard and they obtained good mechanical and water resistance properties that satisfied the relevant standard specifications.

Although soy protein and lignin have their own characteristics and potentials to be good adhesive, there are hardly any research being done on producing adhesive using these two components. In Malaysia, since they can be easily obtained and are cheap, producing adhesive through this method would be another great way in producing a greener and environmental friendly adhesive. Moreover, the long-term outlook for supply and price stability in the oil market are also a concern and composite wood product manufacturers are eager to find a more reliable source and better ways to produce adhesive using better and lasting technologies.

1.2　Problem Statement

1.2.1　Health and Environmental Issues

In 2004, the International Agency for Research on Cancer classified formaldehyde as a potential carcinogen. (IARC, 2004). A carcinogen is a chemical capable of causing cancer. Exposure to low levels of formaldehyde aggravate the eyes, nose and throat and causing allergies that will affect the skin and lungs. Excessive and increased exposure levels can result in throat spasms and a build up of fluid in the lungs which may lead to death. Contact can also cause severe eye and skin burns, leading to permanent damage. Hours after exposure, these symptoms normally appear, even though no pain is felt. Formaldehyde can cause an asthma-like respiratory allergy. Further exposure can cause asthma attacks with shortness of breath, wheezing, cough and chest tightness. Repeated exposures may cause bronchitis, with coughing and shortness of breath.

In terms of environmental issues, formaldehyde dissolves easily in water, and eventually disintegrate. Formaldehyde decomposes in air within 24 hours to form formic acid and carbon monoxide. Formaldehyde does not bioaccumulate in plants and animals. Animals will have chronic effects including shortened lifespan, reproductive problems, lower fertility and changes in appearance or behaviour. Chronic effects can only be seen a long time after the first exposure to a toxic chemical. Formaldehyde poses danger and has high chronic toxicity to aquatic life. Apart from that, it may cause cancer and other chronic illnesses in rodents while exposure of birds and terrestrial animals to formaldehyde could contract similar diseases. (National Protection Agency, 2000).

1.2.2　Non-Renewable Raw Materials

The raw materials for making Urea-formaldehyde and Phenol-formaldehyde resins are derived from natural gas and petroleum which are non-renewable sources. The finite reserve and expanding consumption of petroleum and natural gas will definitely affect the availability of the raw materials for making these formaldehyde-based adhesives in the long run.

1.3   Objective

This research was done in order to achieve the following objectives:

1.   This work aims to produce medium density fibreboard adhesive using soy protein and lignin with better adhesion, mechanical properties and water resistance.
2.   Prepare adhesive which are less harmful towards the environment and human health.

1.4   Scope of Study

The scope of the research listed below is needed to achieve and accomplish the objectives:

1.   Make and produce medium density fibreboard using the modified soy flour and soy -lignin adhesive.
2.   The properties of medium density fibreboard produced using modified soy flour and combination of soy protein and lignin adhesive will be studied.
3.   The effect of different concentration of modified soy flour as adhesive will be studied.
4.   The effect of adding enzyme hydrolase lignin to the modified soy flour will be studied.
5.   Mechanical testing of the medium density fibreboard will be carried out to determine the properties of the board.
6.   Chemical analysis will be done on the adheisve to determine its properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

In this chapter, information regarding and related to this research will be further explained. There are many researches who have studied different ways to make and produce a good wood adhesive using soy protein. These researches have a similar goal in mind which is to find ways to replace the petroleum-based adhesive in a move to contribute to a greener environment. These improvements are usually done by changing the physical and chemical structure of the soy protein through adjustment of the pH, thermal treatment, high pressure, hydrolysis and others.

2.2 Wood Adhesive

2.2.1 Introduction

Wood adhesives are substances used for binding wood to itself or onto other materials. There have been various types of substances that were used historically for bonding wood, but until the late 1940s these adhesives were all made of natural materials . After World War II, synthetic wood adhesive started to appear and has surpassed natural glue for wood binding in modern times. Basically, wood adhesive can be placed into two distinct categories – natural and synthetic. Animal, vegetable, casein, soybean and blood glues are known as natural wood adhesive while petroleum, gas, coal and other synthetic resins are the derivation of synthetic wood adhesives (Mcgraw-Hill Yearbook of Science & Technology, 2010).

2.2.2 Natural Wood Adhesive

2.2.2.1 Animal Glue

Animal glue or also known as hot glue, is made from the hide and bones of cattle, sheep and horses. The low moisture resistance in animal glue will cause the bond to weaken when it is exposed to high humidity. Therefore, it must be applied to wood when it is still hot in order for it to form a strong bond when it cools and loses moisture. The wood should also be kept warm during application in order to prevent the glue to cool too fast thus preventing strong bonds to form. The protein in the animal glues contains a high amount of an amide group (-CONH-), free amino groups (-NH- and -NH$_2$) and a carboxylic acid group (-COOH). These functional groups interact with one aother within and between protein chains in addition to interacting with the wood (Pernollet, 1985). Through these interactions, strength of animal glues and the adhesion is provided for. Proteins in different animal glues have different structures and consists of different amounts of these functional groups. Therefore, different animal glues have properties that vary significantly.

2.2.2.2   Vegetable Glue

According to Charles (1991), vegetable glues are glues that are produced by plants. These materials are dispersible or soluble in water and are usually made from the starches that comprises of many grains and vegetables. The natural gums include agar which is from colloids in marine plants, algin derived from seaweed and gum arabic which is an extract of the acacia tree or also known as gum tree. The substance called marine glue is used to caulk seams. However, it consists of tar or pitch which is not truly a glue.

2.2.2.3   Casein Glue

The use of casein in the gluing of wood is reported to be a very ancient art. European craftsmen understood a method of gluing with a crude casein (possibly the curd of soured milk mixed with quick lime) in the Middle Ages, and the art continued in a small way to the modern days. The manufacture of casein glue as a separate industry, however, seems to have started in Switzerland or Germany in the nineteenth century. In the United States casein glues were not popular and is used only to a very limited extent until the year 1916 or 1917, where the need for a water-resistant glue for the construction of military aircraft suddenly aroused interest in casein glue and promptly led to its extended production and use. The main ingredient of casein glue is casein, which is the chief protein essential to milk. When milk

becomes sour, it will separate into curd and whey. The curd, when washed and dried, is the casein of commerce. When made in this way, it is known as self-soured or naturally soured casein. Casein is also precipitated by mineral acids, such as hydrochloric or sulfuric, and by rennet. In preparing the glue, caseins precipitated by the different methods will require different amounts of water to produce solutions of similar viscosity. The degree and type of alkali influences product behaviour. Satisfactory glues, however, can be produced from caseins precipitated by any of these methods provided the casein is of good quality.In wood bonding, casein glues generally are superior to true animal glues in moisture resistance and aging characteristics (Charles, 1991).

2.2.2.4   Blood Glue

Blood glues are used in much the same manner as casein glues. The proteins from animal blood in slaughtering are precipitate out, dried and sold as powders which are then mixed with water, hydrated lime or sodium hydroxide. Blood glues are used to a limited extent in making softwood plywood, sometimes in combination with casein or soybean proteins. They have also been used as extenders for phenolic-resin glues for interior type softwood plywood. Blood-based adhesives have a higher moisture resistance, but it is still lower strength than casein-based adhesive (Charles & William, 1963).

2.2.2.5   Soybean Glue

2.2.2.5.1   Composition of Soybean

Major storage proteins of soybean are globulins. There are four protein fractions that are classified according to their sedimentation properties. They are 2S, 7S, 11S and 15S fractions and comprise 8%, 35%, 52% and 5% of the total protein content respectively. The principal storage proteins are glycinin (11S) and β-conglycinin (7S) and constitute over 70 % of soluble protein. Their content, ratio and dynamics of biosynthesis vary with soybean varieties and environment (Murphy, 1984). According to Staswick, Hermodson and Nielson (1984), glycinin (m.w ~360 kDa) is a protein with compact quaternary structure stabilized via disulfide, electrostatic and hydrophobic interactions. It is made up of six A-SS-B subunits. Each subunit is composed of an acid (m.w. ~38 kDa) and basic polypeptide (mw ~20 kDa) linked by single disulfide bond, except for the acid polypeptide -A4-. Subunits are packed into

two hexagons placed one over the other to form a hollow oblate cylinder. β- Conglycinin is a major protein of 7S fraction with molecular weight of 150 -180 kDa (Thanh & Shibasaki, 1976). It is composed of three subunits, -α`-, -α- and -β- which interact to produce seven isomers (B0-B6). Molecular weight of these subunits is 72 kDa, 68 kDa and 52 kDa, respectively. The original β-conglycinin is a glycoprotein and it contains the carbohydrates as one unit attached to the aspartic acid residue at the N-terminal end of the molecule. The carbohydrate moiety consists of 38 mannose and 12 glucosamine residues per molecule of protein. Due to the different structure, there are a number of physicochemical differences in the 7S and 11S protein components. For example, 11S protein is insoluble at pH 6.4 and 2-5°C, whereas β-conglycinin is insoluble at pH 4.8. The literature contains numerous references that describe the physicochemical and functional properties of these proteins and their subunits.
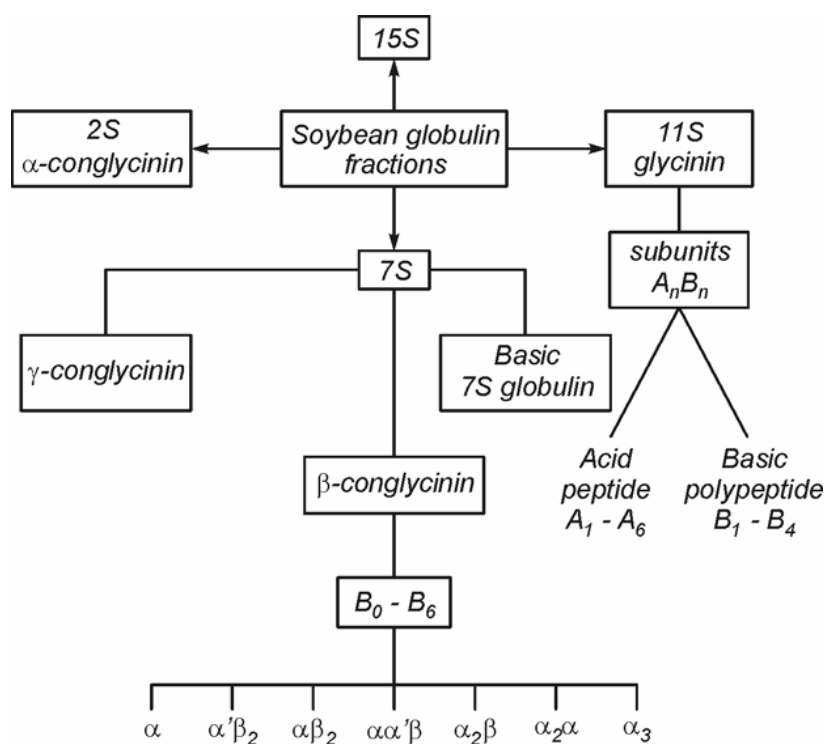

Figure 2.1: Soybean composition

2.2.3   Synthetic Adhesive Derived from Petrochemicals

Petrochemicals are used to produce two types of synthetic resins: thermosetting resins and thermoplastic resins. After being heated at a certain temperature, thermosetting resins become insoluble and infusible materials resulting into an irreversible process. As for thermoplastic resins, they soften or melt when being heated and solidify again when being cooled. The process of softening and solidifying are reversible and can be repeated many times (Eckelman, 1997).

2.2.3.1   Urea-Formaldehyde Resins

Urea-formaldehyde (UF) resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins.2,3 Urea-formaldehyde resins comprise about 80% of the amino resins produced worldwide. (Skeist, 1990, p. 341).

Urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde has initially been studied early in the century. However, due to its complexity, it is still yet to be completely understood at the present time. (Pizzi, 1983). The synthesis of a urea-formaldehyde resin takes place in two stages. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups. This reaction is a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. Tetramethylolurea is apparently not produced, at least not in a detectable quantity. The addition of formaldehyde to urea takes place over the entire pH range. The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1 respectively. The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction. The second stage of urea-formaldehyde resin synthesis consists of the condensation of the methylolureas to low molecular weight polymers. As mentioned, the rate at which these condensation reactions takes place is highly dependent on the pH and, for all practical purposes, occurs only at acidic pHs. The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules; methylene ether linkages by the reaction of two methylol groups; methylene linkages from methylene ether linkages by the splitting out

of formaldehyde; and methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process. The difference between the pH profiles of the two stages of urea-formaldehyde resin synthesis is used to advantage in the production of urea-formaldehyde adhesive resins. (Anthony & Alfred, 1995).

As a wood adhesive, urea-formaldehyde resins are advantageous because they are inexpensive, have good processing and curing properties, and are resistant to fungi and termites. (Meyer, 1979). Greater utilization of urea-formaldehyde resins is impeded, however, because of the emission of formaldehyde which may result in potential health hazards and environmental pollution. (Coutrot, 1986).

2.2.3.2   Phenol-Formaldehyde Resins

Phenol-formaldehyde (PF) are extensively employed as bonding adhesives in the manufacture of composite wood panels, imparting the water resistance required for exterior application such as roofs and external house walls. They are mainly the products of the reaction between phenol and formaldehyde which is catalysed by alkali to provide a thermosetting polymer called resole. (Athanassiadou et al., 2010).

In the preparation of resoles, the molar ratio of formaldehyde to phenol is more than one. Phenol may be substituted with more than one methylol group. These substituted phenols can later react among themselves to form a mixture of polymers with different sizes and different degrees of branching. Resoles will form highly crosslinked polymer networks when cured at a higher temperature. In contrast, the formaldehyde/phenol molar ratio is less than one in the initial stage of preparing novolacs. This is because the methylol group is not stable under an acidic condition and can quickly react with phenol to form polymers. The low formaldehyde/phenol ratio allows the resulting PF resins to have relatively low molecular weight to allow them to flow and penetrate the wood. Extra amount of formaldehyde has to be added to further react the adhesive, resulting in the formation of highly crosslinked polymer networks. With the aid of special catalysts such as divalent metal acetates, phenols can be predominantly linked at ortho-positions, causing novolacs to have a linear structure. (Koch, 1987).

PF resins are mainly used for production of exteriorly used structural wood composite panels such as plywood and laminated veneer lumber (LVL) because of their good durability and

high strength even under harsh weather conditions. After curing, PF resins will have a dark color, which negatively affects the aesthetics of wood composite products. Therefore, PF resins are normally not used for production of interiorly used wood composite panels. (Skeist, 1990).

2.2.4 Lignin

2.2.4.1 Introduction

Lignin is a natural amorphous polymer. It acts as an adhesive to give plants their structural integrity. Lignin is the second most abundant and the only biomass constituent based on aromatic units out of the three major natural polymers that make up ordinary plants namely cellulose, lignin and hemicellulose (Gallezot, 2008). They are derived from trees, plants and agricultural crops and are recovered in large quantities as byproducts from pulping mills mainly in the form of kraft lignin and lignosulfonate.

2.2.4.2 Structure of Lignin

After many years of study, the structure of native lignin still remains unclear. Lignin is actually not one compound but many complex, amorphous, three-dimensional polymers that have in common a phenylpropane structure, that is, a benzene ring with a tail of three carbons. In their natural unprocessed form, none of them has ever been completely described due to its complexity, and having molecular weight reaching up to 15,000 or more. However, the dominant structures in lignin have been elucidated as the methods for identification of the degradation products and for the synthesis of model compounds have improved. The results from these numerous studies have yielded what is believed to be an accurate representation of the structure of lignin. Examples of the elucidated structural features of lignin include the dominant linkages between the phenylpropane units and their abundance, as well as the abundance and frequency of some functional groups. Linkages between the phenylpropane units and the various functional groups on these units give lignin a unique and very complex structure (Ruben et al., 2010).
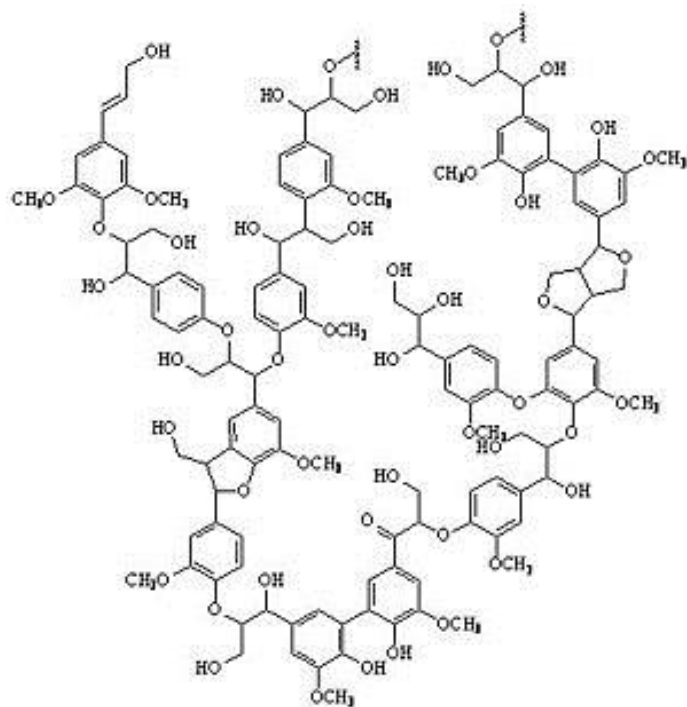
Figure 2.2: Lignin Structure

2.3　　　　Soy Protein Adhesive

Soybean-based adhesives, commonly called soy-based adhesives were widely used in the production of wood composites from the 1930s to the 1960s. Soy-based adhesives have many advantages such as cheaper cost, easier handling and lower pressing temperature (Li et al., 2004). The renewed interest in soy-based adhesives in recent years because soybean is abundant, inexpensive, and readily available. However, wood composite panels bonded with the soy-based adhesives had relatively low strength and low water-resistance, which results in the adhesives to be replaced by formaldehyde-based adhesives.

2.4　　　　Lignin as Adhesive

2.4.1　　　　Introduction

Over the years, lignin has been one of the most intensely researched raw materials for wood adhesives, mainly because of its very low cost. Lignin provides biomass based resins with a phenolic-like molecular structure. Lignin is unusual as a biopolymer resulting in difficulty to adapt to adhesives as compared to starch, cellulose or soy because of its heterogeneity and inexact composition. Native lignin is a crosslinked polymer, but the polymers have to be partially degraded to allow separation from the cellulosics. These degraded lignin resins need to be further polymerized to obtain useful adhesive properties. Lignin from the pulping process does not lead to a useful product because of the cost of separating the lignin from the pulping chemicals and the variability of the product. However, lignin sulfonates, contained in the spent sulfate liquids from sulfite pulping of wood have been found to be a more useful feedstock for the production of reactive lignin. Lignin based wood adhesives have been prepared with formaldehyde or other aldehydes. There have been claimed to provide properties which are up to par with the conventional phenol formaldehyde adhesive, the quality of lignin-based resins diversify significantly depending on wood source, the pulping operation and other considerations (Petrie, 2012).

2.4.2 Production of Synthetic-Resin-Free Wood Panel Adhesives From Mixed Low Molecular Mass Lignin And Tannin

Mansouri et al. (2010) produced mixed interior wood panel tannin adhesive where lignin is in considerable proportion, 50%, of the wood panel binder and in which no "fortification" with synthetic resins, such as isocyanates and phenol-formaldehyde resins as used in the past, was necessary to obtain results satisfying relevant standards. A low molecular mass lignin obtained industrially by formic acid/acetic acid pulping of wheat straw was used. Environment-friendly, non-toxic polymeric materials of natural origin constitute up to 94% of the total panel binder. The wood panel itself is constituted of 99.5% natural materials, the 0.5% balance being composed of glyoxal, a non toxic and non volatile aldehyde, and of hexamine already accepted as a non-formaldehyde-yielding compound when in presence of condensed tannin. The wood was shown to pass the relevant interior standards with such adhesive formulations.

2.4.3 Production of *Vitis Vinifera* Fiberboards using Lignin

In a study by Mancera et al. (2011), lignin was used as an adhesive to fiberboards. Kraft lignin ranging from 5% to 20% was added to the fiberboards that had been steam-exploded under optimized pre-treatment and pressing conditions. The boards were tested to get the water resistance properties in terms of thickness swelling and water absorption. Physical and mechanical characterization of the boards were also carried to study the modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB). The results showed that there is a decrease of fibreboards water absorption as the percentage of lignin increases. In other words, the water resistance of the boards improved. For mechanical properties, as the lignin increased, the fibreboard also increased in strength. Most notably was that with just 5% of lignin, the strength of the boards were double that of the binderless board. From the studies, they concluded that fiberboards with 15% of lignin had good water resistance and mechanical properties that fulfilled the relevant standard speciafications.

2.4.4 Production of Wood using Sodium Hydroxide and Lignin

Young et al. (1985) studied the characteristics of wood surface and made some modification to it by treating it with sodium hydroxide and lignin-formaldehyde or methylolated lignin. Initially, they treated the wood with only sodium hydroxide and found that it can contribute to the wood surfaces strong dry autohesive bonds. However, it has poor water resistance in which they explained that it was due to limited number of secondary hydrogen bonds were formed. Hence, they added metylolated lignin in addition to sodium hydroxide and the end result was that methylolated lignin acted as a reactive gap-filling polymer resulting in excellent dry and wet wood bond strength was obtained. However, there was a need to add an amount of phenol-formaldehyde resin or isocyanate in order to obtain a durable wood bond.

2.4.5 Lignin-phenolformaldehyde Resin Binders

Olivares et al. (1988) studied the copolymerization of lignin with phenol-formaldehyde resin in order to produce anzhesives with that has the same characteristics as phenol-formaldehyde resins. They used lignin from *Pinus radiata* black liquor as a copolymer to produce ligninphenol-formaldehyde resin binders. Different modified lignins were tested and resin composed of 18.8% ultrafiltrated high molecular weight lignin, 22.9% phenol and 58.3% formaldehyde had the best mechanical properties and water resistance.

2.4.6 Sorghum Lignin and Extruded Sorghum Lignin

Xiao et al. (2013) investigated the adhesion properties of sorghum lignin (SL) and extruded sorghum lignin (ESL) that were blended with soy protein adhesive based on soy protein isolate or modified soy protein. They found that the shear strength of the sodium hydroxide suspended soy protein adhesive without lignin was lower as compared to the ones blended with the SL and ESL. The shear strength was seen to be increasing significantly. As for water resistivity, the adhesive without lignin was again relatively low but it increased significantly when it was added with SL and ESL.

2.5 Wood Composite

2.5.1 Introduction

Wood composites are defined as materials that are being bonded and glued. The primary component of wood-based composites is the wood element, often 94% or more by mass (Stark, Cai & Carll, 2010). Common elements for conventional wood-based composites include veneers, strands, particles, and fibers. Properties of composite materials can be changed by changing the size and geometry of the elements and by combining, reorganizing, or stratifying elements. Compared to solid wood, wood composites can provide better mechanical and chemical properties such as higher shear strength, fire resistancy, weathering and biological degradation. Moreover, wood composites can be made with various sizes and shapes that are not easily obtainable from logs. The current wood composites market is mostly occupied by traditional wood composites or also known as panel products such as plywood, oriented strandboard (OSB), particleboard and medium density fiberboard (Maloney, 1996).

2.5.2 Plywood

According to Maloney (1996), plywood is a panel product built up mainly of sheets of veneer called plies. It is made with an odd number of layers with the grain direction of adjacent layers oriented perpendicular to one another. A layer can consist of a single ply or of two or

more plies laminated with their grain direction parallel. A panel can contain an odd or even number of plies but always an odd number of layers. The outside plies are called faces, or face and back plies. Inner plies are plies other than the face or back plies. The outer layers and all odd-numbered layers have their grain direction oriented parallel to the long dimension of the panel. The grain in even-numbered layers is perpendicular to the length of the panel. Plywood panels have significant bending strength both along the panel and across the panel, and the differences in strength and stiffness along the panel length versus across the panel are much smaller than those differences in solid wood. Plywood also has excellent dimensional stability along its length and across its width. Minimal edge-swelling makes plywood a good choice for adhesive-bonded tongue-and-groove joints, even where some wetting is expected. Unlike most panels fabricated from particles, it undergoes minimal irreversible thickness swelling if wetted. The alternating grain direction of its layers makes plywood resistant to splitting, allowing fasteners to be placed very near the edges of a panel (Stark, Cai & Carll, 2010).

Plywood can be divided into two classes, namely construction and industrial plywood; and hardwood and decorative plywood. Most construction and industrial plywood used in the United States is produced domestically, and U.S. manufacturers export some material. The bulk of construction and industrial plywood is used where performance is more important than appearance. However, some grades of construction and industrial plywood are made with faces selected primarily for appearance and are used either with clear natural finishes or lightly pigmented finishes. Hardwood plywood is normally used in applications including decorative wall panels and furniture and cabinet panels where appearance is more important than strength. Most of the production is intended for interior or protected uses, although a very small proportion is made with adhesives suitable for exterior application. (Stark, Cai & Carll, 2010).

2.5.3 Oriented Strandboard

Oriented strandboard (OSB) is made from flakes that are created from debarked round logs by placing the edge of a cutting knife parallel to a length of the log and cutting thin flakes off the log. The cut flakes are subjected to forces that break the flakes into strands having a length parallel to the grain of the wood several times the width of the strand. The strands can be positioned on the board forming machine with the strands predominantly postioned in a single cross machine direction in one layer and predominantly oriented in the generally

perpendicular direction in adjacent layers. The different layers are bonded together by natural or synthetic resin under heat and pressure to produce a finished product.

OSB is easily distinguished by its relatively huge and long wood strands. The arrangement of the surface strands is not always visually obvious, especially in small cut pieces of panel. The main advantage of OSB lie in the field of its mechanical performance, which is directly related to the orientation and shape of the strands and their arrangement and position within the panel. Even though OSB coomprises of relatively large strands of wood, its surface is relatively smooth and this can be further improved by sanding without loosing the aesthetic character which is special to OSB. The colour of OSB varies from a light straw colour to a medium brown depending on wood species used, resin system used and pressing conditions. It contains no knotholes, core voids or points of weakness (Clarke et al., 1996).

Due to its high mechanical properties and the geometry of the strands within panels, OSB is suitable for use in load-bearing applications in construction and for flooring, roof decking and wall sheathing. There is also a wide range of field of other applications where OSB can be utilised as a wood-based panel product. Different grades of the product are available for different levels of loading and different environmental conditions. OSB is a quality, precision-engineered product that can satisfy the same applications and loading conditions as plywood and in some cases a thinner OSB panel may be used allowing lower costing and smaller budget. Huge quantities of OSB are also used for sarking and industrial packaging and in site hoardings and pallet tops (Stark et al., 2010).

2.5.4 Particleboard

Particleboard is manufactured by mechanically reducing the wood raw material into small particles, applying adhesive to the particles, and consolidating a loose mat of the particles with heat and pressure into a panel product. The particleboard industry initially used cut flakes as a raw material. However, due to economic concerns it prompted the development of the ability to use sawdust, planer shavings and to a lesser extent, mill residues and other waste materials. In order to manufacture particleboard with good strength, smooth surfaces, and equal swelling, manufacturers ideally use a homogeneous raw material. Particleboard is typically made in layers. But unlike OSB, the faces of particleboard usually consist of fine wood particles and the core is made of coarser material allowing a smoother surface for

laminating, overlaying, painting or veneering. Particleboard is readily made from virtually any wood material and from a variety of agricultural residues (John, 2012).

Particleboard is widely used in furniture, where it is typically overlaid with other materials for decorative purposes. It is the predominant material used in ready-to-assemble furniture. Particleboard can also be used in flooring systems, in manufactured houses, and as underlayment. Thin panels can also be used as a paneling substrate. Since most applications are interior, particleboard is usually bonded with a UF resin, although PF resins are sometimes used for applications requiring more moisture resistance (Stark et al., 2010).

2.5.5   Medium Density Fibreboard

Medium Density Fibreboard (MDF) is made from lignocellulosic fibres combined with a synthtic resin or other suitable bonding system that are combined together under heat and pressure. Several things differentiate MDF from particleboard, most notably the physical configuration of the wood element. Because wood is fibrous by nature, fiberboard exploits the inherent strength of wood to a greater extent than does particleboard. MDF is denser than plywood and particle boards making it a wider range of applications. Reinforcing a polymer matrix with lignocellulosic materials have been attributed to several advantages such as lower density, high stiffness, less abrasives to equipment, biodegradable and lower cost. Several treatments are used to increase dimensional stability and mechanical performance of hardboard. Heat treatment, tempering, and humidification may be done singularly or in conjunction with one another. Heat treatment, exposure of pressed fiberboard to dry heat improves dimensional stability and mechanical properties, reduces water adsorption, and improves interfiber bonding. Tempering is the heat treatment of pressed boards, preceded by the addition of oil. Tempering improves board surface hardness, resistance to abrasion, scratching, scarring, and water (Mahzan et al. & Stark et al., 2010).

MDF is often used instead of solid wood, plywood, and particleboard in a lot of furniture usage. It is also used for interior door skins, mouldings, and interior trim components (Stark et al., 2010).

2.6   Protein Modification

2.6.1   Introduction

By altering their molecular structure or conformation through physical, chemical or enzymatic agents at the secondary, tertiary and quaternary levels, the functional properties of protein can be improved (Kumar et al., 2002). Various chemical or enzymatic modifications of soy protein were investigated for improving the strength and water-resistance of wood composite panels bonded with soy-based adhesives. Inside the compact protein structure, protein chains are held together by disulfide bonds, hydrogen bonds, electrostatic attraction between oppositely charged groups, and hydrophobic interactions. Other studies suggested that unfolding the soy protein structure can significantly improved the strength and the water-resistance of wood composite panels bonded with modified soy protein (Hettiarachchy et al., 1995; 1998). The mechanisms for this improvement were proposed as follows: when the compact protein structure is unfolded, the protein it enables the chains to be spread well onto wood surfaces allowing to easily penetrate wood. Various functional groups such as amino groups, carboxylic acid groups and hydroxyl groups in the unfolded protein can well interact with wood components, allowing it to form strong bonds with wood. (Lambuth, 1977).

2.6.2   Thermal Treatment

This type of treatment is the oldest and most widely used method for protein modification. When heat treatment is being applied, it will decrease the protease inhibitor activity and eliminate lipoxygenase which will in turn improve the functional properties. When soy protein is being heated to well above 70°C, dissociation will occur at the quaternary structure, denaturing the subunits. This occurrence will change the protein through electrostatic, hydrophobic and disulfide interchange mechanisms (Barac et al., 2004). The thermal susceptibility of the major protein structure, 7S and 11S globulins are different. Glycinin or 11S has a higher thermal transition point of 92°C as compared to β-conglycinin which is 72°C. This is the contributing factor as to why 11S has a more compact and stable structure (German et al., 1982). In another research by Damodaran and Kisella (1982), they mentioned that the insoluble aggregates formed in pure heat treated glycinin solutions comprise only of the basis 11S subunits. They also suggested that during heating treatment, the acid 7S protein

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subunits interact with stabilize the 11S basic subunits to prevent protein aggregation when 7S and 11S soy proteins.

2.6.3 High Pressure Application

The structure of soy protein and its intramolecular hydrophobic and electrostatic interaction can be disrupted when high pressure is applied. Normally, the interuption occurs at the tertiary and quaternary structure (Subirade et al., 1998). According to Galazka et al. (2000), the quarternary structure of the 11S can be altered by the high pressure thereby increasing the protein-protein interactions and interactions between the globulins and polysaccharides. Molina et al. (2001) found out that dissociation of 7S subunits occur at pressure ranging from 200-600 MPa while dissociation of 11S will lead to aggregation due to change in surface hydrophobicity which will also change its solubility.

2.6.4 Chemical Modification

Modifications done to soy protein have the aim to change its properties. These modifications includes the aim to reduce protease activity, phytic acid content, to increase or decrease protein solubility in order to obtain functional properties that are more soluble dependent.

2.6.5 Trypsin-modified Soy Protein

Kalapathy et al. (1995) investigated the properties of trypsin-modified soy protein (TMSP) it has on wood. The adhesive strength of TMSP was measured for cold-pressed and hot-pressed with temperatures varying from 60, 80, 100, and 120°C of woods. Of the woods examined, soft maple gave the highest strength of 743 N at a protein glue concentration of 2 mg/cm^2]. For soft maple and cold-pressing, TMSP at 2 mg/cm^2 gave twice the adhesive strength of unmodified protein controls, 743 vs. 340 N. Also, the adhesive strength of TMSP increased from 284 to 743 N as glue concentration was increased from 1 to 2 mg/cm^2. However, hot-pressing of wood pieces beyond 1 h at 120°C and 30% relative humidity resulted in decreased adhesive strengths of TMSP compared to controls.

2.6.6 Alkali-modified Soy Protein

Hettiarachchy et al. (1995) investigated the properties of soy protein modified by alkali and trypsin. For the alkali-modified soy protein (AMSP) part, suspended soy protein isolate was adjusted to a pH of 8.0, 9.0, 10.0, 11.0, or 12.0 using 1N NaOH and incubated in a shaking incubator at temperature varying from 30°C to 70°C. For the trypsin-modified soy protein (TMSP), Hettiarachchy et al. (1995) used the method as described by Kalapathy et al. (1995). From the results obtained, the optimum treatment conditions (pH/temperature) for producing AMSP with the highest adhesive strengths were 9.0/70, 10.0/50, 11.0/50, and 12.0/40°C. All of these alkali treatments under optimum pH/temperature conditions gave similar adhesive strengths. However, they concluded that a moderate pH/temperature combination of 10.0/50°C was desirable. In the test for water resistance, The total number of blocks delaminated after four cycles using unmodified control soy protein, AMSP, and TMSP were 26, 1, and 11, respectively. This showed that AMSP has improved and better water resistance.

Also from their study, they found out that trypsin modification involves limited hydrolysis of protein molecules, whereas alkali modification involves the unfolding of protein molecules. Furthermore, both trypsin and alkali modifications lead to increased exposure of hydrophobic group. They hypothesise that the pH of the glue may affect its hydrophobic properties.

2.6.7   Urea-modified Soy Protein

Sun and Bian (1999) carried out a research to test the water resistance of adhesives containing modified soy proteins in walnut, poplar and pine plywood applications. In their research, the soy protein was modified into urea-modified and alkali-modified soy protein.

In the urea-modified soy protein, Ten grams of soy protein isolate (SPI) powder was then mixed with 150 mL of the urea/distilled water solution while sodium hydroxide was added to 30 g of SPI powder suspended in distilled water to produce alkali-modified soy protein. Four woods, ranging from soft to hard, were used: pine, maple, poplar, and walnut. The dimension of each wood sample was $3 \times 20 \times 50$ mm (thickness, width, and length). The modified SPI powder was added to distilled water at a ratio of 1:6 (SPI/water) and allowed to disperse at room temperature for about 5 min. The adhesive slurry was brushed onto the wood sample until the entire area was completely wet.

In order to test for water resistivity, Specimens were soaked in tap water at room temperature for 48 h, and then dried at room temperature in a fume hood for 48 h. Soaking and drying cycles were repeated three times, and delamination of the specimen was recorded after each cycle. The dimensions of the wood species were measured before and after soaking in distilled water at room temperature for 48 h.

The gluing strengths of urea and alkali-modified SPI adhesives were high with walnut, maple, and poplar specimens. As for water resistiviy, the water-soaking and drying tests showed that the adhesives made from urea soy protein isolate (U-SPI) had the highest water resistance, as shown by the lowest delamination rates of the glued wood specimens. The gluing strength of the U-SPI adhesive with walnut and pine was reduced about 10% after 24 h of water-soaking and then remained the same after 72 h of water-soaking. The expansion results of the four woods in water-soaking tests showed that maple had the greatest swelling, whereas poplar had zero swelling but the highest linear expansion, resulting in higher total bulk volume expansion. Maple and poplar also had higher linear expansion than walnut and pine. Woods with higher linear or bulk volume expansion would have higher shrinkage stress during drying. They speculate that delamination will occur when the shrinkage stress is higher than the adhesive bonding strength.

2.6.8 Urea and Guanidine Hydrochloride-modified Soy Protein

Huang and Sun (2000) made some ammendments to Sun and Bian (1999) study by adding urea and guanidine hydrochloride to the soy protein. Varying solutions of urea (1, 3, 5, and 8 M) or guanidine hydrochloride (GH) (0.5, 1, and 3 M) were added to soy protein to produce adhesive and applied on walnut, cherry, and pine plywoods.

Shear strengths of wood specimens were determined. Water resistance (for interior application) of the adhesive was tested by following ASTM standard method D-1183. Water resistance (for exterior application) of the adhesive was tested according to the modified method described by Hettiarachchy et al. (1995).

The results obtained showed that the 3 M urea modification gave soy protein the highest shear strength in all wood types. Modifications with 1 and 5M urea had lower shear strength, as compared to the 3 M urea modification, but were still higher than the unmodified proteins.

For GH, The soy proteins modified by GH at 0.5 and 1 M concentrations exhibited greater shear strengths than the unmodified proteins. The incubation test showed that the shear strengths of the wood specimens glued with 1 and 3 M urea-modified soy proteins remained almost the same as the initial strengths. Proteins modified by 3 M urea were found to have the best water resistance (zero delamination rate) in all wood types, as well as higher remaining shear strengths after three water-soaking cycles. Specimens glued with proteins modified by 0.5 and 1 M GH gave higher shear strengths after incubation aging, and zero delamination rate and higher remaining shear strengths after three water-soaking cycles compared with those glued with unmodified proteins and 3 M GH-modified proteins. These results indicated that soy proteins modified by GH at 0.5 and 1 M concentrations had better water resistance.

The Differential Scanning Calorimetry (DSC) analysis suggest that the secondary structure might be desirable for protein adhesion. Proteins modified at relatively lower urea concentrations (1 and 3 M) may have been partly unfolded and had a certain amount of secondary structure, resulting in better shear strengths. As protein molecules disperse and unfold in solution, the partly unfolded molecules with a certain amount of secondary structure increase the contact area and adhesion force onto other surfaces, such as wood materials, and they interact with each other during the curing process to achieve bonding strength. Protein modification also could expose to the surface some hydrophobic amino acids that are buried inside, increasing hydrophobicity and thus increasing water resistance.

2.6.9 Sodium Dodecyl Sulfate (SDS) and Sodium Dodecylbenzene Sulfonate (SDBS) modified Soy Protein

In another study by Huang and Sun (2000), they studied the adhesive properties of soy proteins which was modified by sodium dodecyl sulfate (SDS) and sodium dodecylbenzne sulfonate (SDBS). Solutions of SDS of 0.5, 1, and 3% and SDBS of 0.5, 1, and 3% were prepared at room temperature respectively. 10 g of SPI powder was suspended in each SDS and SDBS solution (100 mL), stirred, and reacted for 6 h.

Wood ranging from hard to soft (walnut, cherry, and pine) were used. The modified protein adhesive slurry was brushed onto both ends of the middle piece and onto one end of the other

two pieces. Adhesive strength test, incubation-aging test and water soaking test were carried out.

From the results, SDS modification of 0.5 and 1% gave the soy protein higher shear strength in all wood types. Three percent SDS modification had lower shear strength, as compared to the 0.5 and 1% SDS modifications, but was still higher than the unmodified proteins in walnut and pine wood samples. The soy protein modified by SDBS at 0.5 and 1% concentrations exhibited greater shear strength than the unmodified proteins . Modification by 3% SDBS had the least effect on adhesive strength although the glue strength for pine wood was still significantly higher than that for the unmodified proteins. Compared to the unmodified protein, the modified proteins also exhibited higher shear strengths after incubation with two cycles of alternating relative humidity and zero delamination rate and higher remaining shear strengths after three cycles of water soaking and drying.

The DSC data for soy proteins treated with SDS at concentrations of 0, 0.5, 1, and 3% showed that as the SDS concentration increased, the total enthalpy decreased; that is, the heat capacity of the modified soy proteins decreased. This indicates that the higher the SDS concentration, the greater the degree of protein unfolding. The lower shear strength of soy proteins modified at higher SDS concentration (3%) might have resulted from the greater extent of unfolding.

2.6.10   Soy Protein Isolate (SPI) modified by Sodium Dodecyl Sulfate (SDS) and Guanidine Hydrochloride (GH)

Zhong et al. (2003) used modified SPI to study the wet strength and water resistance properties. They found out that the SDS-modified SPI containing 91% protein had a water-soluble mass of 1.7%, which met the requirement of less than 2% to be considered a water-resistant adhesive. The wet shear strength test showed 100% cohesive failure within fiberboard, indicating that the modified SPI has good water resistance. The effect of drying treatment on adhesion performance of the SDS-modified SPI on fiberboard was then investigated. Drying treatment significantly affected the final adhesion performance. Shear strength did not change much, but the percentage of cohesive failure within fiberboard increased markedly as drying temperature increased. All the unsoaked, soaked, and wet specimens glued by the adhesives treated at 70° or 90°C had 100% cohesive failure within fibreboard.

2.6.11 Soy Protein Modified by 2-Octen-1-ylsuccinic Anhydride

In a research done by Qi et al. (2013), they used liquid 2-octen-1-ylsuccinic anhydride (OSA) which is oily in nature and has a long hydrophobic alkyl chain to modify the soy protein. From the results that they obtained, they found out that OSA did not significantly affect the dry shear strength. However there were some changes in the wet strength where it increased for concentration up to 3.5% of OSA and then remained constant with any further increased. Adding OSA generated a newly formed hydrophilic carboxyl group and introduced the hydrophobic alkyl long chains to the soy protein thereby enhancing the hydrophobic interactions. They suggested that this hydrophobic nature prevented water from enteringthe interfacial surface of the soy protein adhesive and wood which hinders the formation of hollow cavities. Also, OSA cannot be dissolved in water due to its oily nature. This is why when the wood is being soaked in water, the hydrophilic group will dissolved in water and cavities will be generated between the soy protein and wood surface. This in turn will decreased the adhesive strength.

2.6.12 Soy Protein and Kymene Adhesive

Kaichang et al. (2004) investigate the properties of wood composite made from the combination of soy protein and kymene. Kymene, a commercial product which is widely used, is an aqueous cationic polyamidoamine-epichlorohydrin (PAE) solution. From their research, they found that the adhesive had shear strength which is comparable or better than the commercialized phenol formaldehyde resins. Apart from that, water resistance of the adhesive is relatively better and its strength was even retained after undergoing a water boiling test.

According to Kaichang et al. (2004), the major reaction that occur during the curring of the adhesive is the azetidium group in PAE resins will react with the remaining secondary amines in PAE resin which caused the homo-crosslinking to happen. Apart from that, the azetidium group wil also react with the carboxylic acid groups of glutamic acid and aspartic acid in soy protein. Also, the amino groups in soy protein will also react with the azetidium group. All the possible reaction mentioned will cause a 3D network which is water-insoluble.

2.7   Fourier Transform Infrared

In Fourier Transform Infrared (FTIR), the sample will absorb infrared radiation while some will be transmitted. The spectrum shown represents the molecular absorption and transmission thus showing the fingerprint of the sample. Hence the purpose of performing FTIR analysis is to identify unknown molecule, determine the amount of components present in a mixture and also to determine the quality of the sample. Speed, sensitivity, mechanical simplicity, calibrated internally and along with several other factors result in the accuracy and reproductivity of the measurement therefore making it the most popular and reliable technique that is still widely used today for the identification of any sample (Griffiths and Haseth, 2007).

The basic principle of FTIR starts from the source, the interferometer, the sample, the detector and finally the computer. At first, infrared energy is emitted from the glwoing black body source. This beam passes the aperture which controls the amount of energy presented to the sample. Then, the beam enters the interferometer where the encoding will be taking place. After exiting, the beam enters the sample compartment where it it transmitted through or reflected from the surface of the sample. At this stage, characteristic of the sample will be absorbed. The beam will then pass to the detector for final measurement where the measured signal will eventually be sent to the computer for user to interpret the information and result (Griffiths and Haseth, 2007).

2.8   Differential Scanning Calorimetry

According to Hohne (2003), Differential Scanning Calorimetry (DSC) is defined as the measurement of change in the difference of heat flow rate to the sample and to a reference while being subjected to a controlled temperature program. DSC allows quick and fast measurement of the reaction heats and heat of transition or heat flow rates and their changes at characteristic temperature in at small amount and at a wide of range of temperature a good accuracy. Characterization of materials, comparison measurement, investigation on stability, phase diagram, determination of purity, kinetic and safety invetigations are some of the application of DSC.

2.9   Summary

Basically, many works and research have been done on soy protein and lignin to produce adhesive. However, there have been not many works of adhesive using both soy protein and lignin.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter described the preparation of materials and experiment procedures that has been designed to complete this research project. To accomplish the objectives and scope of this research, the study was carried out in two parts which were the preparation of adhesive using soy protein and using soy-lignin combination. Experimental procedures involve the procedure for running the experiment, obtaining and analyzing the experimental results.

Raw material of the experiment was prepared and different concentration of modified soy protein was also prepared. In the second part, the concentration of modified soy protein that showed the best result from part 1 of the experiment was used to prepare soy-lignin adhesive of that particular concentration. Then, Medium Density Fibreboard (MDF) boards were prepared using hot molding machine. Those boards were then used to carry out water resistant or thickness swelling and mechanical testing. Fourier transform infrared (FTIR) and Differential Scanning Calorimetry (DSC) analysis were carried out to show the different structures and analyse the change in properties when heat is applied.

3.2 Materials

Commercial grade soy flour purchased from Mildura Organic, Malaysia; rubber wood fibers (*Hevea brasiliensis)* provided by Robin Resources (Malaysia) Sdn. Bhd.; Laccase enzyme, Novo WA20040 supplied by Novozyme, Malaysia which was isolated from *Trametesvillosa* with an activity of 70 units per ml (U/ml); Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) were obtained from Sigma Aldrich.

3.3   Preparation of 2N NaOH And 1N HCl

99% of NaOH was used to prepare 2N NaOH. The following calculations were used to obtain 2N NaOH:

2N NaOH = (40 x 2) g/ 1L

        = 80 g/L

37% HCl was used to prepare 1N of HCl. The following calculations were used to obtain 1N HCl:

Density = 1.18 x 1000

        = 1180

Density/Molecular weight = 32.32

0.37 x 32.32 = 11.9 $\approx$ 12N

$M_1V_1 = M_2V_2$

$12V_1 = 1(500)$

$\therefore V_1$ = 42 ml of HCl in 458 ml of H_2O is required to obtain 1N of HCl.

3.4   Protein Modification

Soy flour was suspended in deionized water in the weight ratio of 1:10 and stirred using a magnetic stirrer for 30 minutes to get a uniform dispersion. 2N NaOH was added to the soy flour and was put into the shaking incubator for at least 2 h at temperature of 60°C with pH of 8.5 at 180 rpm. After that, the solution was poured into 45 ml centrifuge tube to be centrifuged for 30 minutes at 15°C and 10000 rpm. The supernatant will then be thrown off and the remaining part would be the precipitate. 1N of HCl will be added to the precipitate and decrease the pH to 4.5. The precipitate was put in the refrigerator for 1 hour at 4°C. After 1 h, it was centrifuged for 30 minutes at 4°C and 10000 rpm. The modified soy flour with 43% moisture content was then used to make 5%, 10% and 20% (w/v) of adhesive to be used to prepare for board making.

In order to determine the moisture content, the modified soy flour was put into the oven at 104°C for 24 hours. Its initial and final weight was recorded. The following formula was used to calculate moisture content:

$$\text{Moisture content} = \frac{W_i - W_f}{W_i} \times 100$$

where W_i = initial weight

W_f = final weight

3.5   Lignin Extraction from Wood Fibers

The method used by Nasir et al. (2013) to extract the lignin was followed. Wood fibers provided by Robin MDF Sdn.Bhd was suspended in deionized water at 5% consistency (mass pulp/ mass suspension). 6 U/g units of Laccase enzyme was added to the mixture. In order to allow uniform enzymatic reaction, the suspension was stirred in the shaking incubator for 2-3 hours at 200 rpm with 24-25°C. After treatment, the pulp was filtered and the left over solution which is known as enzyme hydrolased lignin (EHL) was be retained for soy-lignin adhesive preparation. The fibers were washed till it becomes colourless and pH becomes neutral. As for the extracted EHL, it was transfered to flask to be air-dried in the oven for 1 hour at 65-70°C to stop the enzymatic reaction.

Calculation for lignin extraction:

Step 1: 50 g of wood fibre was suspended in 950 g of water

Step 2: Calculate number of unit for laccase enzyme

50 g x 6 U/g = 300 units

300 units ÷ 70 U/ml = 4.3 ml of laccase were needed to be added to wood fibre suspension.

3.6   Preparation of Soy-Lignin Adhesive

10% suspension (w/v) of soy-lignin adhesive was prepared. Modified soy flour prepared earlier was mixed with EHL and put into the shaking incubator for 2-3 hours to allow uniform mixing at 24-25°C and 200 rpm.

3.7   Preparation of Medium Density Fibreboard

Fibreboard with a desired density of 810 kg/m^3 and dimension of 200 mm x 200 mm x 6 mm was prepared using 194.4 g of wood fibres. 10% of the weight of fibres of modified soy flour adhesive was added to the fibres using air pressure gun and were mixed using a rotating drum mixer. The fibres were then hot-pressed for 4 minutes to the desired thickness of 6 mm at 5 MPa and temperature of 180°C for bottom and upper plate. 6 boards were prepared using adhesive of different parameters (5%, 10%, 20% modified soy flour and 10% soy-lignin).

Table 3.1: Adhesive Description

Adhesive Composition	Preparation
5% Modified soy flour	40 g modified soy flour + 380 ml water
10% Modified soy flour	80 g modified soy flour + 320 ml water
20% Modified soy flour	160 g modified soy flour + 240 ml water
10% Modified soy flour + Enzyme hydrolase lignin	80 g modified soy flour + 320 ml enzyme hydrolase lignin

3.8   Mechanical Testing

Mechanical tests of modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding (IB) was carried out according to ASTM D 1037 to determine and analyze the properties of the board. From the 6 boards prepared, 2 samples were prepared for IB, 2 for the thickness swelling test and 2 for MOR and MOE test. 3-point static bending test was applied to determine the MOE and MOR. A 50 mm x 50 mm x 6 mm specimens were cut for performing internal bonding and thickness swelling test. For MOR and MOE, the 2 samples

were cut into the size of 200 mm x 50 mm x 6 mm. All the testing was done using Shimadzu UTM AG-X plug series while the results was analyzed using the Trapezium X-software.

Modulus of rupture or also known as bending test measures the strength of the board before it ruptures. It is important to determine its overall strength. As for modulus of elasticity which is also known as Young's modulus, it gives information on the properties of the board by giving an indication of the stiffness of the board. Stress-strain curve shows how a material is storing its energy where stress is defined as force per unit area while strain is defined as elongation or contraction per unit length. MOE only measure the board's deflection and not its overall and ultimate strength.

During pressing, the middle part of the board tightens the least therefore resulting in lower strength. Hence, carrying out internal bonding test is important to ensure the internal property of the board. This tensile strength perpendicular to surface test is the measure of the performance of adhesive in wood composites.

In order to calculate MOR, MOE and IB, the following formulas were used:

$$MOR = \frac{3P \times L}{2 \times b \times d^2}$$

Where P = breaking load

L = span length

b = average breadth

d = thickness

$$MOE = \frac{Stress}{Strain}$$

$$IB = \frac{Maximum\ force\ (F)}{Surface\ area\ of\ specimen\ (A)}$$

The unit for MOR, MOE and IB calculated were in MPa.

3.9 Thickness Swelling Test

In order to determine the water resistant property for the board, thickness swelling test was carried out. Boards prepared earlier were cut into specimen size of 50 mm x 50 mm x 6 mm. The specimens were then immersed in water and left aside for 24 hours. After 24 hours, the specimens were taken out of the water and dried. The percentage of increase in the thickness was calculated based on the equation below:

Percentage increased in thickness (%)

$$= \frac{T_f - T_i}{T_i} \times 100\%$$

where T_f = final thickness

T_i = initial thickness

3.10 Chemical Analysis

3.10.1 Fourier Transform Infrared

Fourier Transform Infrared (FTIR) measurement was performed with a Perkin Elmer instrument by direct transmittance using a fitted universal ATR accessory. The spectrums were recorded within the range of 4000-600 cm^{-1} using a resolution of 4 cm^{-1}.

3.10.2 Differential Scanning Calorimeter

Differential Scanning Calorimeter (DSC) is the measurement of endothermic and exothermic transitions as a function of temperature. It was done on the adhesive to determine and study the pattern of the curing kinetics. DSC was carried out using TA/QA 1000 series and its result was analyzed using TA Universal Analysis 2000 software. Before starting the analysis, a standard sample was used for the calibration. Samples of 2-4 mg were put into the hermetic pan and were heated from 40°C to 300°C at a heating rate of 10°C/min with an inert atmosphere of nitrogen at a rate 50 ml/min.
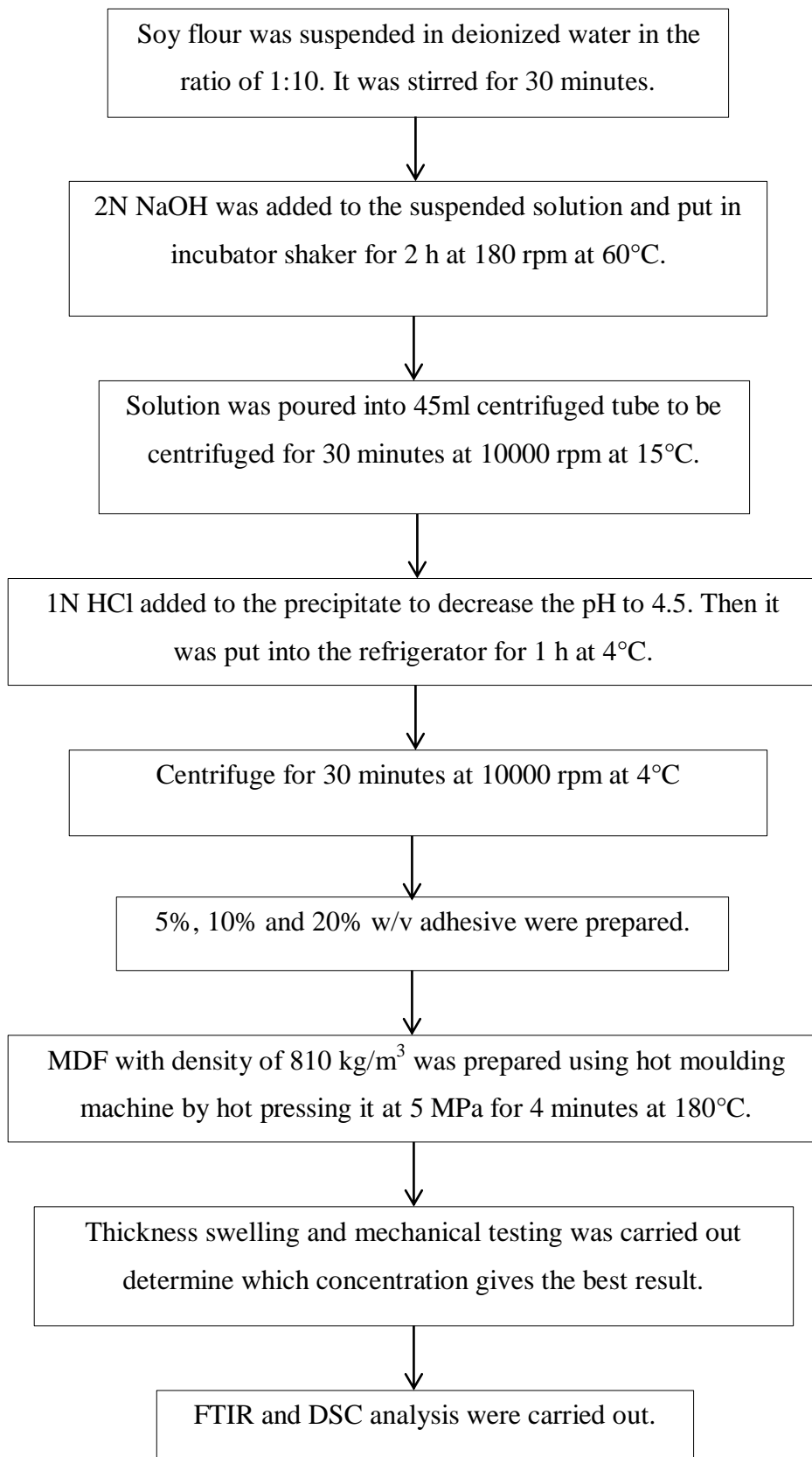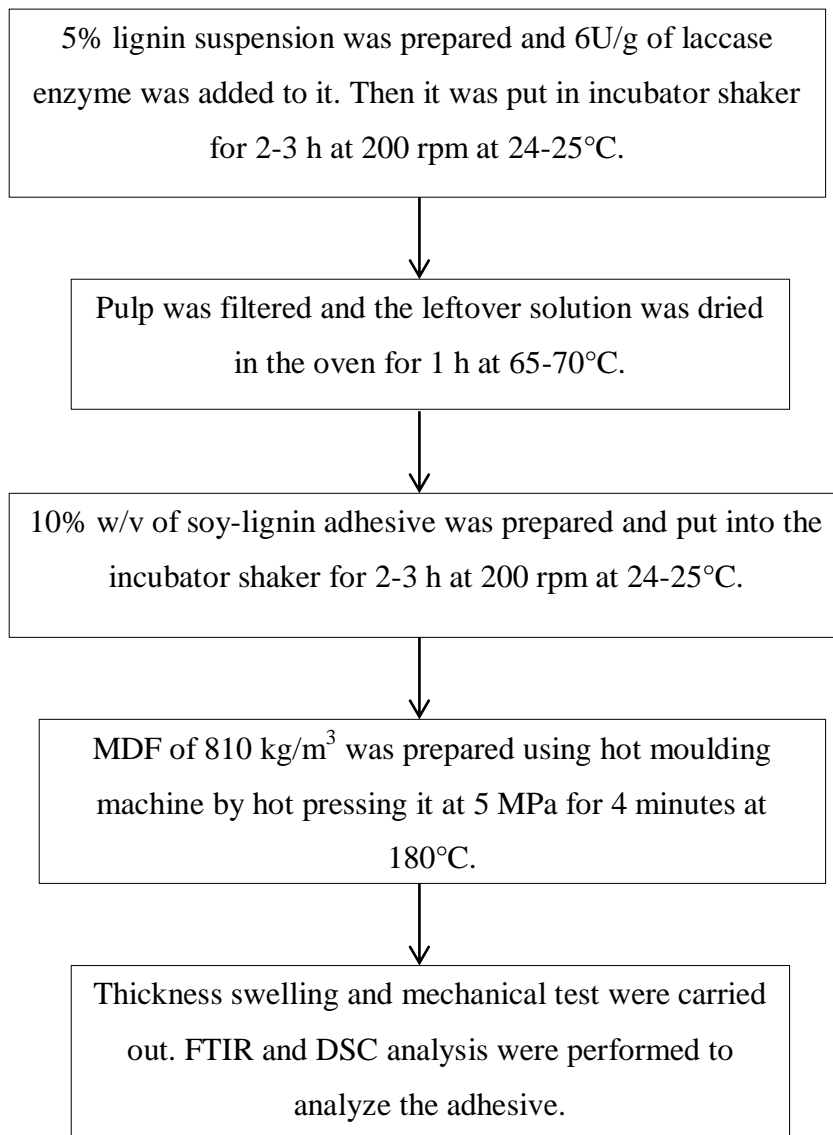
3.11   Summary

```
┌─────────────────────────────────────────────────┐
│   Soy flour was suspended in deionized water     │
│   in the ratio of 1:10. It was stirred for       │
│   30 minutes.                                     │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   2N NaOH was added to the suspended solution    │
│   and put in incubator shaker for 2 h at         │
│   180 rpm at 60°C.                                │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Solution was poured into 45ml centrifuged      │
│   tube to be centrifuged for 30 minutes at       │
│   10000 rpm at 15°C.                              │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   1N HCl added to the precipitate to decrease    │
│   the pH to 4.5. Then it was put into the        │
│   refrigerator for 1 h at 4°C.                    │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Centrifuge for 30 minutes at 10000 rpm at 4°C  │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   5%, 10% and 20% w/v adhesive were prepared.    │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   MDF with density of 810 kg/m³ was prepared     │
│   using hot moulding machine by hot pressing it  │
│   at 5 MPa for 4 minutes at 180°C.                │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Thickness swelling and mechanical testing was  │
│   carried out determine which concentration      │
│   gives the best result.                          │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   FTIR and DSC analysis were carried out.        │
└─────────────────────────────────────────────────┘
```

Soy flour was suspended in deionized water in the ratio of 1:10. It was stirred for 30 minutes.

2N NaOH was added to the suspended solution and put in incubator shaker for 2 h at 180 rpm at 60°C.

Solution was poured into 45ml centrifuged tube to be centrifuged for 30 minutes at 10000 rpm at 15°C.

1N HCl added to the precipitate to decrease the pH to 4.5. Then it was put into the refrigerator for 1 h at 4°C.

Centrifuge for 30 minutes at 10000 rpm at 4°C

5%, 10% and 20% w/v adhesive were prepared.

MDF with density of 810 kg/m^3 was prepared using hot moulding machine by hot pressing it at 5 MPa for 4 minutes at 180°C.

Thickness swelling and mechanical testing was carried out determine which concentration gives the best result.

FTIR and DSC analysis were carried out.

Figure 3.1: Methodology for Part A

5% lignin suspension was prepared and 6U/g of laccase enzyme was added to it. Then it was put in incubator shaker for 2-3 h at 200 rpm at 24-25°C.

Pulp was filtered and the leftover solution was dried in the oven for 1 h at 65-70°C.

10% w/v of soy-lignin adhesive was prepared and put into the incubator shaker for 2-3 h at 200 rpm at 24-25°C.

MDF of 810 kg/m^3 was prepared using hot moulding machine by hot pressing it at 5 MPa for 4 minutes at 180°C.

Thickness swelling and mechanical test were carried out. FTIR and DSC analysis were performed to analyze the adhesive.

Figure 3.2: Methodology for Part B

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

In this chapter, results of the research that were obtained were shown using table and figures. Also, explanation was done based on the result obtained. In the first part, results of modified soy protein were discussed while in the second part, results of adding lignin to the modified soy protein was discussed.

4.2 Results of Thickness Swelling

Table 4.1: Thickness Swelling for 5% Modified Soy Flour

Sample	Thickness before swelling (mm)	Thickness after swelling (mm)	Increase in thickness (%)
A	0.64	1.150	79.68
B	0.64	1.218	90.23
C	0.64	1.195	86.72
D	0.62	1.128	81.85
E	0.62	1.085	75.00
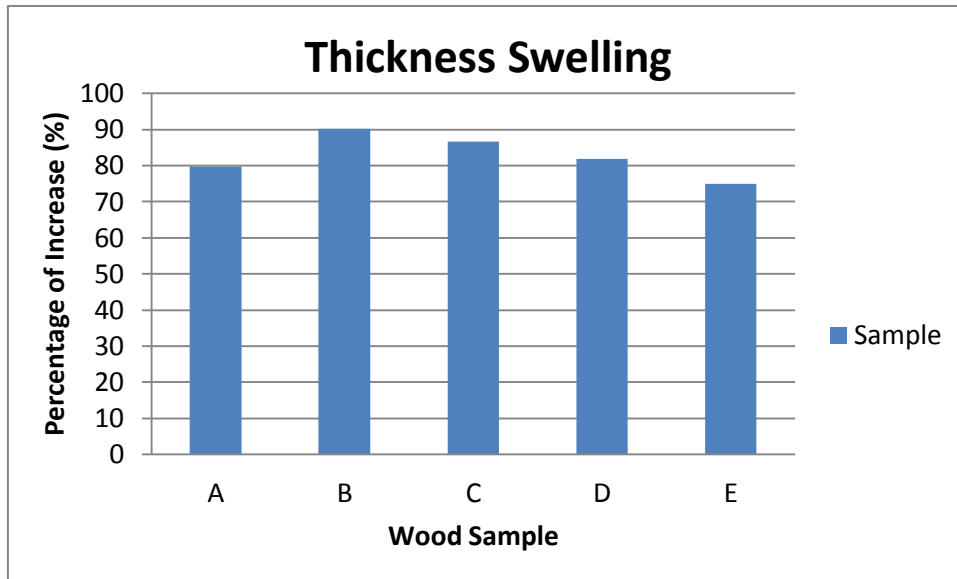
Figure 4.1: Thickness Swelling for 5% Modified Soy Flour

Based on the result above, it can be seen that when the wood samples were immersed in water for 24 h, the wood samples' thickness increased to more than 75%. The highest increased in thickness was 90%. On average, the thickness increment was about 82%.

Table 4.2: Thickness Swelling for 10% Modified Soy Flour

Sample	Thickness before swelling (mm)	Thickness after swelling (mm)	Increase in thickness (%)
A	0.6325	1.2275	94.07
B	0.6425	1.4025	118.29
C	0.6525	1.54	136.02
D	0.64	1.355	111.72
E	0.6375	1.31	105.49
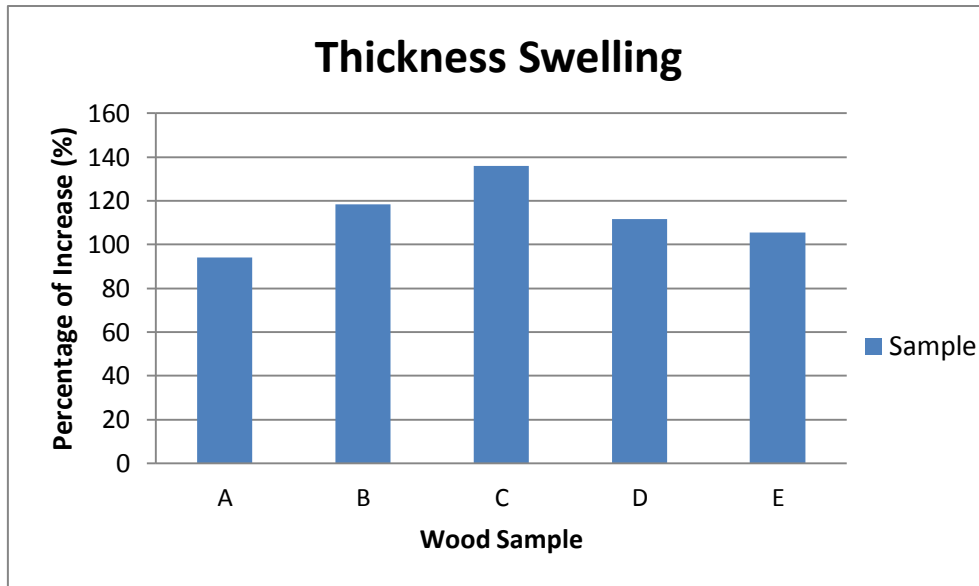
Figure 4.2: Thickness Swelling for 10% Modified Soy Flour

Based on the result in Table and Figure 4.2, it can be seen that when the wood samples were immersed in water for 24 h, the wood samples increased in thickness to more than 94%. The highest increment was 136%. At average, the thickness increment was 113%.

Table 4.3: Thickness Swelling for 20% Modified Soy Flour

Sample	Thickness before swelling (mm)	Thickness after swelling (mm)	Increase in thickness (%)
A	0.655	1.3075	99.62
B	0.65	1.28	96.92
C	0.64	1.3175	105.86
D	0.66	1.2275	85.98
E	0.66	1.22	84.85
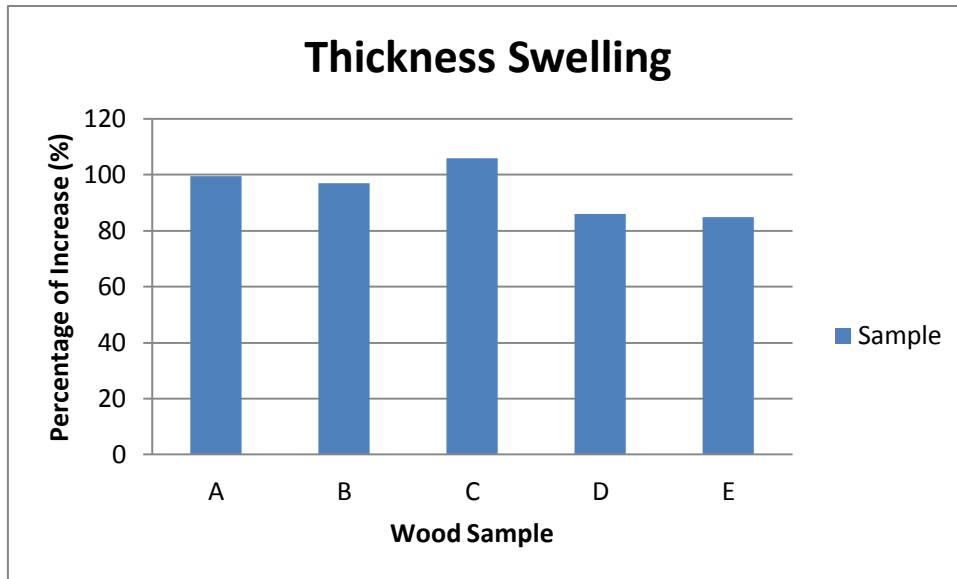
Figure 4.3: Thickness Swelling for 20% Modified Soy Flour

Based on the result in Table and Figure 4.3, it can been seen that when after 24 h of wood samples immersion in water, the wood sample E increased 84% in thickness while sample C had the largest increment which was 105%. Averagely, the increased in thickness was about 94%.

Table 4.4: Thickness Swelling for 10% Modified Soy Flour with Lignin

Sample	Thickness before swelling (mm)	Thickness after swelling (mm)	Increase in thickness (%)
A	0.64	1.15	122.98
B	0.64	1.2175	113.49
C	0.64	1.195	122.35
D	0.62	1.1275	112.09
E	0.62	1.085	112.30
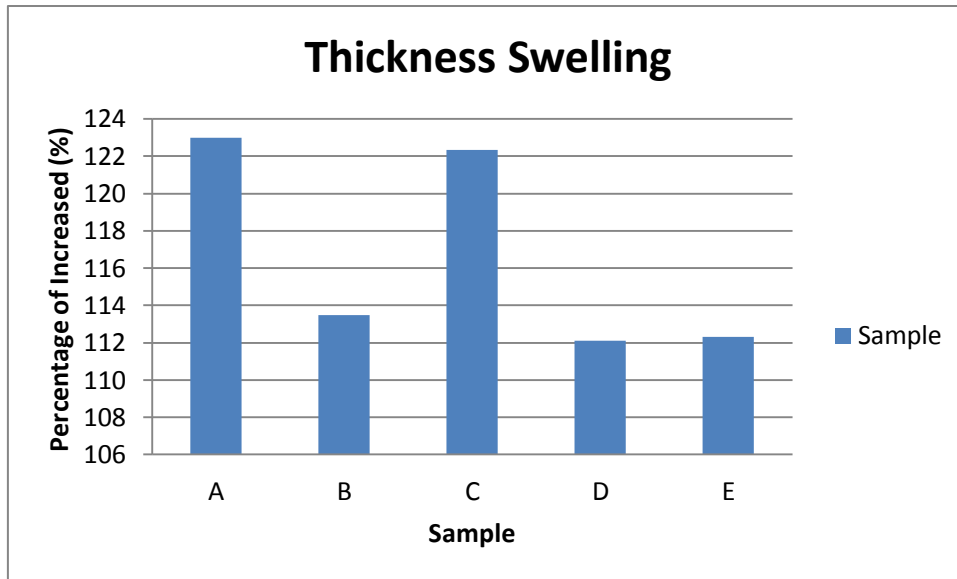
Figure 4.4: Thickness Swelling for 10% Modified Soy Flour with Lignin

Based on results in Table and Figure 4.4, it can be seen that sample D had an increment of 112% while sample A had the largest increment which was 122%. All the samples increased more than 100%. On average, the increased in thickness was around 116%.

4.3   Results for Internal Bonding

Table 4.5: Internal Bonding for 5% Modified Soy Flour

Sample	Density (kg/m³)	Internal Bonding (MPa)
A	720.4862513	0.5405
B	759.0152472	0.5679
C	710.3892694	0.3566
D	736.1783593	0.4893
E	763.2346877	0.4365

Based on the result tabulated, internal bonding for sample A was 0.5679 MPa while sample C had the lowest which was 0.3566 MPa. On average, the internal bonding for 5% modified soy flour was about 0.48 MPa.

Table 4.6: Internal Bonding for 10% Modified Soy Flour

Sample	Density (kg/m^3)	Internal Bonding (MPa)
A	660.3422518	0.6822
B	662.413936	0.7263
C	757.4850012	0.7325
D	733.6393931	0.6991
E	645.8135668	0.7195

Based on the result tabulated, wood sample B had the highest internal bonding of 0.7325 MPa while sample A had the lowest which was 0.6822 MPa. On average, the internal bonding was about 0.71 MPa.

Table 4.7: Internal Bonding for 20% Modified Soy Flour

Sample	Density (kg/m^3)	Internal Bonding (MPa)
A	613.5603527	0.4785
B	585.2093303	0.4046
C	505.5970965	0.4115
D	632.7235233	0.4106
E	676.8444993	0.4846

Based on the result tabulated, wood sample E had the largest internal bond which was 0.4846 MPa while sample B had the lowest of 0.4046 MPa. On average, the internal bond for this concentration was about 0.44 MPa.

Table 4.8: Internal Bonding for 10% Modified Soy Flour with Lignin

Sample	Density (kg/m^3)	Internal Bonding (MPa)
A	523.7974759	0.6940
B	654.0987628	0.7227
C	693.6320656	0.6741
D	543.0763761	0.6246
E	752.9046094	0.6987

Based on the results tabulated in Table 4.8, wood sample B had the largest internal bond which was 0.7227 MPa while sample D had the lowest internal bond of 0.6246 MPa. On average, the internal bond was around 0.68 MPa.

4.4   Results for Modulus of Elasticity and Modulus of Rupture

Table 4.9: MOE and MOR for 5% Modified Soy Flour

Sample	Density (kg/m^3)	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)
A	682.3885896	61768.07	21.520
B	609.70964	62467.83	25.528
C	593.5296493	92053.65	32.310
D	674.3517613	54186.41	23.510
E	738.929569	82765.93	26.843
F	680.0664954	85888.89	27.076
G	588.597561	71103.60	20.407
H	731.2163698	52970.24	16.162

Based on Table 4.9, the highest MOE and MOR were shown by sample C which had MOE of 92053.65 and 32.31 MPa respectively. The lowest was 52790.24 and 16.162 MPa respectively as shown by sample H. The average MOE and MOR was about 80457.80 and 27.62 MPa respectively.

Table 4.10: MOE and MOR for 10% Modified Soy Flour

Sample	Density (kg/m^3)	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)
A	725.4122915	80494.62	30.082
B	661.8096285	71244.56	26.976
C	715.5306567	79977.36	32.719
D	669.5556641	49277.06	25.945
E	694.8852539	71493.06	26.021
F	711.6305444	69874.33	28.899
G	607.9434698	62580.04	24.940
H	757.7680628	104587.36	40.273

Based on Table 4.10, the highest MOE and MOR were shown by sample H with 104587.36 and 40.273 MPa respectively while the lowest was sample D for MOE with 49277.06 MPa and sample G for MOR with 24.94 MPa. On average, 10% modified soy flour had MOE and MOR of 84218.34 MPa and MOR of 33.69 MPa.

Table 4.11: MOE and MOR for 20% Modified Soy Flour

Sample	Density (kg/m^3)	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)
A	607.4664846	92577.20	20.626
B	624.5330487	65772.15	25.141
C	750.7735149	92858.95	26.257
D	671.1014851	54772.81	28.523
E	597.0459414	52891.59	18.780
F	694.7544643	85383.46	18.174
G	644.9004975	65376.84	26.994
H	600.232348	72756.65	32.641

Based on Table 4.11, the highest MOE was shown by sample A with 92577.2 MPa while the lowest was sample E with 52891.59 MPa. For MOR, sample H was the highest with 32.641 MPa while the lowest was sample F with 18.174 MPa. On average, 20% modified soy flour had MOE and MOR of 83198.52 MPa and MOR of 28.162 MPa.

Table 4.12: MOE and MOR for 10% Modified Soy Flour with Lignin

Sample	Density (kg/m^3)	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)
A	607.4664846	79119.53	32.464
B	709.1419319	89208.29	30.727
C	719.3507607	87279.95	30.867
D	711.3574171	79923.45	32.547
E	670.206342	70486.87	28.748
F	722.0319104	87134.08	25.598
G	663.4305979	71908.89	34.954
H	707.0878467	84744.65	28.583

Based on Table 4.12, the highest MOE was shown by sample B with 89208.29 MPa while the lowest was sample E with 70486.87 MPa. For MOR, sample G was the highest with 34.954 MPa while the lowest was sample H with 28.583 MPa. On average, 10% modified soy flour with lignin had MOE and MOR of 92929.39 MPa and MOR of 34.927 MPa.

4.5 Comparison and Discussion

4.5.1 Thickness Swelling
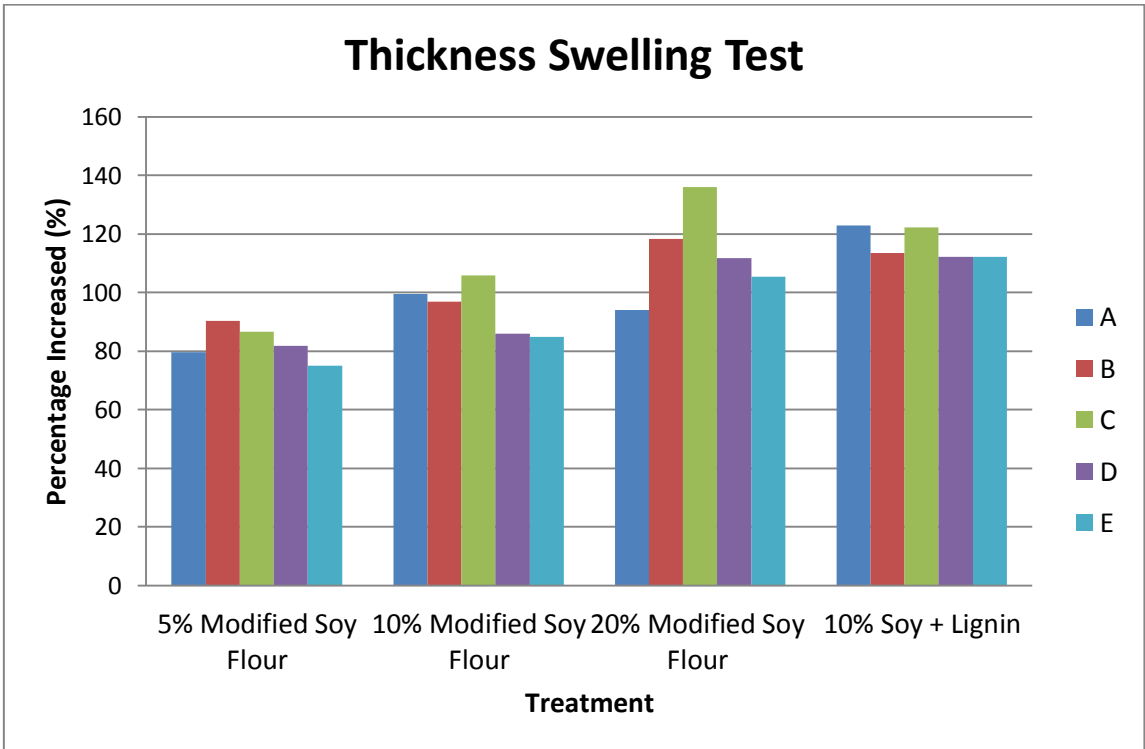
Figure 4.5: Thickness Swelling Comparison

After 24 h immersion in water, the MDF had a sponge-like characteristic. Figure 4.5 showed the result for thickness swelling test for all the different adhesives. It can be seen that 5% modified soy flour had the greatest resistance to water as compared to the 10% and 20%. Even after adding lignin, the water resistance for the MDF did not improve but increased to more than 100% in its thickness. The MDF was easily penetrated by water as the adhesive properties were weak. The reason for the large increment in thickness could be due to the presence of water soluble molecules or components and hydrophilic groups which were still present at large amount in the soy protein. According to Sauter (1996), the presence of large

44

percentage of hydrogen bonds which could form bonds with water thus increasing the thickness swelling. In addition, it could also be the weak bonding strength and rich hydroxyl groups caused by high fiber and carbohydrate content.

4.5.2   Mechanical Testing
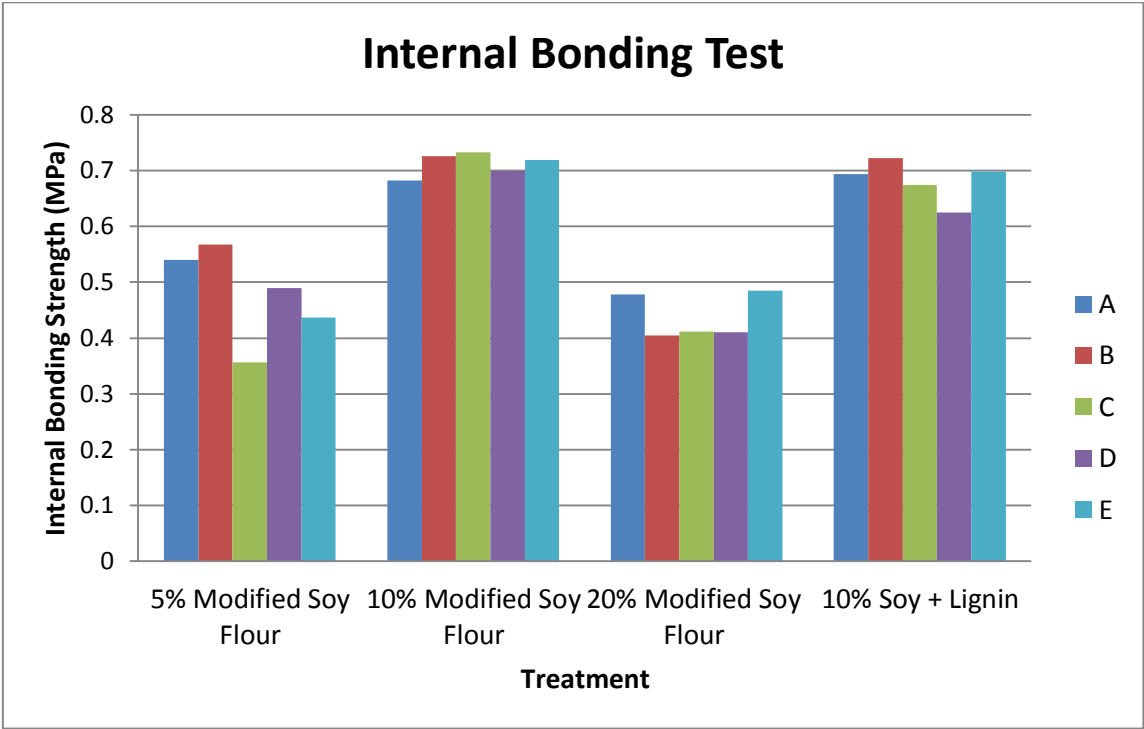
Figure 4.6: Internal Bonding Test Comparison

Figure 4.6 showed the result for the IB of MDF for different types of adhesives. 20% modified soy flour had the worse internal bond at an average of 0.44 MPa. 10% MSF showed results that were near the ASTM standard with an average of 0.71 MPa. After adding lignin, the results were almost similar but slightly less than 10% MSF at 0.68 MPa. The ASTM D 1037 minimum requirement for IB is at least 0.75 MPa. As for UF boards, the IB is around 0.80 MPa (Nasir et al., 2013).
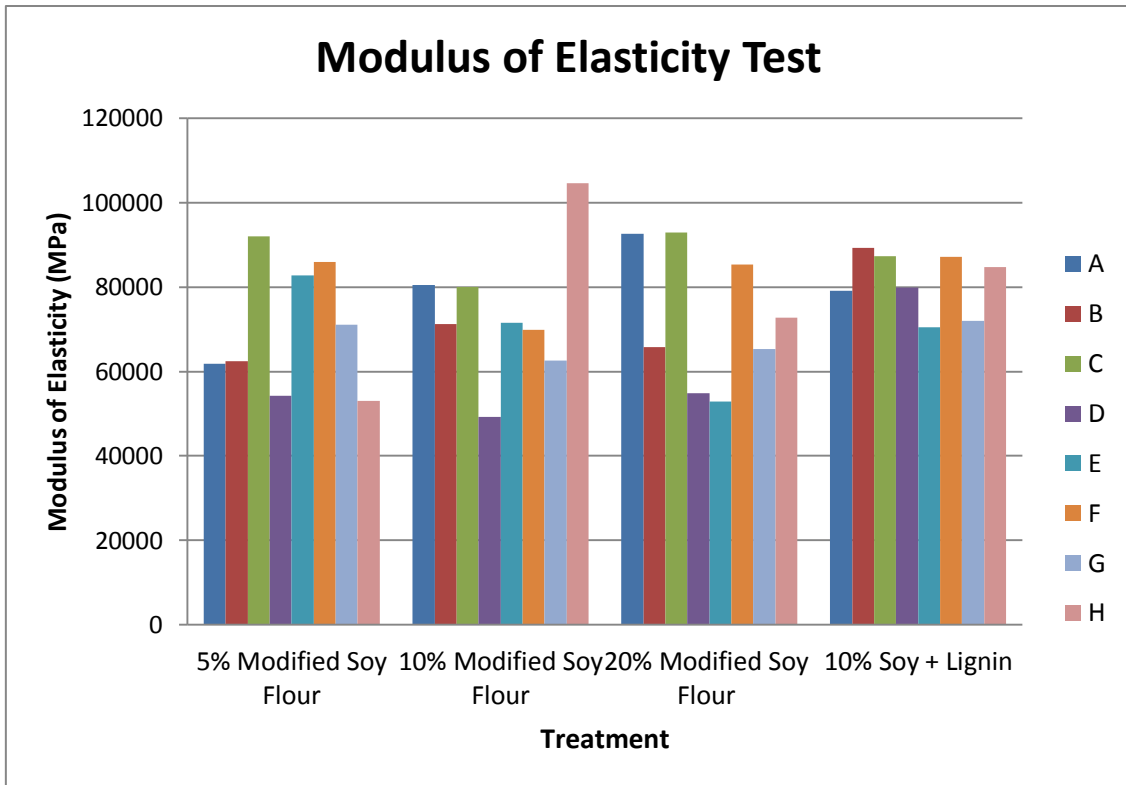
Figure 4.7: Modulus of Elasticity Test Comparison

Figure 4.7 showed the results for MOE of MDF made using different adhesives. 5% and 20% modified soy flour had the worse MOE with average of 80457.80 and 83198.52 MPa respectively. As compared to 10% MSF, MSF-lignin produced MDF of better quality as it had a higher MOE of 92929.39 MPa as compared to the 10% MSF with 84218.34 MPa. These values were higher than the commercial UF boards which has an MOE of 5200 MPa (Nasir et al., 2013).
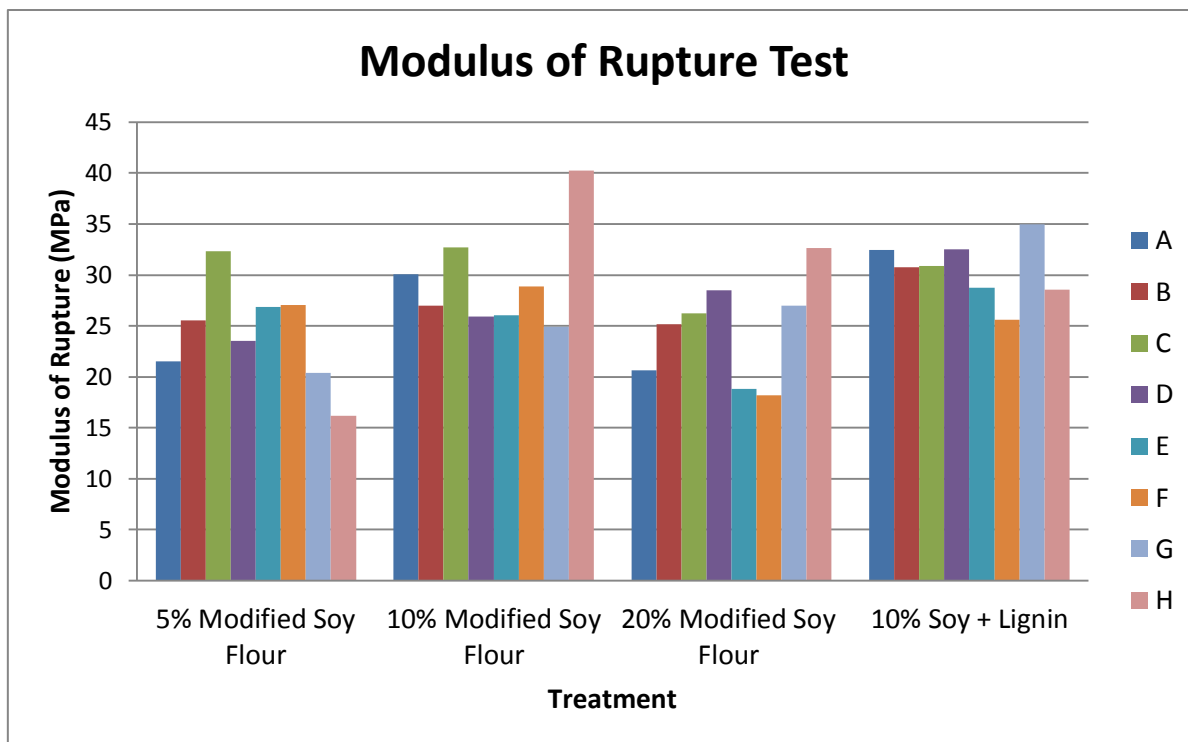
Figure 4.8: Modulus of Rupture Test Comparison

In Figure 4.8, among the three concentrations, 5% MSF had the lowest MOR with an average of 27.62 MPa while 10% had MOR of 33.69 MPa. After adding lignin, the MOR increased slightly, giving a value of 34.927 MPa. Although it was having a lower MOR than the commercial UF boards of 48 MPa (Nasir er al., 2013), at least it was near the 35 MPa which is the passing standard according to ASTM D 1037.

Basically, the strength of adhesive depends on its ability to interact with the wood fibre. Before giving treatments to the soy flour, the polar and non-polar groups are not exposed because of the internal bonding from the Van der Waals forces. That changes when treatment is being done on soy flour, its structure changes by unfolding the molecules thus exposing the polar and apolar groups of the protein making them available to interact. These interaction increases the adhesive strength (Lambuth, 1977).

Another explanation could be the presence of secondary structure of the protein. When soy flour is dispersed and unfolded in a solution, the unfolded section contains a secondary structure which helps in increasing the contact and surface area with the wood fibre. This allows interaction to increase the bonding strength (Huang & Sun, 2000). As for the addition of lignin, the reason behind the high tensile strength and compressive strength could be due to

cross-linking happening. In order for lignin to be used as a type of adhesive, the methyl group present in lignin was removed which is known as demethylation (Ibrahim et al., 2011). The laccase enzyme added to the lignin caused the process of demethylation thus activating the lignin to cross-linked with molecules consisting of the nucleophilic group. Another explanation could be that the lignin degrades partially or extensively thus releasing monomeric subunits that are able to react with other active groups (Filley et al., 2002).

Besides that, another property that could have an effect on the adhesive properties is viscosity. According to Sun and Bian (1999), when protein unfolds more, the viscosity will decrease. When the adhesive has low viscosity, the adhesive will not have any difficulty during spraying to spread uniformly onto the wood fibre thus causing the adhesion property to increasing.

4.5.3 Fourier Transform Infrared
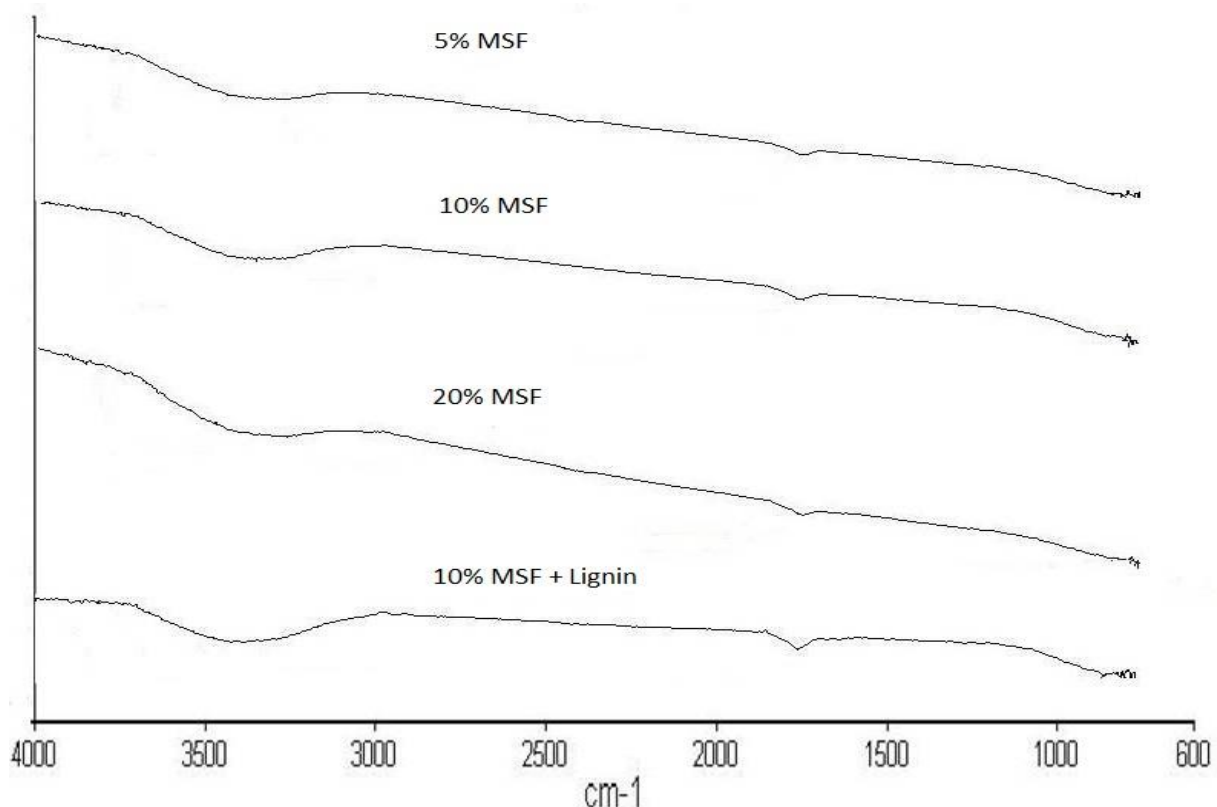
Figure 4.9: FTIR Spectrum for Different Adhesives

Figure 4.9 shows the spectra for 5%, 10% and 20% MSF and 10% MSF with lignin. A wide transmittance band could be observed in all the adhesive ranging from 3600 cm^{-1} to 3300 cm^{-1} resulting from the hydrogen bonding from certain functional group. A strong absorption peak can be observed at 3200 cm^{-1} to 3300 cm^{-1} for all three modified soy flour of different concentrations. It represents the strong O-H group of carboxylic group. The peak's intensity can be seen increasing with increasing concentration. Thus, hydrogen bonding also increased. Also, a sharp peak can be observed from 1637 cm^{-1} to 1640 cm^{-1} indicating the presents of bending primary amide group, N-H$_2$. The presence of O-H and N-H groups increased the chance for a potential intermolecular hydrogen bonding with the hydroxyl groups (Lin et al., 2012).

After adding lignin to the MSF, a sharp peak was observed at 3353.06 cm^{-1} representing the phenol and alcohol hydrogen bonded O-H stretch group conforming the presence of hydrogen bonding. A peak was also observed at 1646.74 cm^{-1} representing alkenes's C=C symmetric bond and amide's C=O stretching bond. It is clear that there is a difference in the structure of the MSF and MSF-lignin. There is a possibility that the amide C=O bonds partially hydrolyzed to form –COOH (Lin et al., 2012).

4.5.4 Differential Scanning Calorimetry

Table 4.13: Results obtained through DSC

Adhesive	Peak Temperature (°C)	Enthalpy of Reaction (ΔH) (J/g)
5% Modified Soy flour	100.19	983.9
10% Modified Soy flour	97.82	1287
20% Modified Soy flour	97.61	1359
10% Modified Soy+Lignin	104.14	1475
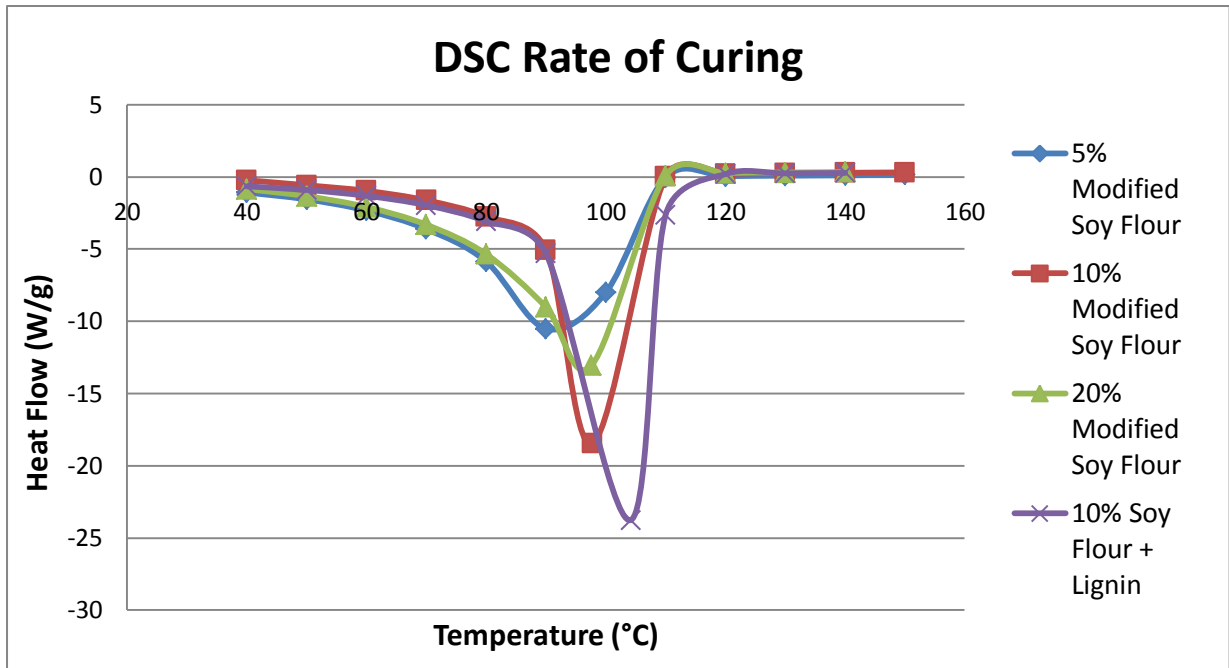
Figure 4.10: DSC Thermograph

Based on Table 4.13 and Figure 4.9, the enthalpy of reaction increased with increasing soy flour concentration. This indicates that more heat was released and generated. When more heat is being released, the rate of heat transfer also increased. This allows the transfer of heat to every parts of the MDF during hot pressing. 10% MSF-lignin showed the highest enthalpy of reaction and also peak temperature. As compared to UF which has an enthalpy of 354.3 J/g, using bio-adhesive instead of UF would not only protect the environment but it can also save energy. As mentioned, heat transfer increased thus the pressing time could be reduced as heat could be transferred to all parts of the MDF at a faster rate.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

For mechanical testing properties, 10% MSF had an IB of 0.71 MPa while 10% MSF-lignin was 0.68 MPa. As compared to 10% MSF, MSF-lignin produced MDF of better quality as MSF-lignin had a higher MOE of 92929.39 MPa as compared to the 10% MSF with 84218.34 MPa. 10% MSF had an MOR of 33.69 MPa which was slightly less than 10% MSF-lignin which had a value of 34.93 MPa. They were all near the passing requirement by ASTM. As for thickness swelling, the MDF made using 5% MSF, 10% MSF, 20% MSF adhesives all had increment of at least 70% to 113%. Even after adding lignin, it did not improve either as it was having thickness swelling of 116%.

Thus, it can be concluded that adhesive made using soy protein and lignin were able to produce MDF of good quality in terms of mechanical properties. As for water resistant properties, the result produced could not accomplish the objective for the water resistant property as did not show promising result.

5.2   Future Work

In order to improve the current result of study, few recommendation could be taken into consideration. Among them, it is recommended to make MSF-lignin adhesive of different weight/volume percent to compare with the 10% MSF-lignin. This is to determine the best w/v percent of the MSF-lignin which can produce the best adhesion properties. Apart from that, it is recommended to study the structure of soy protein to get a better understanding on its interaction with water and how addition of other chemicals or enzymes could change the structure of soy protein. It could be that the hydrophilic part of the soy protein structure that is responsible for the water resistant properties. Therefore, it is advisable to look deeper into the soy protein structure.

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APPENDIX
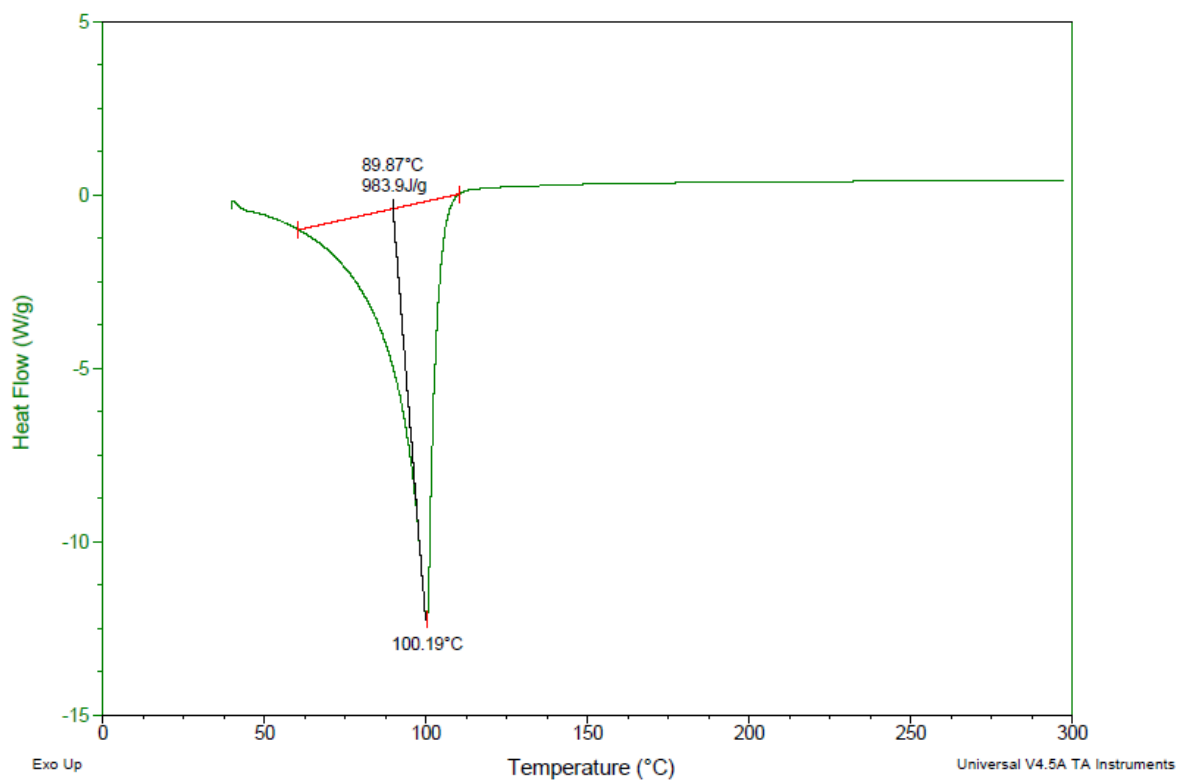
Figure A1: 5% MSF DSC Graph
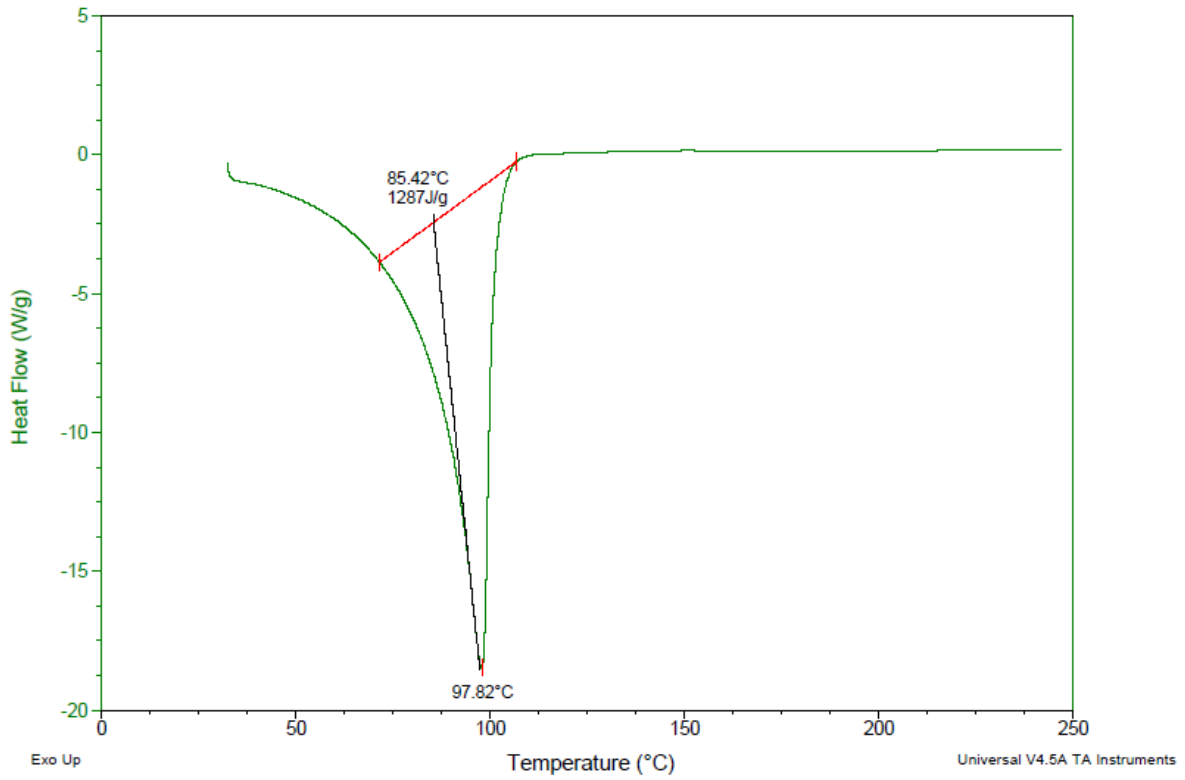
Figure A2: 10% MSF DSC Graph
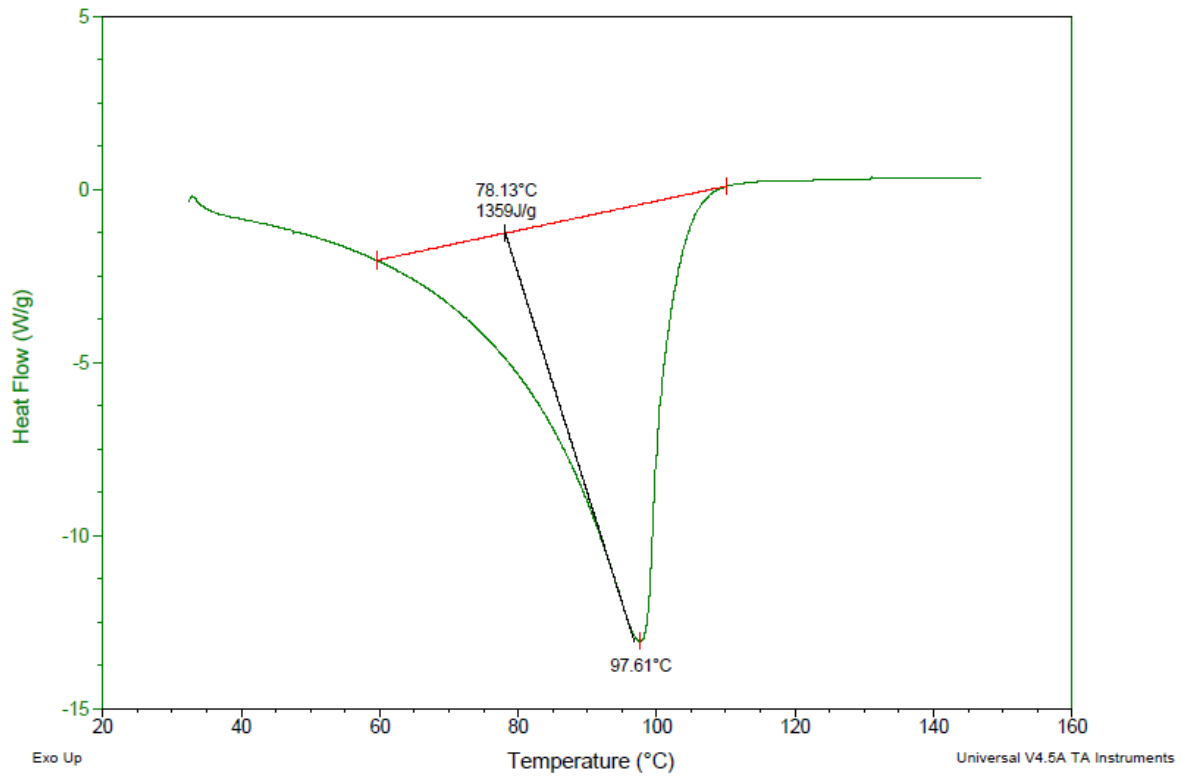
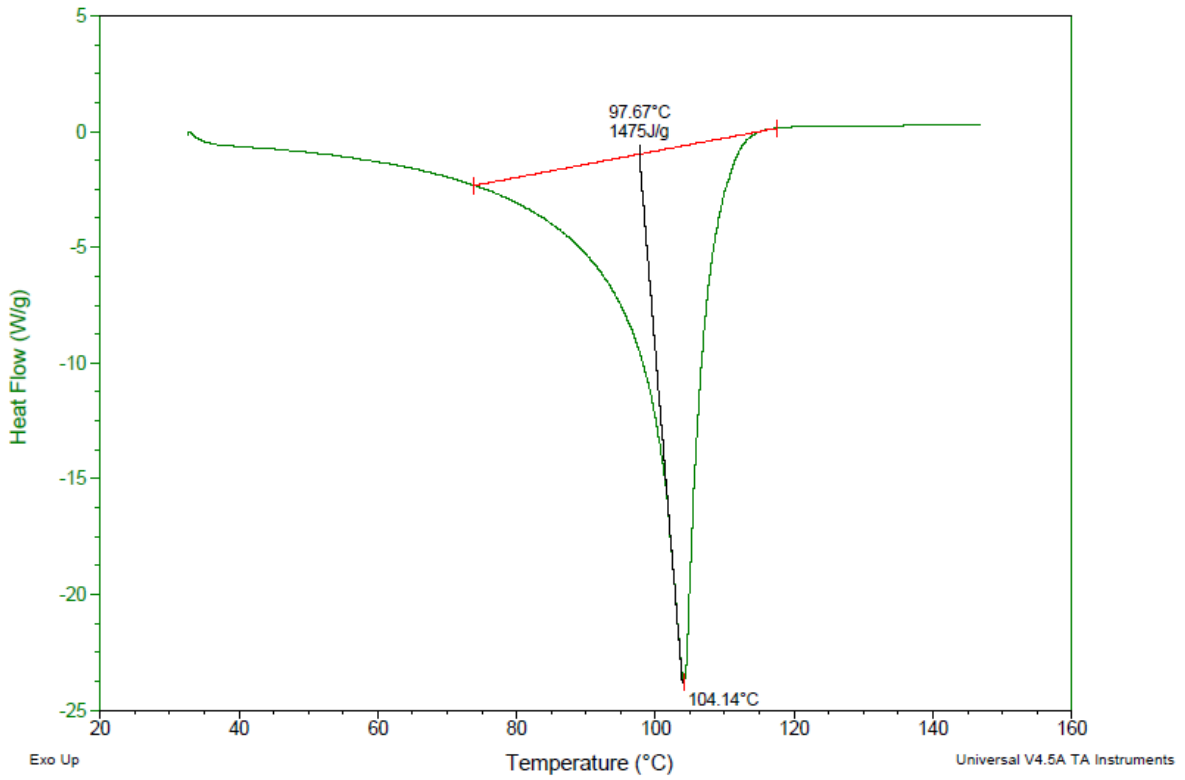**Figure A3: 20% MSF DSC Graph**

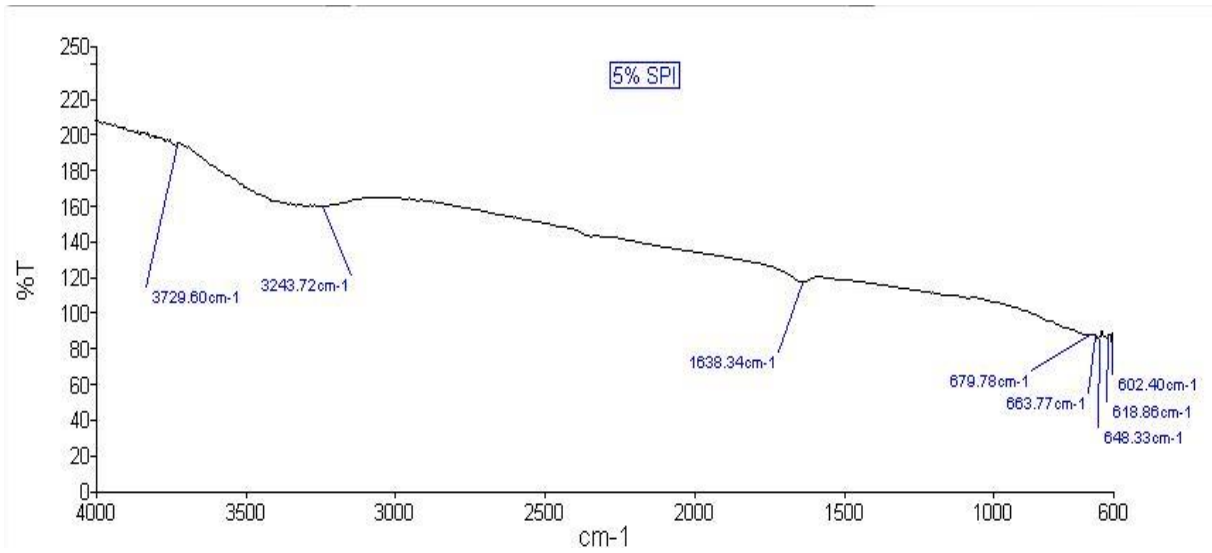**Figure A4: 10% MSF-Lignin DSC Graph**
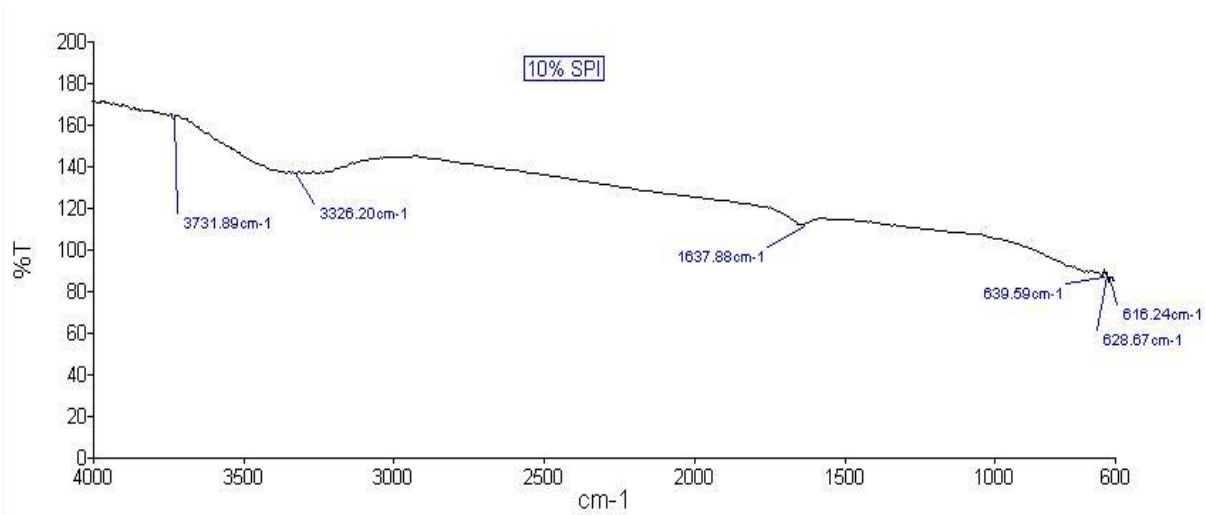

Figure A5: 5% MSF FTIR Graph

Figure A6: 10% MSF FTIR Graph
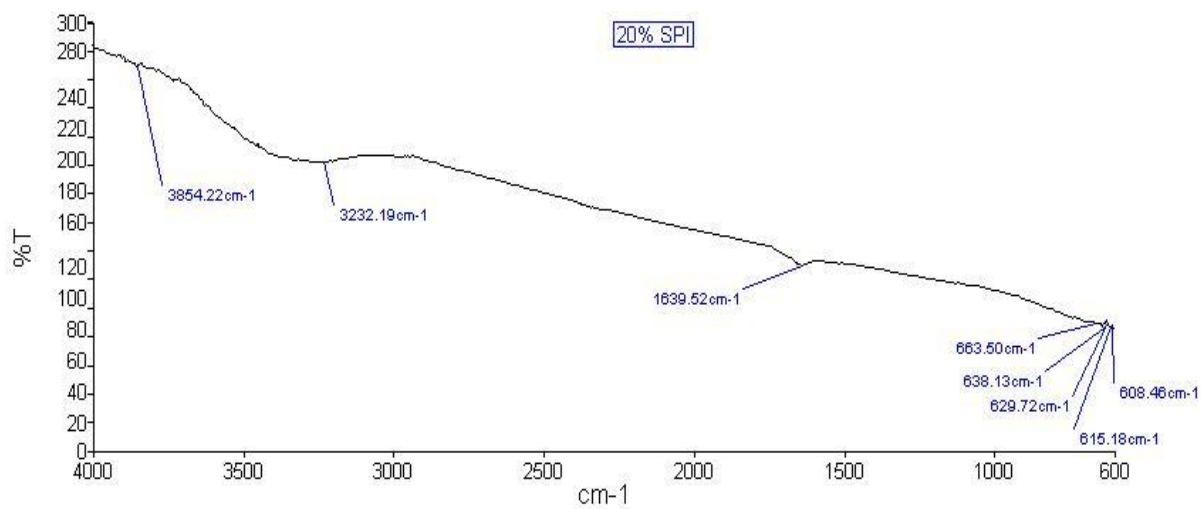

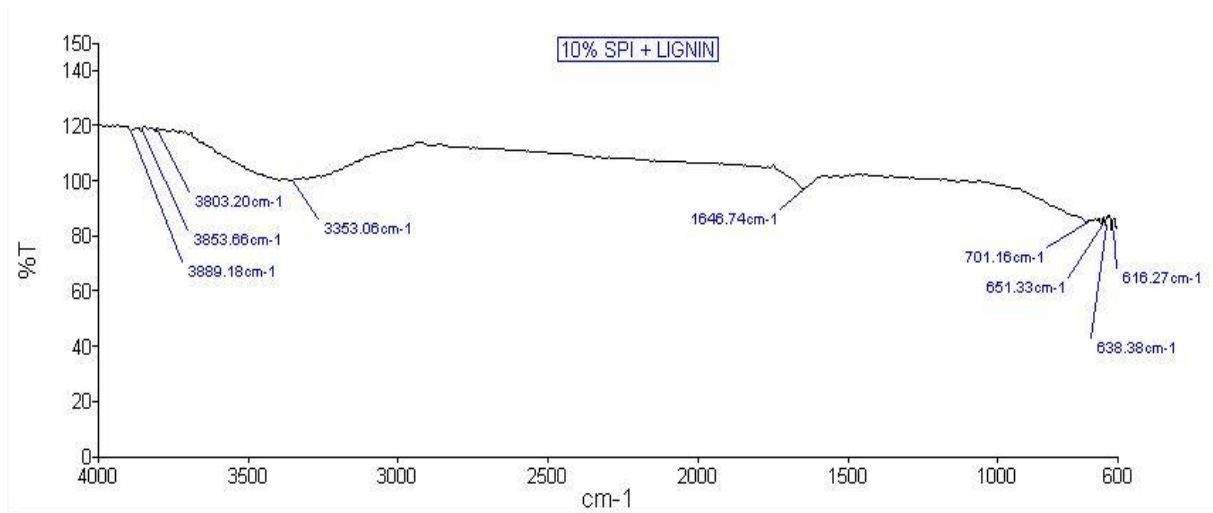**Figure A7: 20% MSF FTIR Graph**

Figure A8: 10% MSF-Lignin FTIR Graph
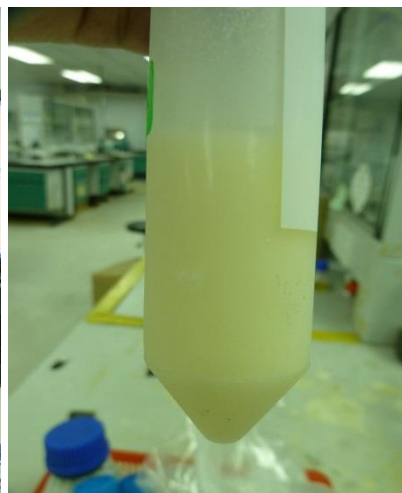

(a) Hot and cold molding press   (b) Mixer   (c) Universal Testing Machine
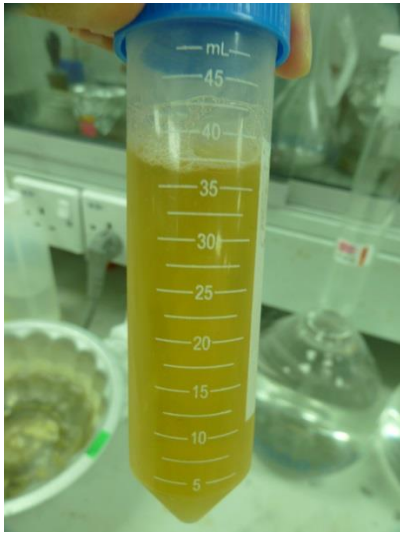

(d) DSC   (e) Modified soy protein   (f) Lignin

(g) Enzymatic hydrolase lignin

Figure A9: Pictures from research