

MECHANICAL PROPERTIES AND WATER RESISTANCE OF CELLULOSIC
FIBERBOARDS WITH SOYBEAN PROTEIN BASED ADHESIVES

by

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Abstract

Large amount of fiberboard are used for packaging applications every year, which generate a large amount of solid wastes causing environmental pollution if these packaging materials are not recycled. Also, a large amount of wood are needed for making fiberboard, which is limited resource in the earth. Reducing the weight of fiberboard and recycling the fiberboard materials are two methods to save quantities of wood fiber in fiberboard manufacture, which benefit the environment and economy. Besides, most adhesives used for producing the fiberboard contain environmental hazardous chemicals. It is necessary to develop new technology to produce cellulosic fiberboards with environmental friendly bio-based adhesives.

The soybean is an agricultural product, and its resource is abundant. Soybean protein is a bio- material that offers an alternative to the existing synthetic adhesives to reduce petroleum dependence of the U.S. energy strategy. The newly developed soy-based adhesive is also competitive in cost. Material cost based on food-grade soybean protein is around 20 cents/Lb. The cost of commercial PF resin is about 14 ~ 17 cents/Lb. Price of hot-melt adhesive for fiberboard is around \$6/Lb.

In this study, soybean protein was modified with sodium dodecyl sulfate as an adhesive for two bio-based fiberboards products, medium density fiberboard by dry processing and light weight cardboard by wet processing. The mechanical and water soaking properties of these cellulosic fiberboards were stronger than or as same as commercial solid fiberboard. This research suggests that these cellulosic fiberboards with modified soybean protein based adhesive have great potential as alternative to current commercial fiberboard.

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CHAPTER 1 - INTRODUCTION

Literature Review

Status of Fiberboard Manufacture and Wood Adhesives

Wood products are integral components of our lives for building, furniture, paper industry, shipping containers and so on. With the needed amount of wood rapidly being increased, the quality of wood is decreasing and the wood price is significantly increasing due to the total amount of trees in the earth being reduced, and older/bigger trees being protected. Therefore, the material of fiberboard products enlarges to all Cellulosic fibers.

Fiberboard is a panel product manufactured from lignocellulosic fibers combined with a synthetic resin or other suitable binder (National Particleboard Association 1980). It is primarily used for industrial applications such as furniture, building material, shipping container, and laminate flooring. It has excellent properties including high strength, easy of machining, good weathering properties, the ability to be made from a wide variety of fibrous products, as well as comparatively cheap price. Traditionally, the density range of MDF is about 40 to 50 lb/ft³; the thickness of MDF (dry processing) is from 3/8 to 1 inch (Suchsland and Woodson 1986); and the strength properties of MDF are in a wide range required for different end-uses (Table 1.1, National Standard for MDF, A208.2). With the development of related science and technology, the density of

fiberboard is gradually decreased with high strength, and lots of light weight fiberboard is used in our lives, especially in package.

The fiberboard could be made by either wet or dry process. Both of them employ formaldehyde-based resins as the adhesive, such as phenol-formaldehyde resins (PF) and urea-formaldehyde resins (UF). There are at least three drawbacks by using formaldehyde-based resins. First, volatile organic compounds (VOCs) are generated from these processes and they last for a long time. The increasing concern about the effect of emissive VOCs, especially for formaldehyde, on human health has prompted a need for using more environment friendly adhesives. Second, PF and UF resins are made from petroleum-derived products (Composite Panel Association, Fifth Edition). The reserves of petroleum are naturally limited. Thirdly, they are usually cross-linked during processing. The cross-linked chemicals make it difficult or impossible for re-pulping the fiberboard during any recycle process. The wood composite industry would be greatly benefited from the development of formaldehyde-free adhesives made from renewable natural resources.

Research Status of Soybean Protein Adhesives in Fiberboard Processing

Soybean protein products were first utilized as adhesives for wood bonding in 1930's (Davidson 1929, Davidson and Laucks 1931). But their usage soon declined by the development of petroleum derived adhesives after War II, because there were several problems when soybean protein was used as the adhesive in wood industry, low moisture resistance, low adhesion strength, and short durability.

Economic and ecological pressures in the 1990's renewed the interest in the practical use of soybean protein products for wood adhesives. From 2001 to present, there have been 19 patents (Table 1.2, 1.3) about soybean protein adhesives in the wood industry. Scientists have made a lot of efforts at soybean protein adhesives; unfortunately, none of these patents can explicitly show the successful applications for the manufacture of cellulosic fiberboard using formaldehyde-free soybean protein based adhesives.

Scientists also investigated how they are applied of soybean protein adhesive in fiberboard manufacture. Kuo et al (1998) applied soybean-based adhesives in making fiberboard (HDF and MDF). They used the dry manufacturing method by spraying synthetic resins and soybean protein to prepare HDF and MDF; the results indicated that because of its high molecular weight, soybean protein isolates (SPI) could not be formulated into sprayable adhesives at the neutral pH for dry-formed fiberboard. Although SPI could be formulated with sodium hydroxide into sprayable 30 percent solid aqueous dispersions, the fiber furnish had very high moisture content and had to be dried before pressing; also, the resultant fiberboards had no moisture resistance. However, their farther research result indicated that SPI could be formulated into sprayable adhesives. Ye, Julson, Kuo and Myers (2005) manufactured hard density fiberboard (HDF) using soybean-based adhesives successfully. The soybean-based adhesive (consisting of 70% defatted soybean flour and 30% phenol-formaldehyde with a pH of 7) was formulated in the Food Science Laboratory and the Wood Chemistry Laboratory at Iowa State University.

The mechanical properties and water resistance of HDF made using soybean-based adhesives were better than corresponding treatments with urea-formaldehyde resin, and

significant effects were detected between 6 and 9% adhesives level for all properties. In their studies, the curing temperature and the pressing time for soybean-based adhesive were higher and longer than UF (138°C, 1min); the hot pressing process might play an important role in affecting the mechanical properties of the fiberboards. Also, their data (unpublished) from another project showed that the soybean-based adhesive in producing MDF is not as good as UF resins. It is necessary to further investigate the effects of the hot pressing conditions and optimize the process.

X. Susan Sun and her group have done lots of studies in this area, and they mainly force on the relationships of adhesion strength of fiberboard with different modification methods of soybean protein. Soybean protein isolate (SPI) (Zhong and Sun 2001), SDS-modified SPI adhesives (Zhong and Sun 2001) and guanidine hydrochloride (GuHCL)-modified SPI (Zhong and Sun 2002) were applied to the fiberboard. The apparent viscosity of GuHCL-modified SPI adhesives (1 M) was 10.65 mPa s at 26 °C at a shear rate of 100.44 S⁻¹ which was close to unmodified SPI adhesives (12.04 mPa s) while clearly lower than the SDS-SPI. The adhesion strength of fiberboard with GuHCL-modified SPI increased with increasing GuHCL concentration to 1.0 M, and then decreased with increasing Gulch concentration higher than 1.0 M. It is markedly different with SDS-modified SPI. Viscosity is related to molecule weight. With GuHCL modification, soybean protein molecules are unfolded from their compact and ordered globular conformation to a loose and random conformation; their molecule weights keep the same or at least are not obviously increased, and the viscosity is the same as unmodified soybean protein. When the concentration is about 1.0 M, SPI molecules are

ideally interact with GuHCL. The GuHCL induces decreasing adhesion strength when its concentration is higher than 1.0 M.

Most of other studies in this area were dedicated to develop soybean protein modifying methods and tried to use in non-fiberboard products, such as particleboard and plywood. Soybean protein could be modified by acid, alkali and salt. Lodha and Netravali (2005) used Phytigel, a poly- carboxylic acid based modifier, to incorporate with SPI. SPI and Phytigel were blended to form an interpenetrating network-like cross-linked complex. The highest tensile strength of 60MPa and Young's modulus of about 900MPa was obtained at 40% (w/w of SPI powder) Phytigel content and 12.5%glycerol (PM-SPI-4 resin). This is a 10-fold increase in both fracture stress and Young's modulus over the control SPI resin. Netravali et al (2004) modified SPI in different ways including the use of stearic acid in near neutral pH, Phytigel, and degradation of SPI, SA-SPI and PM-SPI resin in a compost environment. Liu and Li's study (2002) demonstrated imparting soybean protein with a functional group found in the marine adhesive protein could convert soybean protein to a strong and water – resistant wood adhesive. Choi et al. (2006) developed a biodegradable hot–melt adhesive based on poly- ϵ -caprolactone (PCL) and soybean protein isolate; the thermal and mechanical properties of the blends changed with increasing SPI concentration. When SPI was less than 20% (i.e. <20g/100g), it was miscible with PCL and produced homogenous blend without impairing the lap shear strength. Wescott and Frihart (2004) used soybean-based resin for oriented strandboard, a copolymer of soybean and phenol formaldehyde.

Objectives

The objectives of this research were using soybean protein adhesives to develop medium density bio-based fiberboards, as well as thinning boards with wood fiber, which had high mechanical and water soaking properties could be used for packaging or construction. This research also studied the relationship between process parameters and fiberboard properties.

Table 1-1 Medium Density Fiberboard (MDF) Property Requirement^a

Product class ^b		Nominal thickness (mm)	MOR (MPa)	MOE (MPa)	Internal Bond (MPa)	Screw-holding(N)	
						Face	Edge
Interior MDF	HD		34.5	3450	0.75	1555	1335
	MH	≤21	24.0	2400	0.60	1445	1110
		>21	24.0	2400	0.55	1335	1000
	LD		14.0	1400	0.30	780	670
Exterior MDF	MD-Exterior	≤21	34.5	3450	0.90	1445	1110
	adhesive	>21	31.0	3100	0.70	1335	1000

^aFrom NPA (1994). Metric property values shall be primary in determining product performance requirements.

^bMD-Exterior adhesive panels shall maintain at least 50% of listed MOR after ASTM D1037-1991, accelerated aging (3.3.4). HD = density >800 kg/m³ (>50 lb/ft³), MD = density 640 to 800 kg/m³ (40 to 50 lb/ft³), LD = density <640 kg/m³ (<40 lb/ft³).

Note: from Youngquist.1999. Wood – based Composites and Panel Products, in: Wood handbook — Wood as an engineering material. Gen. Tech. Rep. FPL–GTR–113. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory

Table 1-2 US Patent Application on Soybean Protein Based Adhesive in Wood Industry
(Issued)

Patent No.	Title	Inventor	Composites	Usage	Year
6790271	Soybean protein based adhesive containing a vegetable oil derivative	Thames et al	A mixture of soybean protein isolate, a polyol plasticizer and a vegetable oil derivative	Particle -boards	2004
6497760	Modified soybean protein adhesives	Sun; Xiuzhi; Bian; Ke	Soybean protein, water, urea, sodium dodecylbenzene sulfonate, sodium dodecyl sulfate, and guanidine hydrochloride		2004
6518387	Soybean-based adhesive resins and composite products utilizing such adhesives	Kuo et al	soybean flour and a cross-linking agent		2003
6306997					2001
6365650	Heat and radio frequency-curable two - pack soybean protein-based polyurethane adhesive compositions	Chen, Gang- Fung; Day, David E. Jones, David	Isocyanate-terminated prepolymer and hydrolyzed soybean protein having a pH of at least about 9	Wood	2002
6231985					2001

Note: from USPTO PATENT FULL-TEXT AND IMAGE DATABASE

Table 1-3 Current US Patent application on Soybean Protein Based Adhesive in Wood Industry

Application No.	Title	Inventor	Composites	Usage
20050282988 20040089418	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Li, Kaichang	Soybean protein; at least one amine, amide, imine, imide, or nitrogen-containing heterocyclic functional group	
20050277733 20050222358	Water-resistant vegetable protein adhesive dispersion compositions	Wescott et al.	Soybean flour, functionalized with methylol groups with one or more reactive comonomers, and preparing an acidic dispersion of the adhesive.	wood
20050272892	Hydrolyzates of soybeans or other soybean products as components of thermosetting resins	Hse, Chung Yun Lin, Liangzhen	converting processed soybean into phenol-formaldehyde-like, water resistant thermosetting resin adhesives	structural composite panel
20050234156	Soybean protein based adhesive and particleboard	Thames et al	Aqueous mixture of soybean protein, zinc sulfate heptahydrate, calcium oxide, sodium benzoate, pine oil, wax emulsion and non-sulfonated kraft lignin.	Particle-boards and other composites
20050166796	Adhesives from modified <i>soybean</i> protein	Sun et al	a protein portion and modifying ingredient portion selected from the group consisting of carboxyl -containing compounds, aldehyde -containing compounds, epoxy group-containing compounds	
20050070635	Wood composites bonded with protein-modified urea-formaldehyde resin adhesive	Breyer et al	A urea-formaldehyde resin modified with a protein	particleboard
20050070186	Urea-formaldehyde binder composition and process	Shoemaker, Kelly ; et al	urea-formaldehyde resin modified with a source of <i>soybean</i> protein	Binder for preparing fiber mats
20040173306	Particleboard and method for forming a particleboard	Thames, Shelby F., et al	the binder includes soybean protein isolate, a plasticizer such as glycerol and a vegetable oil derivative such as maleinized methyl ester of tung oil	Particleboard
20040037906	Modified protein adhesives and lignocellulosic composites made from the adhesives	Li, Kaichang; Liu, Yuan	Additional phenolic hydroxyl functional groups, amine functional groups, and/or thiol functional groups into the soybean protein structure.	
20030148084	Vegetable protein adhesive compositions	Trocino, Frank S. SR	Copolymerizing hydrolyzed vegetable protein that has been functionalized with methylol groups and one or more co-monomers also having methylol functional groups	

Note: from USPTO PATENT FULL-TEXT AND IMAGE DATABASE

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CHAPTER 2 - MECHANICAL AND WATER SOAKING PROPERTIES OF MEDIUM DENSITY FIBERBOARD WITH WOOD FIBER AND SOYBEAN PROTEIN ADHESIVE¹

Abstract

Soybean protein is a renewable and abundant material that offers an alternative to formaldehyde-based resins. In this study, soybean protein was modified with sodium dodecyl sulfate as an adhesive for wood fiber medium density fiberboard (MDF) preparation. Second-order response surface regression models were used to study the effects and interactions of initial moisture content (IMC) of coated wood fiber, press time and temperature on mechanical and water soaking properties of MDF. Results showed that IMC of coated fiber was the dominant influencing factor. Mechanical and soaking properties improved as IMC increased and reached their highest point at an IMC of 35%. Press time and temperature also had a significant effect on mechanical and water soaking properties of MDF. Second-order regression results showed that there were strong relationships between mechanical and soaking properties of MDF and processing parameters. Properties of MDF made using soybean protein adhesive are similar to those of commercial board.

Introduction

Medium density fiberboard (MDF) is primarily used for industrial applications such as furniture, building material, and laminate flooring because of its good mechanical and

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economical aspects—is usually high in strength, easy to machine, and has good weathering properties (Suchsland and Woodson, 1986). Formaldehyde-based adhesives are currently used for MDF manufacture. Two major drawbacks of using formaldehyde-based resins are 1) they contain volatile organic compounds harmful to human health and 2) petroleum feedstocks for producing formaldehyde are limited. Soybean protein, however, is an inexpensive and renewable material. Soybean protein adhesives were first developed in the 1920s but were replaced by petroleum-based adhesives after World War II because soybean protein had relatively low bonding strength and less water resistance (Kumar et al., 2002). Recently, research interest in modifying soybean protein as an adhesive to improve bonding strength and water resistance has increased. Native soybean proteins have a highly ordered global structure with hydrophilic groups exposed outside and hydrophobic groups buried inside. When the internal bonds are broken by chemical modification, protein molecules unfold, promoting adhesion potential of the protein complex and making reactive groups available to interact with cellulosic materials (Mo et al., 2004). Alkaline (Kalapathy et al., 1995), urea (Sun and Bian, 1999), guanidine hydrochloride (Huang and Sun, 2000b), sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (Huang and Sun, 2000a), polyamide-epichlorohydrin (Zhong et al., 2007), etherification by ethanol and HCL solution (Wang et al., 2006), Phytigel (Lodha and Netravali, 2005), and stearic acid (Netravali, 2003) have been used to modify soybean protein and improve the properties of bonding strength and water resistance. Huang and Sun (2000a) showed that 1% SDS modification had significantly enhanced adhesive strength as well as water resistance.

Soybean protein adhesives have been used for wood board preparation such as cardboard (Zhong et al., 2001a), oriented strandboard (Wescott and Frihart, 2004), wheat straw particleboard (Mo et al., 2001, 2003; Cheng et al., 2004), and low density particleboard from wheat straw and corn pith (Wang and Sun, 2002). Little information is available in wood fiberboard bonded by soybean protein adhesives, particularly MDF. Kuo et al. (1998) prepared wood fiberboards that had no moisture resistance. Ye et al. (2005) stated that the hot press process might play an important role in fiberboard preparation in terms of mechanical properties. The objective of this work was to determine the effects of processing parameters on mechanical and water soaking properties of wood fiber MDF with soybean protein adhesive.

Materials and Methods

Materials

Defatted soybean flour with 4.6% moisture content was purchased from Cargill Inc. (Minneapolis, MN). Southern yellow pine wood fiber (length of 2 mm to 5 mm, diameter of 25 μm to 70 μm) with about 10% moisture content was provided by the fiberboard division of Georgia-Pacific Co. (Holly Hill, SC). Sodium hydroxide, hydrochloric acid, and SDS from Sigma Chemical Co. (St. Louis, MO) were used.

Preparation of Soybean Protein Adhesive

Soybean protein was extracted from defatted soybean flour following the procedure described by Huang and Sun (2000b). The soybean flour contained 88% protein (dry basis)

with 90% of particles passing through a 150 μm sieve opening. Soybean protein (64.5 g) was gradually added to 1% SDS solution (365.5 g) with stirring. The slurry was stirred for 3 h at room temperature before coating onto wood fiber.

MDF Panel Preparation

Wood fibers (300 g) were coated with 430 g of the modified soybean protein slurry in a rotary blender (Patterson-Kelly Co., East Stroudsburg, PA) for 12 min, then the fiber was dried with an aeration dryer at room temperature to adjust the initial moisture content (IMC) of the coated fiber. The IMC of the coated fiber was determined with the air oven method at 130 °C for 1 h. Coated fibers with different IMC (52 g, dry basis) were manually loaded into a single fiber mat using a 152.4 mm x 152.4 mm aluminum mold. Then, the coated fibers were pressed into fiberboard using a Hot-Press (Model 3890 Auto “M”, Carver Inc, Wabash, IN) at force of 116.6 KN. A programmed hot-pressing schedule was used to control the press time and temperature. In this process, the aluminum mold was equipped with stops so that a constant gap was always achieved to control the thickness of the board. The final thickness of the fiberboard was about 3.2 mm. The fiberboard was placed in a constant humidity chamber with 50% relative humidity at 23 °C for 2 days for further analysis.

Property Characterization

The density of each fiberboard panel was obtained by dividing the fiberboard mass (wet basis) by its volume. Average bulk density was 0.74 g/cm³. Each MDF panel was cut into five pieces of 25.4 mm x 25.4 mm specimens and four pieces of 25.4 mm x 127 mm rectangular testing specimens for evaluation (Fig. 2-1).

Mechanical Properties

Mechanical properties were determined following ASTM standard method D1037-99 (American Society for Testing and Materials, 2000) using an Instron testing machine (Model 4466, Canton, MA). Tensile strength (TSH) was obtained by tensioning the specimen (25.4 mm x 127 mm) at a crosshead speed of 4 mm/min. Internal bonding strength (IB) was measured by pulling the specimen (25.4 mm x 25.4 mm) apart in the cross section direction at a crosshead speed of 0.5 mm/min; both side surfaces of the specimen panel were mounted onto the testing accessory with Speed Bond #1 glue (Prime Resins Inc., Conyers, GA). Modulus of rupture (MOR) and modulus of elasticity (MOE) of the fiberboard (25.4 mm x 127 mm) were obtained by performing the three-point flex test at a crosshead speed of 3 mm/min.

Water Soaking Properties

Thickness swell (TS), linear expansion (LE) and water absorption (WA) were measured according to ASTM standard method D1037-99 (American Society for Testing and Materials, 2000). The 25.4 mm x 127 mm specimens were soaked in water for 24 ± 1 h at room temperature. Thickness, length and weight were measured before and immediately after soaking. The dimensional size and weight measured before and after soaking were used to calculate TS, LE and WA, which were expressed as percentages of the data after soaking to data before soaking. Wet MOR (W-MOR) and wet MOE (W-MOE) after soaking were measured using the same methods described in the mechanical properties section.

Microscope Images

The microstructures of the fracture surface of MDF were observed with scanning electron microscopy (SEM) (Hitachi S – 3500N, Hitachi Science Systems, Ltd., Ibaraki, Japan). The specimens were first mounted on aluminum stubs, and then fracture surfaces were coated with a mixture of 60% gold particles and 40% palladium with a sputter coater (Desk II sputter/etch unit, Denton Vacuum, Moorestown, NJ) before observation.

Experimental Design

Response surface methodology (RSM) was used to study the influence of IMC of coated fiber, press time (PT), and press temperature (PTT) on properties of MDF. The second order model used in this research is:

$$Y = a_0 + a_1X_{IMC} + a_2X_{PT} + a_3X_{PTT} + a_{11}X_{IMC}^2 + a_{22}X_{PT}^2 + a_{33}X_{PTT}^2 + a_{12}X_{IMC}X_{PT} + a_{13}X_{IMC}X_{PTT} + a_{23}X_{PT}X_{PTT} \quad (1)$$

Where a is constant, X represents all the variables, and the subscribed acronym of the X is the variable name: IMC = initial moisture content of the coated fiber (%), PT = press time (min), PTT = press temperature ($^{\circ}$ C), and Y represents the response variables including tensile strength (TSH) in MPa, modulus of rupture (MOR) in MPa, modulus of elasticity (MOE) in MPa, internal bonding (IB) in MPa, thickness swell (TS) in %, linear extension (LE) in %, water absorption (WA) in %, and wet MOR (W-MOR) and wet MOE (W-MOE) in MPa, respectively.

A central composite design was applied as an approach to analyze the effects of three variables on mechanical and water soaking properties. Each of the five levels of a variable is scaled separately to -1.68, -1, 0, 1, and 1.68.

According to preliminary experiments and previous research results (Mo et al., 1999, 2003), the zero level of IMC was defined as 22.5%, press time as 10 min, and press temperature as 170 °C. The hot–pressing variables and experimental design are shown in Table 2-1. All data reported were means of five replications. The standard error and coefficients of determination obtained were based on the six replicated runs conducted at center points (zero level). Statistical software (Minitab of Minitab Inc.) was used to analyze experimental data.

Results and Discussion

Processing variables and their interactions on mechanical and water soaking properties of MDF were empirically expressed with statistical equations. After adjusting the model (Eq. 1) using significance test and lack-of-fit values, all variables in the final models were required or significant at the level of 0.1. These equations and their R^2 values and standard deviation (SD) values were shown in Table 2-2. The models fit experimental data very well. Almost all R^2 were higher than 0.9, except for LE ($R^2 = 0.74$), which was caused by board density effect on the LE (Ganev et al., 2005). These models were then used to predict mechanical and water soaking properties as functions of the three processing variables. To show the main effect and interaction of processing parameters on mechanical and water soaking properties, curves were plotted for each responsive property as a function of variables.

Effect of IMC on Mechanical and Water Soaking Properties

For hot press processing, if the IMC of coated fiber approaches 40%, the board can blow and crack in the middle layer because of the higher water vapor pressure produced (Mo et al., 2001); this also was observed in our preliminary experiments. To avoid board cracking, we designed the IMC of coated fiber to be lower than 36%. The regression models (2 - 10) indicated that the influence of IMC on mechanical and water soaking properties was the most significant, except for IB (Table 2-2). In the variable range of this experiment, as IMC increased, TSH, MOR and MOE increased significantly, and IB also increased from 0 to 0.44 MPa (Fig. 2-2a); W-MOR and W-MOE followed the same traces as MOR and MOE (Fig. 2b). The water soaking properties of MDF improved as IMC of soybean protein adhesive coated fiber increased (Fig. 2-2c). All mechanical and water soaking properties reached the optimum values at 35% IMC (Fig. 2-2).

In the soybean protein system, water acts as a plasticizer, which reduces protein exothermic temperature (Mo et al., 1999) and improves mobility of soybean protein polypeptide chains, which might then interact easily with other polymers. Compared with the round and curly shape of fracture structure with low IMC (10%; Fig. 2-3a), SEM images showed, after hot press, the shape of fiber with high IMC (35%; Fig. 2-3b) became to flat and straight, and the adhesion between coated fibers with high IMC was significantly stronger than coated fibers with low IMC. Moisture was a promoter for the adhesion behavior of soybean adhesive and fiber in hot press processing and led to better entanglements at higher IMC.

Effect of PTT and PT on Mechanical and Water Soaking Properties

The denaturation temperature of SDS-modified soybean protein is 73 °C and 90°C caused by conglycinin (7S) and glycinin (11S) components, respectively. During thermal denaturation, the ordered structure of soybean protein is changed to a relatively loose and random structure (Zhong et al., 2001b), which improves interactions between protein adhesive and fiber. However, when the temperature of soybean protein increases to 200 °C, which is above the protein exothermic temperature (192 °C), the protein becomes overheated and degraded, resulting in some small fragments and voids in the protein phase (Mo et al., 1999). In this study, soybean protein demonstrated strong adhesive strength in the temperature range between denaturation and exothermic point. Considering that a temperature gradient existed from the outer to the inner surface of the panel during hot processing, in this study we used a press temperature from 130 °C to 200 °C and press time from 1.6 min to 18 min. Optimum strength occurred at 35% IMC; therefore, the effects of press time and temperature on properties of MDF prepared with 35% IMC are discussed here.

In the temperature range between denaturation and exothermic point, press temperature and press time had significant effects on properties of MDF. In general, a long press time promoted the interaction between protein polymer and fiber surface and led to higher mechanical strength (Fig. 2-4). A longer press time not only allowed the water residues evaporated from the board, but also improved the mechanical strength. At a short press time (i.e., 2 min), water vapor could not completely evaporate to the surface of the panel but coagulated and assembled inside the panel, reducing mechanical and soaking properties.

No interactive effects of press time and temperature were observed on TSH (Fig. 2-4a), MOR (Fig. 2-4b) and MOE (Fig. 2-4c). TSH, MOR and MOE all increased as press time increased. However, TSH reached its highest value at a press temperature of about 180 °C and then leveled off in the press time range of 2 to 18 min (Fig. 2-4a). As mentioned previously, press temperature promoted soybean protein entanglements that enhanced adhesion strength. At press temperatures above 180 °C, protein became partially denatured, resulting in no increase in adhesion strength. We assumed that TSH would decrease at press temperatures above 200 °C. Press temperature had no significant effect on MOR (Fig. 2-4b) but had a negative proportional effect on MOE (Fig. 2-4c). As press temperature increased, adhesion strength was enhanced by the higher degree of entanglements of soybean proteins. The morphology of fiberboard at higher press temperatures is similar to that at higher moisture content as shown in Fig. 2-3b. The improved adhesion resulted in a tougher material. Because the MOE is the ratio of stress (σ) and strain (ϵ) before proportional limit, MOE could be different when the MOR remains the same. For example, as shown in Fig. 2-5, both samples (a) and (b) had 30% moisture content, but sample (a) was pressed at 190 °C for 5 min and sample (b) was pressed at 150 °C for 5 min. The area under the curve of sample (a) was bigger than that of sample (b), which means that sample (a) is tougher than sample (b). In this case, sample (b) should have larger MOE than sample (a). We observed similar trends for all other samples.

Press time and temperature had interactive effects on IB (Fig. 2-4d). At low temperature (i.e., 140 °C), IB increased as press time increased. At high temperature (i.e.,

200 °C), IB decreased as press time increased and then increased slowly at press times of about 12 min and beyond. At lower temperatures, a longer press time promoted soybean protein entanglements, leading to higher adhesion, which had morphology similar to that shown in Fig. 2-3b. In addition, water vapor pressure was lower at lower temperature, and water vapor could appropriately evaporate with a longer press time, which also resulted in higher IB. At higher temperatures, soybean protein became denatured at longer press times, decreasing adhesion. At press times of 12 min and beyond, vapor was completely evaporated; therefore, IB slightly increased.

Both wet strength (W-MOR and W-MOE) of the MDF proportionally increased as press time and temperature increased after 24 h of water soaking (Fig. 2-6). As discussed previously, longer press times and higher temperatures promoted protein molecular entanglements; this improved water resistance and, in turn, wet mechanical strength. Linear expansion was significantly reduced with press time and temperature (Fig. 2-7a) because the crosslink degree between soybean proteins and wood fibers was improved at longer press times and higher press temperatures. Thickness swell and water absorption of the MDF were not significantly affected by press time and temperature (Fig. 2-7b, c), respectively.

Optimum MDF Processing Parameters

Optimum processing parameter ranges for MDF were obtained using equations 2–10 derived from surface response experiments at 35% IMC with Minitab statistics software. The optimum operation zone was a narrow irregular shape with press temperature from

192 to 200 °C and press time from 13.0 to 14.5 min. The values of mechanical and water soaking properties predicted from the optimum zone are summarized in Table 2-3. To verify the predicted optimum point, MDF panels were prepared using the parameters from the optimum zone: IMC was 35%, press temperature was 195 °C and press time was 13 min. The experimental data of mechanical and water soaking properties of the MDF had good agreement with the predicted properties (Table 2-3), indicating these models can be used to predict the properties of MDF as functions of IMC, press time and temperature in the variable range tested in this research. Compared with the commercial MDF standard (ANSI A208.2-2002), MDF made with soybean protein adhesive has IB and MOR that are significantly stronger than Grade 210 and the same as Grade 230 (Table 2-4). The MDF with soybean protein adhesive has great potential as an alternative to current commercial board.

Conclusions

Processing parameters influenced mechanical and water soaking properties. The effect of IMC was significant because moisture was a promoter for the adhesion behavior of soybean protein adhesive and wood fiber. Press temperature and press time had effects on properties. In general, a long press time promoted the interaction between protein polymer and fiber surface leading to higher mechanical strength. Overall, MDF with wood fiber and soybean protein adhesive gave high mechanical and water soaking performance that was stronger than commercial fiberboard Grade 210 and similar to Grade 230. Replacing petroleum-based resin with soybean protein adhesive in MDF applications including

indoor construction and furniture would solve problems related to emission of toxic formaldehyde.

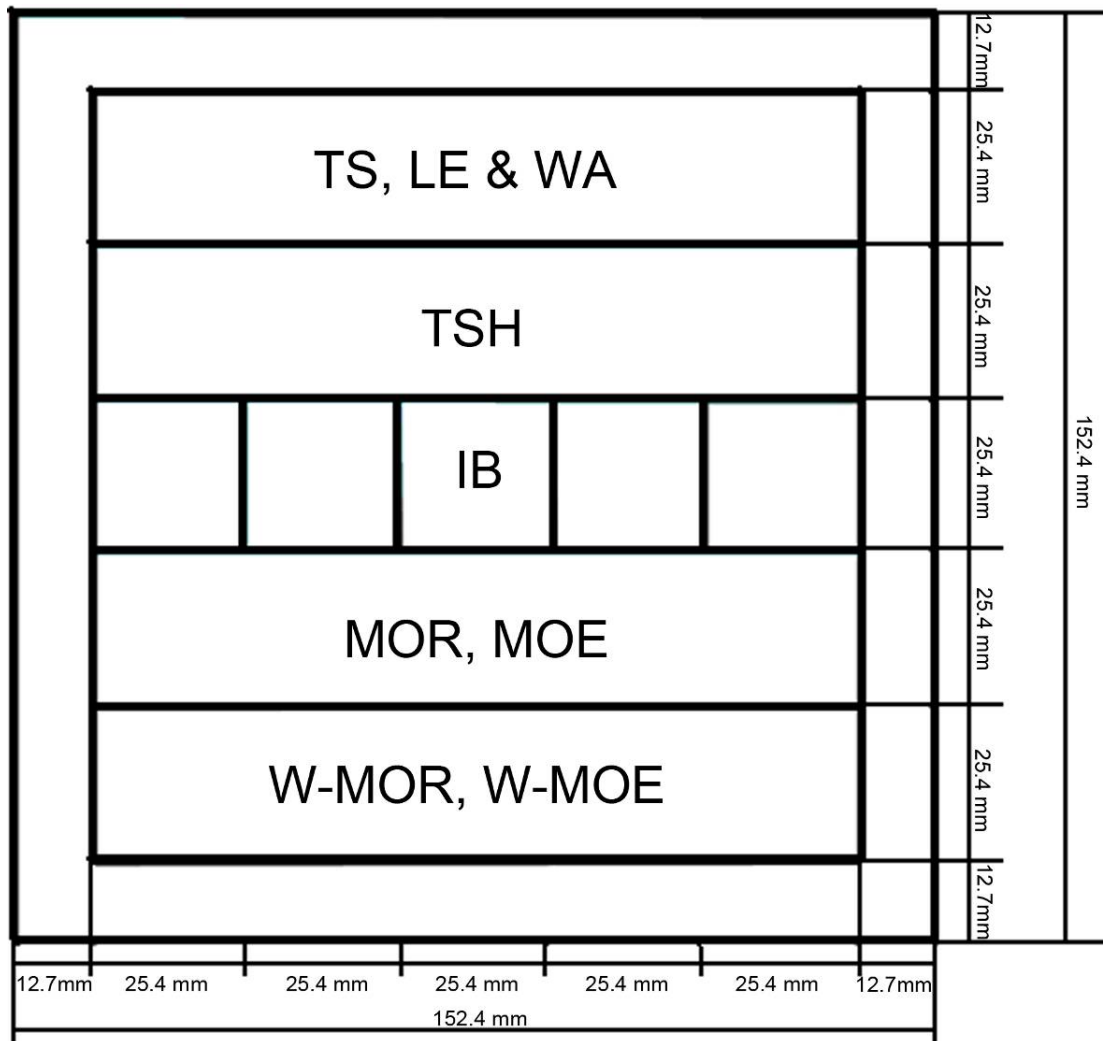


Figure 2-1 Dimensions of Cutting Method for Testing Specimens from a Medium Density Fiberboard Panel.

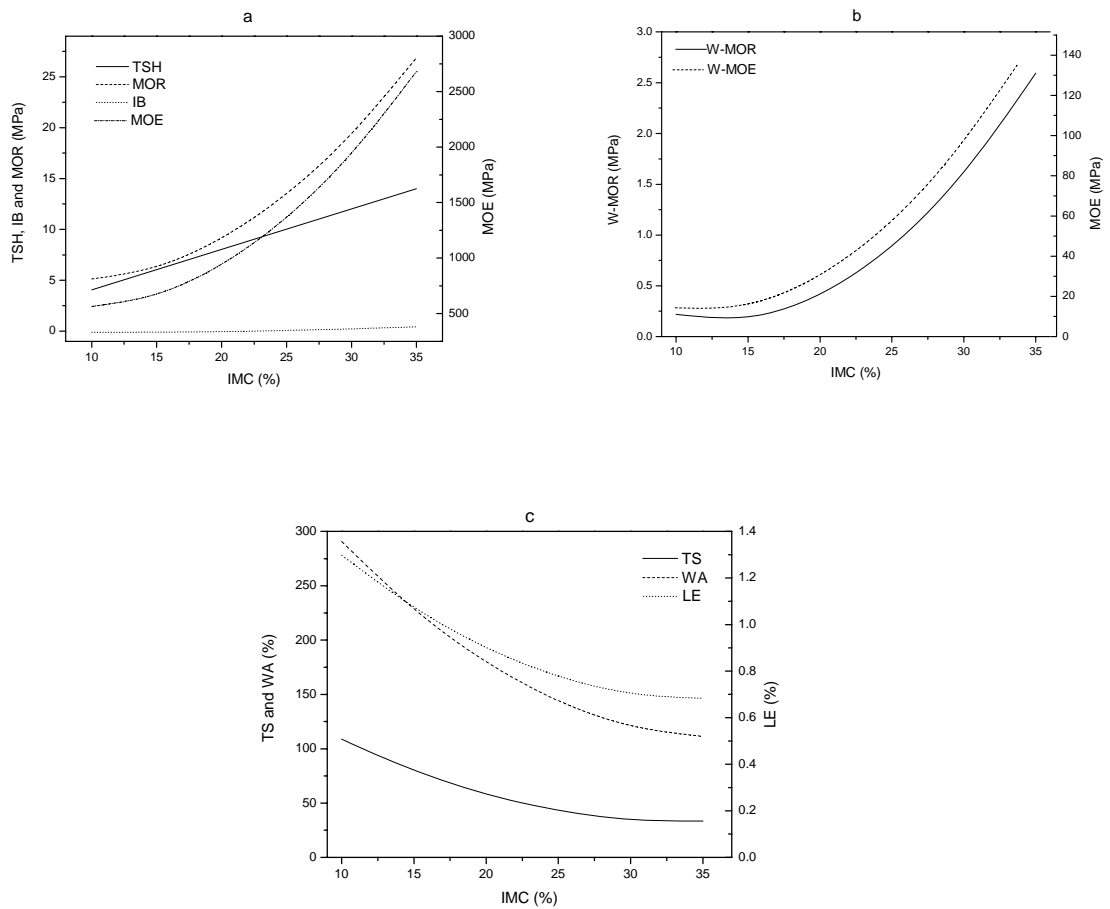
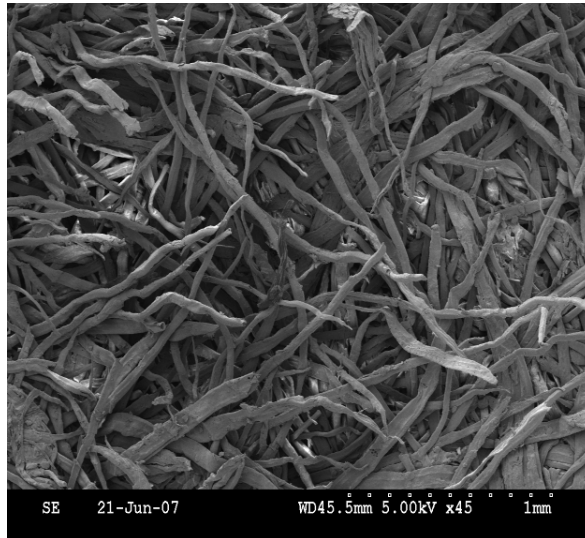


Figure 2-2 Initial Moisture Content of 1% SDS Modified Soybean Protein Adhesive Coated Wood Fiber With a) Tensile Strength (TSH), Internal Bonding Strength (IB), Modulus of rupture (MOR) and Modulus of Elasticity (MOE); b) Wet Modulus of Rupture (W-MOR) and Wet Modulus of Elasticity After 24 h Water Soaking (W-MOE); c) Linear Expansion (LE), Thickness Swell (TS) and Water Absorption (WA) of Wood Medium Density Fiberboard ($\rho = 0.74 \text{ g/cm}^3$), Made at 170 °C Press Temperature and 10 min Press Time

a



b



Figure 2-3 Scanning Electron Micrographs of the Fractured Surface of Wood Fiberboards.

Note: Pressed at 170 ° C for 10 min with a) 10% and b) 35% initial moisture content of coated wood fiber

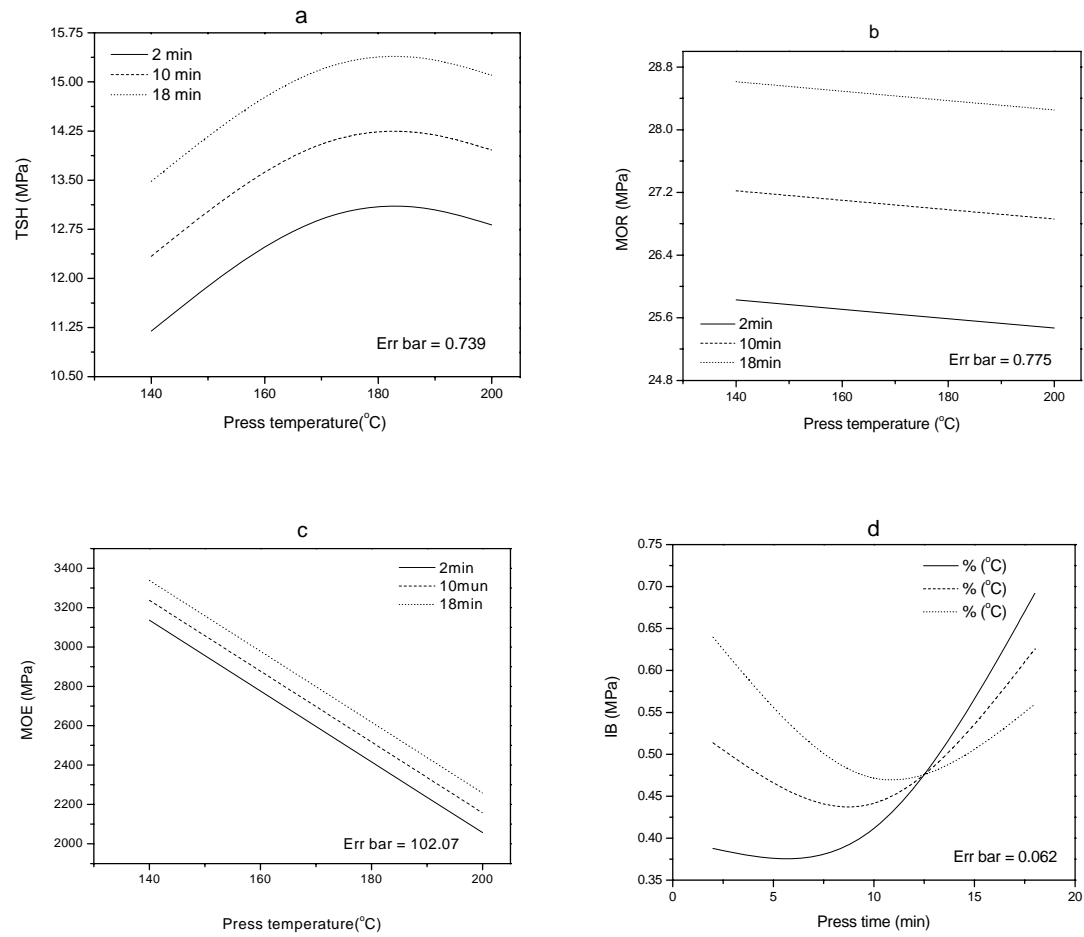


Figure 2-4 Interactive Effects of Press Time and Temperature on a) Tensile Strength (TSH), b) Modulus of Rupture (MOR), c) Modulus of Elasticity (MOE) and d) Internal Bonding Strength (IB) with 35% Initial Moisture Content of Coated Wood Fiber

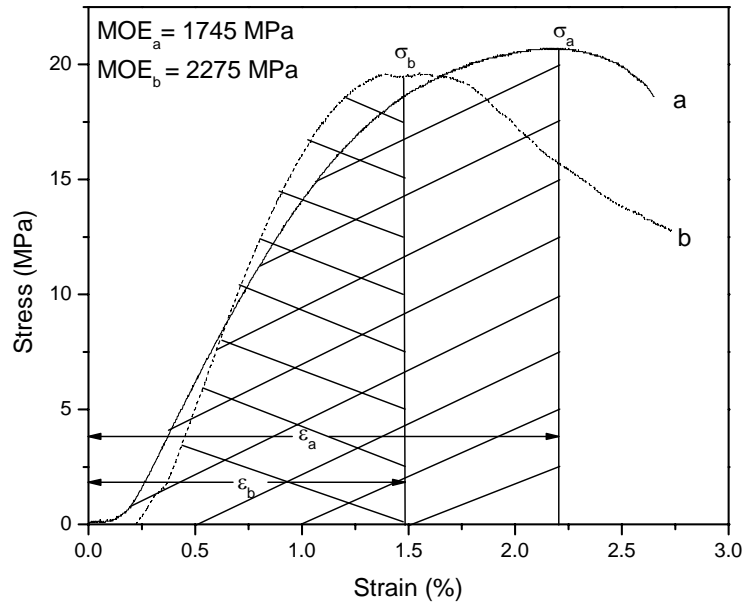


Figure 2-5 Stress–Strain Curves of Wood Fiberboards.
Recorded during three-point bending test of samples with 30% initial moisture content pressed at a) 190 °C and b) 150°C for 5 min.

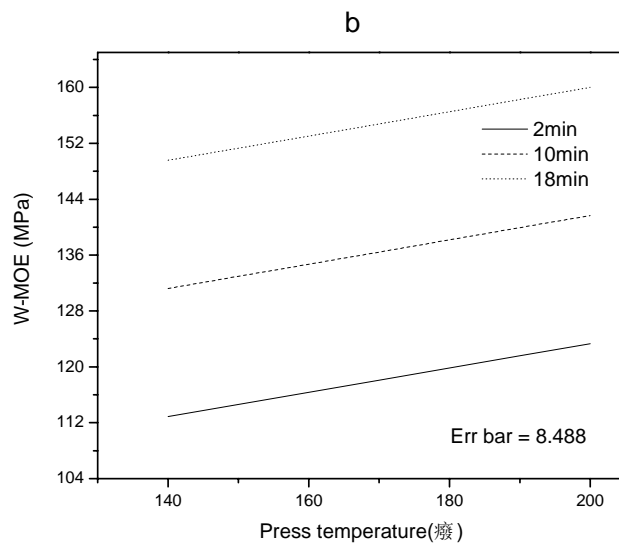
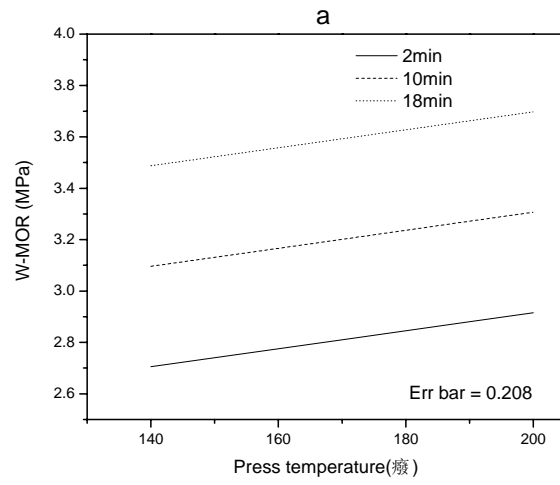


Figure 2-6 Interactive Effect of Press Time and Temperature on a) Wet Modulus of Rupture (W-MOR) and b) Wet Modulus of Elasticity (W-MOE) after 24 h Water Soaking with 35% Initial Moisture Content of Coated Wood Fiber

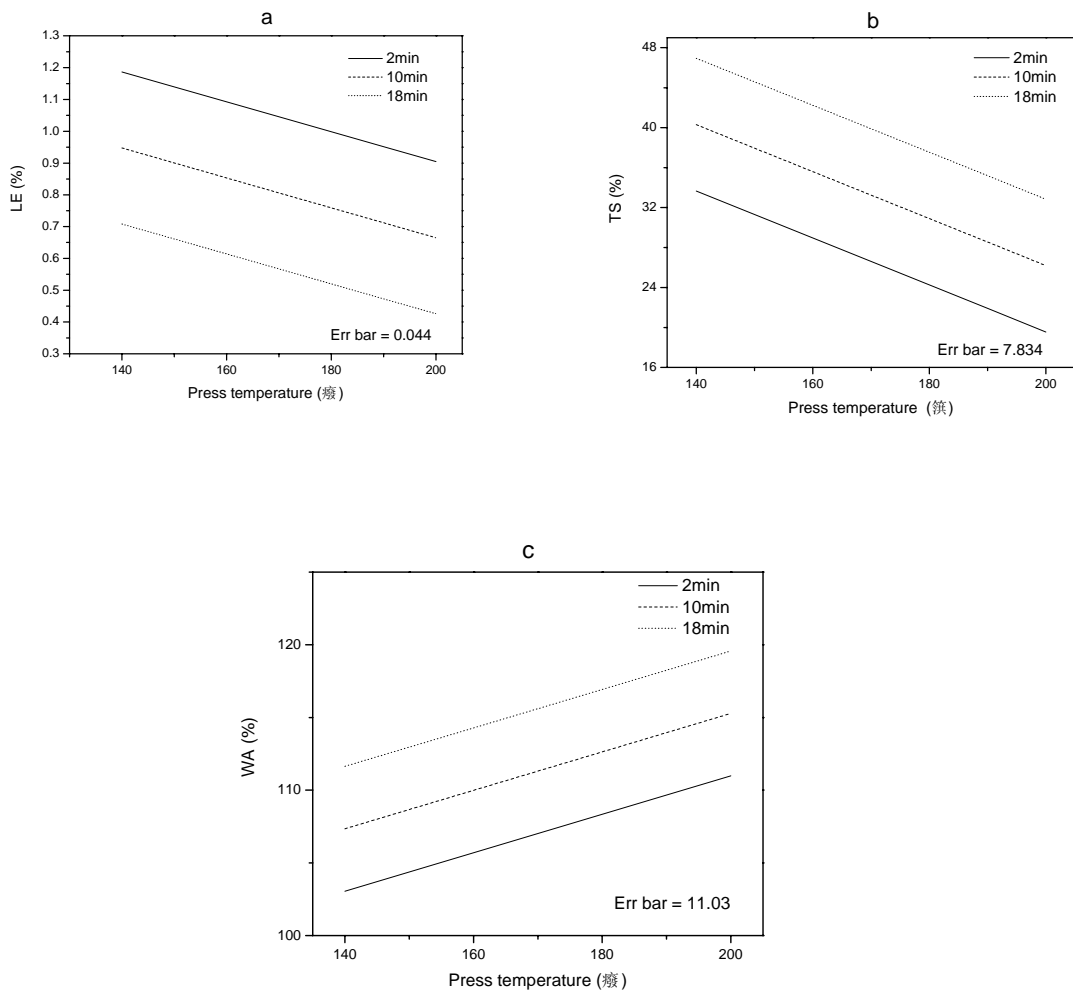


Figure 2-7 Interactive Effect of Press Time and Temperature on Dimension Stability.
a) Linear expansion (LE), b) Thickness swell (TS) and c) Water absorption after 24 h
water soaking with 35% initial moisture content of coated wood fiber

Table 2-1 Surface Response Experimental Design to Study the Effects of Processing Parameters on Mechanical and Water Soaking Properties of Medium Density Fiberboard. Processing Parameters Include Initial Moisture Content (IMC) of Wood fiber Coated with Soybean Protein Adhesives, Press Time (PT) and Press temperature (PTT)

Run Order	IMC (%)	Temperature (°C)	Time (min)	Density (g/cm ³)	TSH (MPa)	IB (MPa)	MOR (MPa)	MOE (MPa)	LE (%)	TS (%)	WA (%)	MOR-W (MPa)	MOE-W (MPa)
1	22.5	170.0	18.4	0.792	10.301	0.490	14.403	1532.92	0.703	47.037	150.473	1.307	67.333
2	30.0	190.0	15.0	0.722	10.985	0.577	15.495	1538.76	0.611	33.759	131.566	2.016	88.48
3	30.0	150.0	5.0	0.756	8.774	0.419	17.552	2252.82	0.980	43.093	132.861	1.303	64.733
4	22.5	203.6	10.0	0.758	7.465	0.307	11.153	1163.09	0.844	46.857	160.333	0.930	47.163
5	15.0	190.0	15.0	0.716	5.947	0.101	8.667	946.66	0.737	48.755	207.639	0.604	40.249
6	22.5	136.4	10.0	0.796	6.181	0.154	11.810	1555.19	1.091	61.854	167.861	0.537	38.325
7	15.0	190.0	5.0	0.672	5.461	0.058	6.196	570.78	1.000	93.582	264.082	0.341	7.766
8	22.5	170.0	10.0	0.738	8.282	0.153	11.701	1182.57	0.820	60.277	170.567	0.842	30.211
9	15.0	150.0	5.0	0.705	4.873	0.076	6.373	829.75	1.213	90.977	236.234	0.218	11.144
10	22.5	170.0	10.0	0.736	9.154	0.155	12.089	1159.06	0.832	50.513	169.314	0.737	32.443
11	22.5	170.0	1.6	0.725	6.489	0.288	7.866	943.86	1.426	63.574	184.286	0.454	17.621
12	22.5	170.0	10.0	0.718	7.551	0.285	10.784	957.38	0.889	32.664	149.368	1.213	48.629
13	30.0	190.0	5.0	0.758	11.508	0.659	18.376	1745.91	0.986	34.101	129.052	1.765	67.666
14	9.9	170.0	10.0	0.643	2.993	0.010	3.627	428.66	1.487	115.313	296.52	0.172	4.127
15	15.0	150.0	15.0	0.714	5.464	0.075	5.919	669.01	1.151	78.002	203.403	0.483	13.568

16	35.1	170.0	10.0	0.776	14.457	0.866	29.656	2992.11	0.705	28.432	101.272	3.536	162.311
17	22.5	170.0	10.0	0.730	7.030	0.192	12.178	1248.89	0.861	44.647	154.975	1.194	44.535
18	22.5	170.0	10.0	0.726	7.848	0.267	10.381	1073.09	0.760	46.311	144.893	1.209	48.094
19	22.5	170.0	10.0	0.726	7.540	0.278	10.715	1082.04	0.811	49.159	143.077	0.977	48.517
20	30.0	150.0	15.0	0.778	11.786	0.707	19.317	2113.81	0.854	37.089	111.12	2.43	81.985

Table 2-2 Second-order Regression Models for Mechanical and Water Soaking Properties of Medium Density Fiberboard.

Equation No.	Second-order regression models	R ²	SD
2	$TSH = -34.841 + 0.398X_{IMC} + 0.143X_{PT} + 0.367X_{PTT} - 0.001X_{PTT}^2$	0.920	0.739
3	$MOR = 6.556 - 0.525X_{IMC} + 0.174X_{PT} - 0.006X_{PTT} + 0.031^2_{IMC}$	0.927	0.775
4	$MOE = -1752.9 + 101.4X_{IMC} + 12.6X_{PT} + 14.3X_{PTT} + 3.2X_{IMC}^2 - 0.92X_{IMC}X_{PTT}$	0.931	102.07
5	$IB = -0.703 - 0.023X_{IMC} + 0.035X_{PT} + 0.005X_{PTT} + 0.001X_{IMC}^2 + 0.002X_{PT}^2 - 0.0004X_{PT}X_{PTT}$	0.951	0.062
6	$LE = 2.993 - 0.0697X_{IMC} - 0.0299X_{PT} - 0.0047X_{PTT} + 0.001X_{IMC}^2$	0.737	0.044
7	$TS = 278.18 - 10.78X_{IMC} - 5.207X_{PT} - 0.235X_{PTT} + 0.134X_{IMC}^2 + 0.172X_{IMC}X_{PT}$	0.904	7.834
8	$WA = 507.45 - 21.169X_{IMC} - 7.677X_{PT} + 0.132X_{PTT} + 0.259X_{IMC}^2 + 0.234X_{IMC}X_{PT}$	0.962	11.03
9	$W - MOR = 0.0198 - 0.1300X_{IMC} + 0.0489X_{PT} + 0.0035X_{PTT} + 0.0054X_{IMC}^2$	0.925	0.208
10	$W - MOR = -6.960 - 5.388X_{IMC} + 2.294X_{PT} + 0.174X_{PTT} + 0.227X_{IMC}^2$	0.908	8.488

Table 2-3 Comparison of the Actual Results of Mechanical and Water Soaking Properties of Medium Density Fiberboard and the Predicted Data Using Statistical Software (Minitab) at the Optimum Condition of 35% Initial Moisture Content, 195 °C Press Temperature and 13 min Press Time

Mechanical and water soaking propertied of MDF	Experimental data	Predicted data
Density, g/cm ²	0.80 ±0.05	---
Tensile strength, MPa	22.8 ±2.0	>15
Internal bonding strength, MPa	1.03 ±0.43	>0.8
Modulus of rupture (MOR), MPa	33.7 ±7.4	>25
Modulus of elasticity (MOE), MPa	2847 ±654	>2300
Thickness swell, %	23.9 ±2.8	<30
Linear expansion , %	0.95 ± 0.23	< 1.1
Water absorption, %	64.3 ± 9.6	<80
MOR after soaking, MPa	7.87±0.68	>3.0
MOE after soaking, MPa	380.3 ± 58.7	>155

Table 2-4 The Mechanical Properties of Medium Density Fiberboard Made at 35% Initial Moisture Content, 195 °C Press Temperature and 13 min Press Time Meet or Better Than These Properties Required by American National Standard (ANSI A208.2-2002) for Grades 210, 220, and 230.

Mechanical properties	Experimental data	ANSI A208.2		
		210	220	230
Internal bonding strength, MPa	1.03 ±0.43	0.35	0.60	1.00
Modulus of rupture (MOR), MPa	33.7 ±7.4	21.0	31.0	31.0

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CHAPTER 3 - HIGH STRENGTH, THIN-LAYERED, PULP FIBERBOARD USING SOYBEAN PROTEIN ADHESIVES

Abstract

Making thin-layered fiberboard and recycling fiberboard materials are two major approaches to save quantities of wood fiber in fiberboard manufacture, which offer both environmental and economic benefits to our society and industry. The objective of this research was to develop high-strength, thin-layered, pulp fiberboard using sodium dodecyl sulfate (SDS) modified soybean protein adhesives for packaging applications. SDS modified soybean protein adhesives had a significantly higher bonding strength than that of unmodified soybean protein adhesive. Results showed that the thin-layered pulp fiberboard with SDS modified soybean flour adhesive (0.05 g/cm² of area density and 0.6 mm of thickness) had stronger tensile strength, similar burst index, and better/similar water soaking properties in comparison to commercial solid fiberboard (0.124 g/cm² of area density and 1.7 mm of thickness).

Introduction

Currently, a large amount of pulp-based fiberboard such as cardboard and corrugated boards are used for packaging applications, especially for food and drink packaging market with a high strength and good water resistance. Triantafyllou reported that fiberboard for food and drink packaging accounts for 48% of all packaging market in the United States [1]. Using pulp-based fiberboard for packaging applications generates a huge amount of solid wastes because these packages are always one-off way for food and drink packaging applications. Reducing the amount of pulp fiber in these packages

without affecting and using quality and recycling these packaging materials are two main approaches to resolve the problem. Development of thin-layered pulp fiberboard using biodegradable adhesives could be one of the solutions.

Most adhesives used for manufacturing the fiberboard contain environmentally hazardous chemicals that are usually cross-linked during processing. The cross-linked chemicals make it difficult or impossible for re-pulping the fiberboard during any recycle process. Soybean protein, a byproduct after oil extraction, has been used as bio-based adhesives in wood industry back to 1920'. In recent years, a lot of research showed that modified soybean protein-based adhesives had high adhesion strengths as well as high water resistances [2-5], and had a great potential in bonding multiform wood boards, such as plywood[6], cardboard[7], and oriented strandboard[8], but little research on manufacturing pulp fiberboard. In this study, sodium dodecyl sulfate (SDS) was used as a denaturation agent for protein modification. At low concentration, SDS binds with protein molecules and induces a drastic cooperative conformation change in soybean protein [9]. The objective of this research was to develop high-strength, thin-layered pulp fiberboards using soybean protein-based adhesives for packaging applications.

Materials and Methods

Materials

Virgin pine pulp (made through an unbleached Kraft process) with 88% moisture content was provided by Interstate Paper LLC (Riceboro, GA). Defatted soybean flour, containing 48.5% (dry basis) protein and 4.6% moisture, is a product of Cargill Inc. (Minneapolis, MN). Sodium hydroxide, hydrochloric acid, and sodium dodecyl sulfate (SDS) are products of Sigma Chemical Co (St. Louis, MO).

Soybean Protein-based Adhesives Preparation

Five soybean protein-based adhesives (SPA) were prepared from defatted soybean flour with and without SDS modifications. **SPA-I:** SDS was added to regular tap water at 1%(w/w) concentration to prepare SDS-water solution. Then soybean flour was mixed with the SDS-water solution at 40:60 (soybean flour:solution) ratio to develop on adhesive dough. The adhesive dough was then shaped into a 1 inch thick and 2 inches wide bar and dried in a continuous microwave chamber for 30 sec. Then the dried sample was milled into powder with average particle size of 100 μm . Then the SDS modified soybean flour powder, containing 47.7% (w/w, dry basis) protein, was gradually added to distilled water at 5% (w/w) solid content and stirred for 1 h at room temperature and then readied for further use (pH \approx 7.1). **SPA-II:** Defatted soybean flour was gradually added to a 1% SDS solution at 5% solid content and stirred for 3 h at room temperature and then was ready for further use (pH \approx 6.9). **SPA-III:** Defatted soybean flour was gradually added to distilled water at 5% solid content and stirred for 30 min at room temperature and then readied for further use (pH \approx 6.5). **SPA-IV:** Soybean protein isolates (SPI) containing 88% protein (dry basis) was extracted from defatted soybean flour following the procedure described by Huang and Sun [10]. SPI was gradually added to 1% SDS solution at 5% solid content and stirred for 3 h at room temperature and then readied for further use (pH \approx 7.7). **SPA-V:** SPI was gradually added to distilled water at 5% solid content and stirred for 30 min at room temperature and then readied for further use (pH \approx 7.4).

Pulp Fiberboard Panel Preparation

Paper mat preparation: Pulp fiber was dispersed in distilled water at 4% solid content (wet basis) by using a blender (Osterizer, Sunbeam Products Inc., Mexico) at low speed for 16 ~ 18 sec. Then SPA slurry, as described in the SPA preparation section, was added into the pulp fiber slurry and mixed manually for 20 sec at room temperature. The pulp fiber–SPA slurry was transferred into a mold having dimensions of 152.4 mm by 152.4 mm. After the fiber precipitated to the bottom of the mold, a metal screen with a fine nylon cloth was covered on the slurry in the mold. Then water was drained out from the slurry through the metal screen to form a fiber mat. The paper mat was obtained by drying the fiber mat at 60°C for 5 hours, and then was conditioned in a humidity chamber at 23°C and 50% RH for 48 h before testing the properties of pulp fiberboard. Varied amount of pulp fiber and SPA concentration for preparing paper mat were designed to study the effects of different SPA concentrations on the properties of paper mat (Table 3-1).

Pulp Fiberboard panel preparation: The paper mat was used to prepare the pulp fiberboard panel in a pair of special designed molds: a female mold as a sample holder (Fig. 3-1a) and a male mold as a cover (Fig. 3-1b) with dimensions of 152.4 mm by 152.4 mm. To allow water vapor to evaporate easily, the pair of molds was designed with the following features: 1) there are three vertical notches (2mm width by 1 mm depth, Fig 1a-enlarged A,B) at each side of the female mold; and three horizontal notches connected with the vertical notches (2mm width by 1 mm depth, Fig 1a-enlarge B) at two face-to-face sides of the female mold, these vertical notches match the eaves on the male mold (Fib 3-1b) in application; 2) there are three vertical and three horizontal notches (2

mm width by 1 mm depth, Fig 3-1b) on the top surface of the male mold, and nine round holes for penetrating the male mold on each cross point (Fig 3-1b-enlarge A).

The paper mats (5-8 mats depending on the thickness of board) were layered together in the female mold, and 1.75 ± 0.25 g water was added between two mats. The male mold was placed into female mold, and then the layered paper mats were hot pressed using a hot press (Model 3890 Auto “M”, Carver Inc, Wabash, IN) at 66.7 KN force and 160 °C. The thickness of fiberboard was controlled by the gap adjustment in the mold using metal sheets. The density of the pulp fiberboard was controlled by the amount of fiber used and the thickness of board. The panels were conditioned in a humidity chamber at 23 °C and 50% of RH for 5 day before testing the properties of fiberboard.

Characterization of SPA Properties

Viscosity measurement: The rheological properties of the SPA slurries were determined using a Brookfield Programmable Rheometer (DV-III+) equipped with a small sample adapter (SC4-21/13R) (Brookfield Engineering Laboratories, Inc., Middleboro, MA) with bob and cylinder arrangement. The SPA slurry was prepared as described previously in SPA preparation section. About 8 mL of SPA slurry was transferred into the sample holder of the rheometer, and its viscosity was recorded every 60 sec from 80 sec to 680 sec at a shear rate of 93.0 s^{-1} at room temperature.

Contact angle measurement: The contact angle was monitored by an optical contact angle meter (CAM 100, KSV Instruments, Helsinki, Finland). A droplet (about 2 μL) of SPA slurry, prepared as described in SPA preparation section, was dropped on the

surface of the substrate. The substrate was prepared by hot pressing three pieces of paper mat at 66.7KN and 105 °C for 5 min, which mat was prepared as described in paper mat preparation section. Contact angles were measured immediately after the droplet dropped on the substrate. The values reported were averages of five replications.

Thermal property: Thermal properties of SPA were determined by a differential scanning calorimeter (DSC) (Pyris-1, Perkin-Elmer, Norwalk, CT, USA). The instrument was calibrated with indium and zinc standards before measurements, and all measurements were conducted under a nitrogen atmosphere. About 35 mg SPA slurry, prepared as described in SPA Preparation with 10% solid content instead of 5% of that, was sealed in a large-volume DSC pan. All samples were held at 30°C for 1 min and then scanned to 150°C at a heating rate of 10°C/min. The enthalpy of denaturation (ΔH_d) was determined by integrating the area under the endothermic peak. All experiments were made in duplicate and average values were reported.

Characterization of Fiberboard Panel Properties

Mechanical properties: Mechanical properties were determined following ASTM standard method D1037-99 [11] using an Instron testing machine (Model 4466, Canton, MA). Tensile strength (TSH) was obtained by tensioning the specimen (25.4 mm × 127.0 mm) at a crosshead speed of 4 mm/min. The shear strength at maximum load was recorded. Modulus of rupture (MOR) of the fiberboards (25.4 mm × 127.0 mm) were obtained by performing three-point bending test at a crosshead speed of 3 mm/min. The wet TSH (W-TSH) and wet MOR (W-MOR) were obtained after 24±1 h water soaking.

Burst strength was determined following TAPPI method T 810 om-06[12] using a Burst Tester (MTA 2000, West Berlin, NJ). A specimen (152.4 mm by 152.4 mm) was clamped in a pair circular plate with a pneumatic system, then a constantly increasing pressure acted on the unsupported area of specimen until the specimen was burst; the force required to burst the specimen was recorded. The hydraulic system rate of flow was 170 ± 15 mL/min. The burst index (BI) was obtained by dividing burst strength by its weight. All values reported were averages of three replications.

Dimension stability: Thickness swell (TS), linear expansion (LE), and water absorption (WA) were measured according to ASTM standard method D1037-99. The 25.4 mm × 127 mm specimens were soaked in water for 24 ± 1 h at room temperature. The dimensional size and weight before and after soaking were measured to calculate the values of TS, LE and WA, which were expressed as percentages of the data after soaking to that of before soaking.

Experimental Design and Statistical Analysis

A one-way factorial experimental design was used to study the effects of different soybean protein-based adhesives on the properties of pulp fiberboard. Statistical Analysis Software (SAS Institute, Cary, NC) was used to calculate ANOVA and least significant difference (LSD) of results.

Results and Discussion

Properties of Different Soybean Protein- based Adhesives

To investigate the influence of soybean protein-based adhesives on properties of fiberboard, the viscosity, contact angle and enthalpy of denaturation of five type soybean protein-based adhesives (SPAs) were tested (Table 3-3). The viscosities of SPA-IV and SPA-V were significantly higher than the other types of SPAs, because they were made from SPI, and the protein content of SPI (88%) is significant higher than defatted soybean flour (48.5%). In general, the viscosities of five SPAs were very low (less than 7 MPa s). The low viscosity makes all of the SPAs easy to handle and mix with pulp fibers during paper mat and fiberboard preparation. Thermal property testing results showed that the enthalpy of denaturation for SPA-IV and SPA-V was significantly higher than others due to the higher protein content of SPI (88%). Compared to the enthalpy of denaturation between the SPAs with and without SDS modification, the enthalpy of denaturation decreased significantly after SDS modification but it still exist, showing that soybean protein native structure was partly unfolded during SDS modification [13]. The SDS-modified soybean flour powder (SPA-I) was unfolded slightly less than the SDS-modified soybean flour solution (SPA-II).

Contact angle characterizes the spreading or wetting properties of soybean adhesive on the surface of wood fiber. A lower value of contact angle indicates that the liquid spreads or wets the surface better than a liquid with a higher value. SPA-IV had the best spreading or wetting properties, which was almost similar as water, then followed by SPA-II, SPA-I, SPA-V, and SPA-III. The native soybean protein (SPA-V and SPA-III) had a poor spreading and wetting properties on the wood fiber surface. However, after modified by SDS, the spreading or wetting properties of those SPAs was significantly improved to as well as water, from 62.99° to 41.36° and from 78.59° to 45.59°,

respectively. There was no significant difference between two different modified SPAs: SPA-I and SPA-II. At the low SPA solid content (5%), the native protein content affected the contact angle. High protein content resulted in a lower value of contact angle. The contact value of SPA-V was higher than that of SPA-III. However, after modified by SDS, there was no significant difference between different protein content (SPA-II and SPA-IV).

Effect of Concentration of Soybean Protein-based Adhesive on Mechanical Properties of Pulp Fiberboard

The pulp fiberboards were prepared with different concentrations (from 0 to 0.15%) of SPA-I (Fig. 3-2). TSH increased as the adhesive concentration in pulp slurry increased from 0 to 0.1%, and then slightly decreased when the adhesive concentration increased from 0.1 to 0.15%. However, there was no significant difference among the adhesives concentrations from 0.05% to 0.15%. MOE increased as the adhesive concentration in pulp slurry increased from 0% to 0.05%, and then leveled off with the adhesive concentration increased to 0.15%. SPA-I could increase TSH, MOR, and MOE significantly compared with the pulp fiberboard without SPA-I. Since there was no significant difference in mechanical properties of fiberboard among different SPA concentrations and from economic point view, 0.05% of soybean protein-based adhesive was preferred.

Effect of Press Time on Tensile Strength of Bio-based Fiberboard

Table 3-4 showed the tensile strength of pulp fiberboards prepared by different press time at 66.7 KN force and 160 °C with 0.05% of SPA-1. The board panels with press time of 1.5 min and of 2.0 min were still wet after hot pressing and continuous evaporation of moisture during the condition period is needed. Pressing time of 3.0 min gave a relative dry fiberboard panels. After 5 day conditioned in a constant chamber, the water content of fiberboards reached equilibrium. The mechanical testing results showed that pressing time did not have a significant effect on tensile strength of the fiberboard panels from 1.5 min to 5.0 min. Concerning the effect of press time on moisture content of fiberboard; a press time of 3 min is preferred.

Different Soybean Protein- based Adhesives on Pulp Fiberboard Properties

Table 3-5 shows the influence of different soybean protein-based adhesives on physical and mechanical properties of pulp fiberboard. The thickness of the fiberboard ranged from 1.10 to 1.21 mm and area density ranged from 0.088 to 0.094 g/mm². Fiberboard with SPA-I had the strongest TSH among the five types of adhesives. Fiberboard with SPA-III resulted in the weakest TSH similar to control. No significant difference of TSH among the Fiberboards with SPA-II, SPA-IV, and SPA-V. For MOR, the SPAs were clearly separated into the two groups. The group of SPA-I, SPA-II, SPA-IV and SPA-V had a significant higher MOR than the group of SPA-III and control. The results indicate that both protein content and SDS modification had a significant effect on MOR. At low protein level (soybean flour), SDS modified SPA (SPA-I and SPA-II) had higher MOR than unmodified SPA (SPA-III). For unmodified SPA, the SPA with higher

protein content (SPA-V) yielded a higher MOR than that of SPA with less protein content (SPA-III). At higher protein level, the effect of protein with or without SDS modification on MOR was not significant; SPA-IV and SPA-V had the similar MOR. For soaked samples, fiberboards made with SPAs were significant higher in both W-TSH and W-MOR than control. This result indicates that, as an adhesive, soybean protein enhanced water resistance of fiberboard.

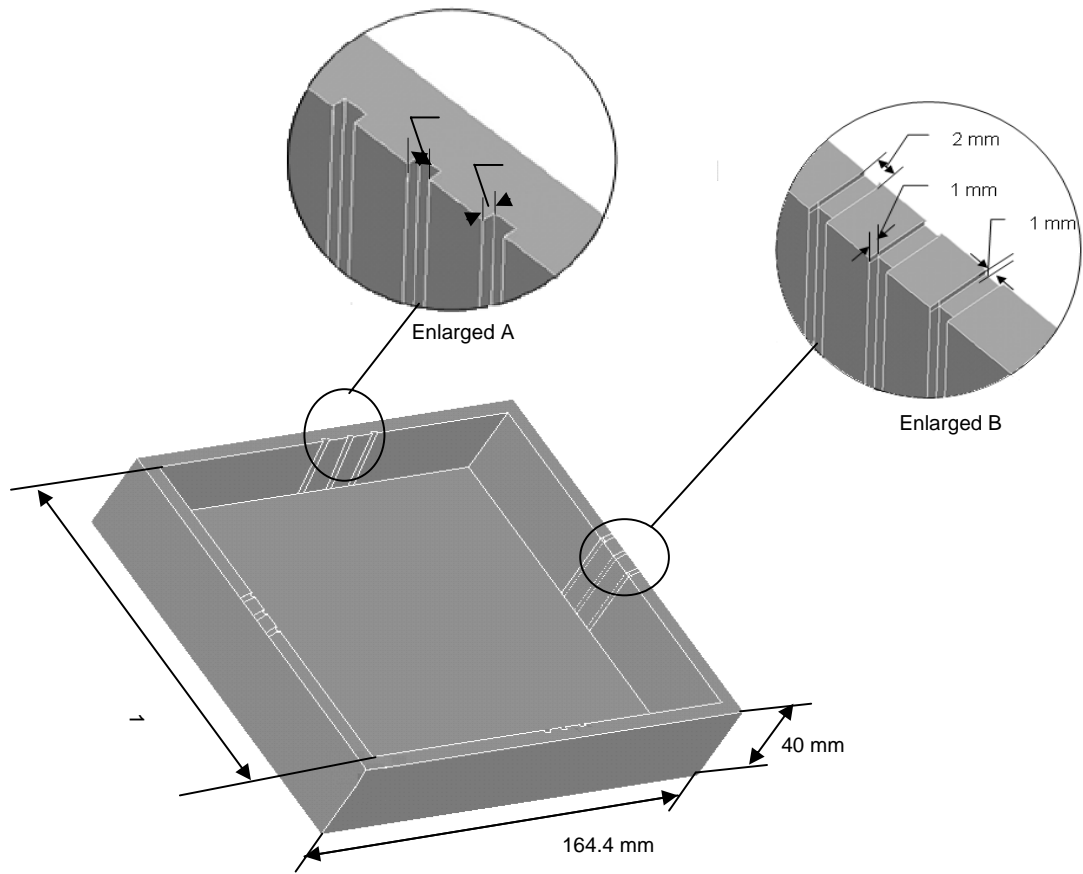
Comparison of Pulp Fiberboard with Commercial Solid Fiberboard (SF)

The two thin-layered pulp fiberboards (0.09 g/ cm² and 0.05 g/ cm² area density, 1.1 mm and 0.6 mm thickness) had a significant higher TSH than that of commercial solid fiberboard (SF) measured at perpendicular section and slightly higher than that of SF measured at parallel section, even the SF has higher area density (1.24 g/cm²) and thickness (1.7 mm). Also the specific TSH of thin-layered pulp fiberboards were higher than that of SF. After 24 h water soaking, TSH of thin-layered fiberboards was also stronger than or similar as SF. The burst index of the thin-layered fiberboards was as high as SF, indicating multi-directional tensile strength of the thin-layered fiberboards was as strong as SF. In addition, the two thin-layered pulp fiberboards also showed the similar or lower thickness swell and linear expansion compared with SF (Table 3-6). The developed thin-layered fiberboards with high mechanical strength and water resistance have a great potential to replace current commercial solid fiberboard.

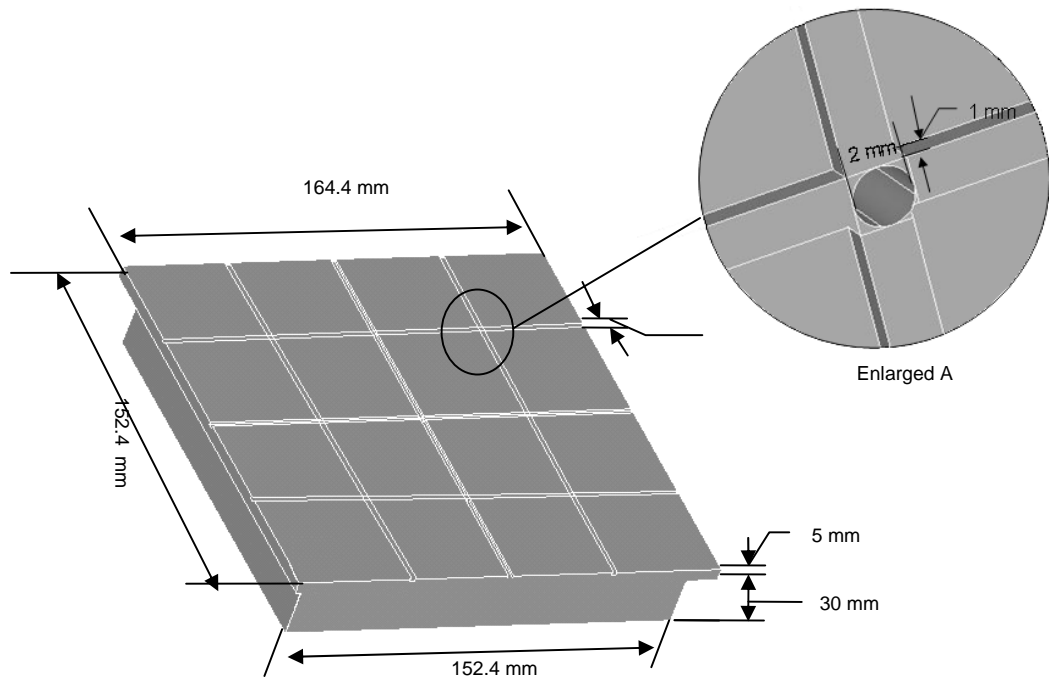
Conclusions

In general, the thin-layered pulp fiberboards made with SPAs had a strong mechanical properties as well as water resistance. SDS modified soybean flour yielded

the similar mechanical strengths as SDS modified SPI in both dry and wet TSH and MOR. The thin-layered pulp fiberboard using soybean flour adhesive modified with 1% SDS and 0.05 to 0.1% pulp slurry had the similar burst index, significantly stronger tensile strength, and stronger or similar tensile strength after 24 hrs soaking; lower or similar linear expansion and thickness swell, compared with commercial solid fiberboard. This research suggests that the thin-layered pulp fiberboard with soybean flour adhesive has great potential as alternative to current commercial solid fiberboard.



a



b

Figure 3-1 A Pair of Special Designed Molds: a) Male Mold and b) Female Mold.

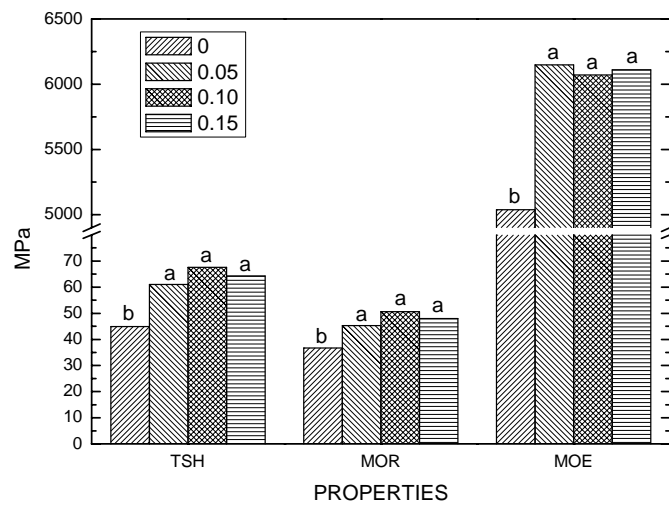


Figure 3-2 Mechanical Properties of Thin-layered Pulp Fiberboard Made at 66.7 KN Force and 160 °C for 3.5 min with 1.0 g/cm² of Area Density and 1.2 mm of Thickness Prepared by Different Concentrations of SPA-I (0% to 0.15%).

Table 3-1 SPA and Pulp Fiber Concentrations Used for Preparation of Paper Mat

SPA slurry (wb, %)	SPA content (db, %)	Pulp fiber slurry (wb, %)	Pulp fiber solid (db, %)
0	0	4.00	0.48
1.0	0.050	3.67	0.44
1.5	0.075	3.50	0.42
2.0	0.100	3.33	0.40

**Table 3-2 Method for Controlling the Thickness of the Thin-layered Pulp
Fiberboard Panel and Hot Press Conditions**

Target thickness of fiberboard (mm)	Weight of total paper mat (g)	No. of paper mat	Hot Press	
			Time (min)	Temp. (°C)
0.6	14±0.5	5	3.0	160
1.2	23±0.5	8	3.5	160

Table 3-3 Properties of Different Soybean Protein-based Adhesives¹

Formula	Viscosity at 93/s of shear rate (MPa s, 5 % solution)	Contact angle on wood fiber mat (°, 5 % solution)	Enthalpy of denaturation (J/g SPA, 10 % slurry)
SPA-I	3.59±0.54 ^{c, d}	49.47±4.78 ^c	2.78±0.26 ^d
SPA-II	3.77±0.41 ^c	45.59±3.57 ^{c, d}	2.03±0.11 ^e
SPA-III	3.41±0.38 ^d	78.46±4.72 ^a	4.04±0.03 ^c
SPA-IV	6.82±0.40 ^a	41.36±5.11 ^d	6.03±0.04 ^b
SPA-V	6.27±0.26 ^b	62.99±3.09 ^b	7.97±0.04 ^a
water	---	41.4±2.78 ^d	---

¹ANOVA and LSD tests were performed using SAS. Means in the same column followed by different superscript letters are significantly different at P>0.05.

Table 3-4 Effect of Press Time on Tensile Strength, Area Density, and Thickness of Pulp Fiberboards with 0.05% SPA-I Pressed at 66.7 KN force and 160 °C

Press time (min)	Area density (g/mm ²)	Thickness (mm)	TSH (MPa)
1.5	1.07	0.57	66.0
2.0	1.04	0.56	68.0
3.0	1.00	0.59	65.9
4.0	1.06	0.60	60.0
5.0	1.08	0.50	62.2

Table 3-5 Effect of Type of Soybean Protein Adhesives on Area Density, Thickness, and Mechanical Properties of Thin-layered Pulp Fiberboard¹

Formula	Area density	Thickness	TSH	MOR	W-TSH	W-MOR
	(g/cm ²)	(mm)	MPa	MPa	Mpa	MPa
SPA-I	0.090	1.10	61.0 ^a	46.7 ^a	4.12 ^a	3.53 ^a
SPA-II	0.090	1.18	51.7 ^b	45.2 ^a	3.73 ^a	3.28 ^a
SPA-III	0.088	1.15	39.9 ^c	37.9 ^b	4.14 ^a	3.17 ^a
SPA-IV	0.094	1.13	54.2 ^b	47.5 ^a	3.81 ^a	3.34 ^a
SPA-V	0.089	1.13	51.9 ^b	48.0 ^a	4.23 ^a	3.30 ^a
Control	0.090	1.21	42.8 ^c	36.7 ^b	2.60 ^b	2.10 ^b

¹ANOVA and LSD tests were performed using SAS. Means in the same column followed by different superscript letters are significantly different at P> 0.05.

Table 3-6 Comparison of Area Density, Thickness, and Mechanical Properties between the Thin-layered Pulp Fiberboards (TLPB) and Commercial Solid Fiberboard (SF)

	Area density (g/cm ²)	Thickness (mm)	TSH (MPa)	Burst Index (KPa m ² /g)	TSH after soaking (MPa)	Linear expansion (%)	Thickness swell (%)	Specific TSH MPa cm ³ /g
TLPB 1	0.09	1.1	65	2.8	3.1	0.6	60	79.46
TLPB 2	0.05	0.6	68	2	5.5	0.4	69.3	81.63
SF (perpendicular)	0.124	1.7	23	2.8	2.5	2.5	55.6	30.79
SF (Parallel)	0.124	1.7	50	2.8	3.5	0.1	56.3	66.93

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CHAPTER 4 - SUMMARY

Medium density wood fiberboard and thin-layered pulp fiberboard were developed with soybean protein based adhesives, which were used as well as formaldehyde-free, bio-based adhesives. MDF gave high mechanical properties and good water soaking performances, which were stronger than those of commercial fiberboard Grade 210, and similar to Grade 230. Furthermore, thin-layered pulp fiberboards with soybean protein based adhesives had better strength and soaking properties than without soybean protein based adhesives. Comparing to the commercial solid fiberboard, thin-layered pulp fiberboards with soybean protein based adhesives had better mechanical properties and water resistance with lower weight in same unit area.