CHAPTER II

THEORY AND LITERATURE REVIEW

"Wood is a friend of mine; the best friend on earth of man is the tree" Frank Floyd Wright, American architects, has said. Values of wood as a building material are a renewable abundance of supply, a wide variety of types, a durable material, a strong material, an attractive material, an easily worked material, and a versatile material. [17]

2.1 Particleboards

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Particleboard industry has grown rapidly because the demand for wood is on the increase and the supply of wood from natural forest is unable to keep with it (Table 2.1). Furthermore, the economic need to recover higher percentages of unusable material from forest resources and need to use higher small, low-quality trees. In this respect, the softwood, small, and low-quality trees of the world have vast potentialities in supplying wood. These are the cheap sources of wood to effective substitutes for wood panel industries.

Matformed particleboard is an engineered panel product of machined particles bonded together with a binder under controlled heat and pressure. The gross macrostructure of the wood is retained in the component particles of particleboard and an external binder is required for interparticle bonding. A wide range of particle sizes, from sawdust granules to flakes three inches long is commonly used, although rarely is the entire size distribution included in a single panel [18]

2.1.1 General Definitions

Particleboard: a generic term for a panel manufactured from lignocellulosic materials (usually wood), primarily in the form of discrete pieces or particles, as distinguished from fibers, combined with a synthetic resin or other

suitable binder and bonded together under heat and pressure in a hot press by a process in which the entire interparticle bond is created by the added binder, and to which other materials may have been added during manufacture to improve certain properties. Particleboards are defined by the method of pressing. When the pressure is applied in the direction perpendicular to the faces, as in conventional multi-platen hot press, they are defined as flat-platen-pressed; and when the applied pressure is parallel to the faces, they are defined as extruded.

Table 2.1 World production of wood based panels, 1990-1994.[19]

Products	Unit 1,000	1990	1991	1992	1993	1994
Plywood	m ³	48,258	46,394	48,127	48,534	48,851
Particleboard	m ³	50,413	48,574	49,188	50,780	51,982
Fiberboard	m ³	20,254	20,016	17,939	18,956	19,748

2.2.2 Classifications of Particleboards

Low-density particleboard: A particleboard with a density of less than 590 kg/m³.

Medium-density particleboard: A particleboard with a density between 590-800 kg/m³.

High-density particleboard: A particleboard with a density greater than 800 kg/m³.[20]

2.1.3 Properties of Isocyanate Bonded Particleboard

The properties of polyisocyanate-bonded particleboard depend upon the nature of polyisocyanate and flake characteristics. Table: 2.2 shows a comparison of pMDI and TDI binders. The pMDI based binders produce moisture-stable particleboards of high strength and high dimensional stability. These boards are permanently resistant to boiling water and free of alkali and formaldehyde. The pMDI-bonded particleboards are also free from objectionable or toxic odours and, unlike some boards bonded with phenolic resins, they are neutral and non-corrosive. [21, 22, 23]

Table 2.2	Properties of 3 layer laboratory particleboard, 16 mm, with various
	polyisocyanates.[21]

Type of	Content of the polyisocyanate	Density (kg/m ³)		kness ing (%)		ernal (MPa)	Flexural strength
cyanate	(% on dry chip)		2 hr.	24 hr.	V20	V100	(MPa)
pMDI	6	650	10.4	16.1	1.09	0.33	26
TDI	6	650	5.7	20.1	0.28	-	12
	6	850	4.3	, 19.5	0.91	0.08	26

The performance of particleboard manufactured with pMDI under changing climate condition, is expressed by weight change vs. time over three years of outdoor weathering exposure. Figure 2.1 shows the superior performance of pMDI base particleboard compared with conventionally bonded board. The differing sorption-isotherm of particleboard bonded with pMDI, urea-formaldehyde, and phenol-formaldehyde are shown in Figure 2.2. The lower water absorption of pMDI bonded particleboards under conditions of high relative humidity is clear apparent.

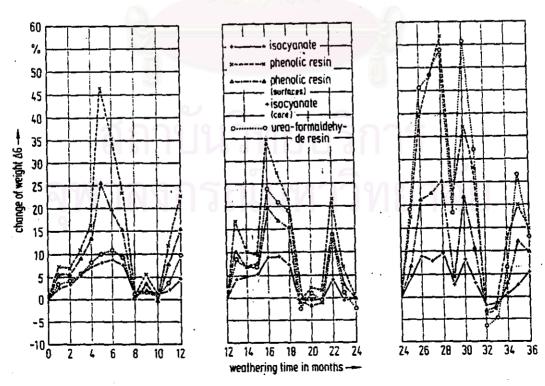


Figure 2.1 Average monthly weight change (%) of laboratory made particleboard exposed to outdoor weathering.[21]

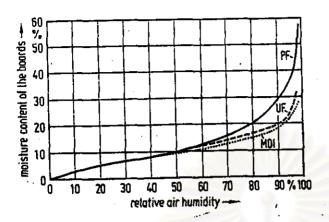


Figure 2.2 Sorption-isotherms (20 °C) of particleboard (20 mm) bonded with polyisocyante (pMDI), ureaformaldehyde resin (UF) and phenol formaldehyde (PF).[21]

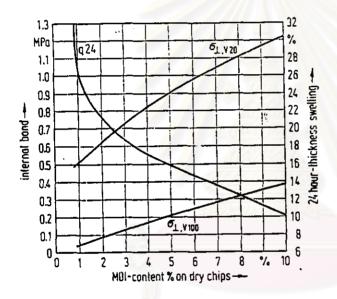


Figure 2.3 Internal bond and 24 hours thickness swelling of 16 mm laboratory made particleboard versus the quality of binder. [21]

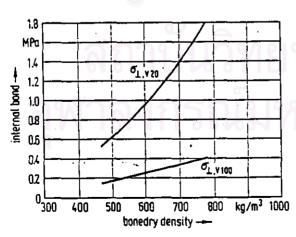


Figure 2.4 Internal bond of 16 mm laboratory made particleboard versus density (6% pMDI).[21]

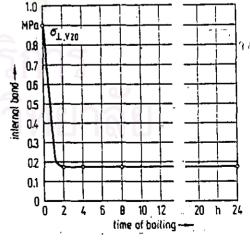


Figure 2.5 Internal bond of air classified particleboard versus time of boiling in water (7% pMDI).[21]

The internal bonding quality in panels depends on the quantity of pMDI binder used. Figure 2.3 and 2.4 show that, at low densities and low pMDI contents, surprisingly good quality panel can be produced.

Table 2.3 Properties of 3 layer laboratory particleboard with various binders (16 mm, 170 °C).[21]

Type of Binder	pl	MDI	Phenol-Formaldehyde Resin		
Content of the Binder (%) (based on dry chips)	8/6	12/8	8/6	12/8	
Content of Paraffin (%) (based on dry chips)	1	1	1	1	
Density of the panel (kg/m ³)	650	650	650	650 '	
Moisture content of the panels (%)	6.5	6.2	6.5	7.0	
Thickness swelling (q ₂ -%)	3.0	2.4	14.3	12.3	
Thickness swelling (q ₂₄ -%)	10.1	8.9	16.8	14.9	
Internal bond V20 (MPa)	1.08	1.21	0.73	0.83	
Internal bond V100 (MPa)	0.25	0.35	0.17	0.22	
Flexural strength (MPa)	27	31	23	24	
_ , ,	3,020	3,430	3,000	3,000	

The exceptional hydrolytic stability of the polyurea bond has been demonstrated through immersion experiments in boiling water. After two hours of immersion, no further reduction of the internal bond occurred (Fig. 2.5). To show the extraordinary bonding strength of the pMDI, some of the test results are shown in Table 2.3 in comparison to a commercial PF-resin at equal dosages. The quality of polyisocyanate bond can be affected by the species of the wood being bonded. Table 2.4 compares the physical properties of particleboard made from Pine, Beech, Oak, and Spanish Chestnut woods.[21]

2.1.4 Safety of Isocyanate Bonded Particleboard

The smoke density during combustion of particleboard bonded with polyisocyanate is between that of UF and PF resins. However, the inhalation toxicity of the combustion gases is lower as compared to the conventionally bonded boards. The Federal Public Health Department in the Federal Republic of Germany, has approved particleboard bonded with polyisocyanate for the transportation and storage

of dry food. Also, the Federal Public Environment Department in the Federal Republic of Germany affirmed that there no factors opposing the use of pMDI as a binder in particleboard.[21]

Table 2.4 Physical properties of single layer, 20 mm isocyanate bonded particle-board made from chips of various species of wood with a density of approximately 700 kg/m³; content of binder 6% (referring to dry chips), press temperature 190 °C.[21]

Species of wood	Press time	Internal bond (MPa)		Thickness s	Thickness swelling	
	(min.)			(%)	1.4	
		V20	V100_	2 hr.	24 hr	
Scotch pine	5	1.14	0.24	10.4	18.9	
(Pinus silvestris)	7	1.19	0.24	9.9	17.9	
Beech (Fagus)	5	0.94	0.16	3.8	15.2	
, ,	7	1.13	0.29	3.5	14.2	
Young Oak with ba	ark 5	0.83	0.13	2.4	11.8	
	7	0.93	0.16	2.4	11.8	
Spanish chestnut	5	0.83	0.12	2.2	8.9	
(Castanea Sativa)	7	0.97	0.17	1.9	8.5	

2.2 Wood Materials

Wood is a three-dimensional, polymeric composite made up primarily of cellulose, hemicellulose, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Wood is a preferred building and engineering material because it is economical, low in processing energy, renewable, strong, and aesthetically pleasing. [24] Nowadays, the forests of the world are progressively dwindling as the countries of the world are rapidly developing and their populations fast increasing. As a result, the demand for wood is on the increase and the supply is unable to keep pace with it. Furthermore, the production of logs and sawnwood have declined (Table 2.5). So that, new sources of wood supplies have to be exploited so as to maintain the industries in which wood is the starting material. [1, 25]

Figure 2.6 The partial molecular structure of cellulose and hemicellulose.[26]

Table 2.5 The world production of sawlogs and sawnwood between 1990-1994.[19]

Year	World Production (1000 m ³)			
	Sawlogs	Sawnwood		
1990	1,055,921	505,172		
1991	927,600	455,486		
1992	903,543	436,479		
1993	893,597	420,220		
1994	895,067	413,319		

Whatever the process or type of board, the first consideration is naturally the raw material, the wood, flax or other ligno-cellulosic substance which is the main constituent of board, together with the resin binder and any other additive.[27]

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The raw material for board industry can be roundwood, slabs edgings, end trim, shavings, sawdust, annual plants, etc. Many wood species, both hardwoods and softwoods, are use for particleboard. It is probable that over 95% of world production utilizes wood in some form or another. However, the density of the particleboard should be higher than the density of the raw material to efficiently utilize the binder system. The wood content on a dry basis for most particleboard is between 90-95%. The main wood and ligno-cellulosic raw materials are forest products, industrial wood residues, and agricultural products.[21, 27]

2.2.1 Forest Products

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Logs and timbers are the main product from forests, the timber of any softwood species is an excellent raw material for particleboard, also, branches and low quality trees. They are being increasingly used, particularly in the newer plants. In the coniferous areas of temperate climate, conifers are used as raw material due to the fact that ample supplies of these species are available, softwoods are also preferred as being easier to break down to particle size, less friable when broken down and more compatible chemically one with another over the common range of species, than are hardwoods. In tropical countries, where perhaps hardwood forests predominate and coniferous resource are meagre, will result in increasing quantities of boards based on hardwoods although softwood boards will always be in the majority on a word basis.

2.2.2 Industrial Wood Residues

Apart from the very large quantities of forests available in roundwood form, the normal conversion of timber to the sizes required by the carpenter and joiner gives rise to slab wood and offcuts on initial conversion, and to shavings from planer, spindle and other woodworking machinery at a later stage. The principal types of raw material available at the present time are veneer peeler core, cull lumber, lumber slabs and edgings, lumber mill end trim (green), lumber planer end trims (mostly dry), veneer log roundup (green), veneer clippings (green), pulp ships (green), lumber planer shavings (dry), sawmill sawdust (green), miscellaneous dry woodworking residues from molding and furniture-type plants, planner mill and similar dry sawdust, ply wood trim, plywood sander dust, and miscellaneous woodworking sander dust. All these material, suitably processed, can be utilized in the manufacture of particleboard. [20, 27]

2.2.3 Agricultural Product Residues

Agricultural waste materials, such as straw, rice hull, flax, linen, etc., which accrue and grow again yearly, can be bonded with greatly difficulty or not at all, with the existing common aqueous binders. The utilization of these valuable raw materials is currently meaningful and should become more so in future. Through the development of polyisocyanates binders, it has become possible to produce

particleboard and molded parts from this materials for the fist time. Under pressure and heat, polyisocyanates are able to penetrate the hydrophobic layer of wax and silicates which often exist in such natural products.[21]

Table 2.6 Summary of the major types of raw materials used in north american particleboard plants.[20]

Wood Material	Proportion of total particleboard raw material supply (%)		
Softwood			
Roundwood	4.2		
Pulp chips	3.7		
Planer shavings	47.7		
Sawdust	11.8		
Hogged mill waste:			
Sawmill & planing mill	1.7		
Plywood plant	9.3		
Millwork plant	0.2		
Furniture plant	0.3		
Particleboard plant	0.9		
Unspecified	4.8		
Total hogged wood mill waste	17.2		
Total softwoods	84.6		
Hardwoods			
Roundwood	6.7		
Pulp chips	2.1		
Planer shavings	3.1		
Sawdust	0.4		
Hogged mill waste:	311.19		
Sawmill & planing mill	0.2		
Plywood plant	0.1		
Furniture plant	2.5		
Flooring plant	0.3		
Total hogged wood mill waste	3.1		
Total hardwoods	15.4 100.0		

2.2.4 Rubber Wood in Wood Industries

Due to the demand for wood is on the increase but the supply is unable to keep pace with it. Furthermore, the production of logs and sawnwood have declined. So that, new sources of wood supplies have to be exploited so as to maintain the industries in which wood is the starting material. In this respect, the softwood, small, and low-quality trees of the world have vast potentialities in supplying wood. These are the cheap sources of wood to effective substitutes for wood panel industries.

Rubber trees are a hardwood species, rubber plantations of the word have vast potentialities, in supplying wood, which is at present a waste product of rubber replantation schemes after it turn out the economic life. Nowadays, there are attempts to maximum using of rubber wood. Rubber wood has been more important role in furniture industry and wood-type equipments because of a cream colored wood and attractive grain. [5, 28] The chemical and mechanical properties of rubber wood were shown in Table 2.7 and 2.8.

At present, Thailand have rubber plantation area about 11.6 million rais and tend to continue increasingly every year (Table 2.9), particularly in east-northern part. Average economic life of rubber trees is 25 years. The cut down rubber tree can be used for substitute import sawlogs and sawnwood from the neighbouring countries. Around the country, there are uneconomic rubber trees which cut down about 200,000 rais for annum, calculated to volume of wood about 9.8 million cubicmetre.[8, 10] Since 1989, the manufacturers found that it can substitute the natural wood from natural forest, the export market prefers furnitures made from rubber wood. Today, rubber wood products have increasing value and make income to country more than 10,000 million baht for annum.[10, 26]

2.3 Binders

Binders play an important role in the wood products industry. In 1988, this industry accounted for a 25% share of total U.S. consumption of binders. The use of binders can increase the utilization of small and low-quality trees in a variety of bond wood products. The economic imperative to use available timber resources in efficient

a manner as possible will undoubtedly increase the demand for binders.[4] About 50-60% of total producing costs are the cost of binders, others are wood 30-40%, additives 5%, and the rest 5%. [29]

A large and growing share of structural wood products are composed of pieces of wood held together by binders. In a few cases, natural glues such as animal glues, casein, and starch are still used. Currently, however, most wood-to-wood bonds in composite wood panel products are produced by a variety of synthetic resins (primarily formaldehyde-based thermosetting resins).

Any binder use in the bonding of wood must be able to provide a strong, durable bond at a reasonable price. Binder color, storage life, and ease of application are also important factors. Because wood is not homogeneous substance, the resins used as wood binder also must be effective over a wide range of bonding conditions. Important wood quality variables such as moisture content, density, and surface properties can vary considerably among different types of wood and wood pieces. To adjust for such changes, a number of different specific resin formulations are required.

2.3.1 Conventional Binders

Almost all of the binders currently used to manufacture composite wood panel products are synthetic polymer resins based on the consideration reaction of formaldehyde with compounds derived from either benzene or ammonia. Four major conventional wood binder thermosetting resins used in wood industries are phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), urea-formaldehyde (UF), and melamine-formaldehyde (MF). All four resins are available in wide range of formulations to satisfy different operating conditions and product requirements.[5, 30]

2.3.2 Nonconventional Binders

The conventional formaldehyde binders for composite wood panel products have several shortcomings that have become increasingly important over the last decade. For example, phenol-formaldehyde form a brittle glueline that for some end-use applications can become detrimental over time. Urea-formaldehyde resins are

Table 2.7 General chemical properties of rubber wood.[31]

Chemical Composition	Chemical Content (%)
Holocellulose	75.61-78.72
Cellulose	49.41-59.87
Pentosan	17.17-18.57
Lignin	18.06-19.03
Solubility in:	
Alcohol-benzene	2.87-3.51
Hot-water	1.08-7.91
Cold-water	0.96-2.45
1% NaOH	17.54-19.92
Ash	0.42-0.86

Table 2.8 General mechanical properties of rubber wood.[32]

Mechanical Properties	
Moisture content (%)	12
Specific gravity	0.70
Bending strength (kg/cm ²)	973
Compressive strength (kg/cm ²)	478
Shearing strength (kg/cm ²)	162
Stiffness (X100 kg/cm ²)	960
Toughness from impact bending (kg-m)	2.86
Hardness (kg)	538
Durability (year)	1.9 (0.5-3.8)

Table 2.9 Rubber plantation area of Thailand from 1993-1997.[33, 34]

Year	Total Rubber Plantation Area (rais)
1993	11,194,945
1994	11,307,810
1995	11,376,193
1996	11,443,575
1997	11,454,261

coming under increasing attack because of formaldehyde emissions and resulting indoor air pollution problems. Formaldehyde binders also have long pressing times, intensive energy consumption, and health risk for workers. Attempts to formulate new non-conventional bonding systems have explored ways to emulate the behavior of conventional binders. [5, 35, 36]

Lignins, tannins, and isocyanate are the new binders that would overcome these problems. They have shown the most promise as potential substitutes for conventional binders. Also, they have received the greater share of attention and funding. [5]

2.3.3 Isocyanate in Wood Industry

Isocyanates have been used in the manufacture of polyurethane resins for more than 40 years; however, their use in wood binder is relatively new. Manufacturing process of isocyanate is shown in Figure 2.7. Although isocyanate differs from other non-conventional binders because it is petroleum-derived, the novelty of its adhesion system and it improved technical performance increase its potential as an important substitute for thermosetting resins binders in the near term. Isocyanate can be used as coupling agent for wood filled thermoplastics. [5, 37, 38]

All isocyanates of industrial importance contain two or more isocyanate groups per molecule to enable polymers to be formed by condensation with other polyfunctional molecules. Only a limited number of isocyanate compounds have gained technical significance. Their selection is governed by such factors as reaction behavior, physiological properties, availability of starting materials, and economics of production.[5, 39]

Panels, and molded parts from wood chips, fibers, and veneers are used extensively in the furniture, building, packaging, and automotive industries. These article are produced under heat and pressure using a variety of organic binders. In the past these binders were primarily aqueous condensation polymers based on formaldehyde and urea, melamine, or various phenols. Today, polyisocyanate bonding agents are replacing these binder in many applications.

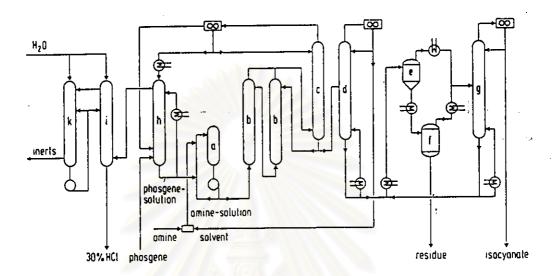


Figure 2.7 Manufacturing process of isocyanate, low pressure phosgenation.[21] a = cold phosgenator, b = hot phosgenator, c = wash column, d = solvent distillation, e = preflasher, f = evaporator, g = isocyanate distillation, h = phosgene removal column, i = HCl absorber, k = phosgene decomposition

Polymeric diphenylmethane diisocyanates (pMDI) are found increasing use because of their inherent value as bonding agents. Improved processing and end use performance compared to other bonding technologies account for the increasing volumes of polyurea being used.

$$\begin{array}{c|c} & \text{CH}_2 & \\ \hline & \text{OCN} - \text{CH}_2 & \\ \hline & \text{NCO} \end{array} \Big]_n$$

Figure 2.8 Polymeric diphenylmethane diisocyanates (pMDI). [40]

Because curing takes place when moisture reacts with polyisocyanate, polyureas are formed. For that reason the term "polyurea-bonded" particleboards is often used. pMDI binders offer significant processing and physical property advantages. These advantages can more than offset the higher costs of polyisocyanate binders.

pMDI has been accepted as a standard binder for construction particleboard. This reflects the excellent results obtained when pMDI is employed as a binder. The demand for control of formaldehyde emissions further intensifies the interest in formaldehyde free polyisocyanate binders.

Many forest and agricultural by-products, which were thought to be unsuitable for bonding, can in fact, be used effectively with polyisocyanate binders. This broadens the source of raw materials for bond composites and better utilizes environmental resources.[21]

2.2.3.1 Health and Safety

In general, the intrinsic toxicity of the main chemicals, isocyanates and polyols, by ingestion, absorption or implantation, is low although some isocyanates can cause skin irritation, which can be severe for some aliphatic isocyanates. The main hazard arises from the possible inhalation of isocyanate vapour, dust or aerosol droplets. All isocyanates are respiratory irritations and potential sensitisers, that is, they may cause allergic symptoms in susceptible people. Additionally, from more than 30 years of polyurethane industrial experience handling isocyanates there is nothing to suggest that they are human carcinogens. Inhalation studies of TDI in animals has shown that TDI is not a carcinogen at exposure levels up to 7.5 times the recommended maximum exposure level in workplace. [22]

Table 2.9 Vapour pressure of some isocyanates at their usual processing temperature.
[22]

Isocyanate	Melting Point	Vapour Pressure (at stated Temperature) (Pa)
Polymeric MDI	Liquid at 25 °C	6X10 ⁻⁴ (25 °C)
Monomeric MDI (pure MDI)	42 ºC	2.5X10 ⁻³ (42 °C)
IPDI, (Isophorone diisocyanate)	Liquid at 25 ^o C	4X10 ⁻² (25 °C)
TDI	Liquid at 25 °C	3.3 (25 ⁰ C)
HMDI, (Hexamethylene diisocyanate)	Liquid at 25 °C	6.7 (25 °C)
CHDI, (1,4-Cyclohexane diisocyanate)	- 62 °C	40 (62 °C)
NDI, (1,5-Naphalene diisocyanate)	130 ⁰ C	150 (130 ⁰ C)
PPDI, (p-Phenylene diisocyanate)	95 ºC	300 (95 °C)

2,2.3.2 Handling Isocyanates

The objectives of handling procedures are to avoid the inhalation of isocyanate vapour or aerosols and to protect eyes and skin from contact with isocyanates. Polymeric MDIs which are liquid at ordinary temperatures, are usually handled at room temperature when the vapour pressure is so low that the TLV-TWA is unlikely to be exceeded - unless the isocyanate is sprayed or airborne aerosol particles are created in some other way

Splashes into the eye will cause mild to severe irritation, and should be treated by immediate flushing the eye with copious amounts of clean, cold water or preferably using the contents of several sterile eye-wash bottles, which should be stored in a readily accessible position in the workplace. The eye should then be examined by a physician. Contamination of the skin should be treated by immediately washing with ordinary soap and water. The soap not only helps to emulsify and remove traces of isocyanate but also decontaminates by catalyzing the reaction between the isocyanate and water. [22]

2.3.4 Adhesion to Wood

The creation of bond between a binder resin and the wood substrate requires adequate interpenetration of the resin and wood components, and the development of links between the resin and the exposed wood surfaces. Adequate resin-wood contact in the binder application process is a necessary prerequisite to producing a good binder bond. The basic resin-wood contact is made in three phases: penetration, wetting, and diffusion. The liquid resin binder is applied to the wood; for wood flakes or particles, the resin is atomized and sprayed onto the surface.

At a minimum, the resin must penetrate the wood surface to the level of solidly attached wood fibers without destroying the continuity of the resin remaining in the binder film layer. Wetting must then occur between the binder and the solidly attached wood fibers; the surface tension of the binder film must be low enough to allow easy contact between the binder and wood molecules. Then, the molecular weight fractions of the binder must be diffused sufficiently into the wood

fiber cell walls to establish a molecular "hold" on a wood constituent. This diffusion is accomplished by some combination of solvent, heat, and/or pressure

The exact nature of the attractive force between the resin and wood molecule, which produce the actual adhesive bond, has not been clearly determined. In general, it is though that when resin molecules are brought into contact with wood molecules, a bond forms between reactive polar molecule groups of the resin and wood molecules. The three basic chemical processes are involved in binder bonding:

- 1) Van Der Waals forces: intermolecular forces caused by the creation of temporary positive and negative electrical fields (polarities) in adjacent nonpolar molecules.
- 2) <u>Hydrogen bonds</u>: electrostatic attraction between the hydrogen atom of one molecule and the fluorine, oxygen, or nitrogen atom of another. These particular intermolecular bonds are an specially strong type of dipole attraction between molecular molecules. In binder terminology, hydrogen is called "specific adhesion".
- 3) <u>Covalent bonds</u>: electrons are shared between two atoms; in wood adhesion, the formation of covalent bonds between parts of resins molecules and wood fiber molecules.

Mechanical forces have also hypothesized, but are usually not considered a major contributor to the wood binder bond. Studies have proven that all three types of bonds are possible in wood-resin adhesion, but the existence and/or relative importance of these bonding forces in final wood bonds is not yet known.

Since wood-resin adhesion is essentially chemical in nature, it is important that the resin contain sufficient numbers of reactive groups and that the wood surface present a significant number of reactive sites to able bonding.[5]

2.3.5 Bonding Reactions of Isocyanate

The chemistry of isocyanate and it ability to bond to wood are inextricably tied to the formulation of polyurethanes. The two major reactions in the

preparation of polyurethane are the reaction between isocyanate and hydroxyl-containing compounds and that of isocyanate and water (Figure 2.9 and 2.10). Other reactions that foster wood adhesion are the reaction of isocyanate group with amines and the formation of linkages with urethane. These reaction causes branching and crosslinking. These crosslinking also occurs from trimerisation, which leads to the formation of isocyanurate rings that are hydrolytically and thermally very stable. Isocyanates form various length bridges with the alkyl and phenolic hydroxy groups in wood cellulose and lignin. The reactions that take place between isocyanate and wood are displayed in Figure 2.11.

Figure 2.9 The reaction between isocyanate and hydroxyl-containing compounds. [22]

R-NCO + H
$$\stackrel{\text{H}}{\longrightarrow}$$
 H $\stackrel{\text{COH}}{\longrightarrow}$ R-NH₂ + CO₂ (2.2)

Carbarmic Acid $\stackrel{\text{H}}{\longrightarrow}$ O $\stackrel{\text{H}}{\longrightarrow}$ R-NCO $\stackrel{\text{H}}{\longrightarrow}$ R-NCO $\stackrel{\text{H}}{\longrightarrow}$ R-NCO $\stackrel{\text{H}}{\longrightarrow}$ R-NCO $\stackrel{\text{H}}{\longrightarrow}$ R-NCO $\stackrel{\text{H}}{\longrightarrow}$ Biuret

Figure 2.10 The reaction between isocyanate and water.[40]

Though the formation of polyureas, variation in the isocyanate polymer length occurs and contributes to successful wood bonding. One impediment on this process is water, which must be controlled. If too much of water is present, a large amount of isocyanate is deactivated and the system loss many of its binder qualities. The urethane linkages become too few in number to create adequate bonding between the wood surface and the binder.[5]

Figure 2.11 Generalized reaction scheme showing the possible reactions which are thought to occur in the curing pMDI-wood bondline.[40]

2.4 Wax Emulsions

The final component in most particleboard is a sizing agent to reduce the absorption of liquid water. This normally a paraffin wax emulsion which is supplied to the particleboard manufacturers at approximately a 50% wax solids in water. Less than 1% wax solids based on the ovendry weight is used in most particleboards; levels above 1% tend to interfere with interparticle bonding while levels below 0.75% do not offer maximum water resistance.[18, 41]

2.5 Manufacturing Process

Particleboard is produced in large, capital intensive plants with highly automated equipment. Processing steps during manufacturing are particle preparation, particle drying, binder-particle blending, mat formation, hot pressing, and finishing. A relatively small quantity of particleboard is produced annually by an extrusion process whereby the binder treated particles are forced between heated dies which polymerizes the binder and forms a continuous particleboard ribbon, which is then cut into desired lengths. The production of extruded particleboard has been steadily decreasing and, due to the limited mechanical properties, the use of this material is basically restricted to that of corestock for furniture.[18, 42] Figure 2.12 shows the flow diagram of the manufacture of particleboard.

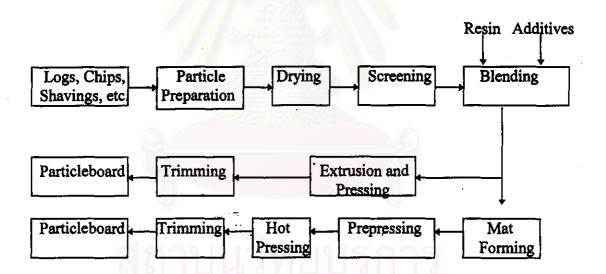


Figure 2.12 Flow diagram of the manufacture particleboard.[27]

2.6 Literature Review

The use of waste wood product, small and low-quality tree for particleboard production appears to gain in importance, at least, judging from the increasing number of research work in this area. Despite the large number of literature reference, systematic studies of various aspect of this area appear to be relatively rare. This is also the case with rubber wood flakes and various types of isocyanate materials used as binders for particleboard. In this literature survey, the various types of binders and wood composite are summarized as follows:

Wendler, S. L. and Frazier, Ch. E. [40] studied the effects of cure temperature and time on the isocyanate-wood adhesive bondline by ¹⁵N CP/MAS NMR. In this work, a 99% ¹⁵N-labelled polymeric methylenebis(phenylisocyanate) (pMDI) resin was used to make a series of wood-¹⁵N-pMDI composites cured as a function of temperature and time. Bonding chemistry was monitored using ¹⁵N CP/MAS NMR. Urea linkages were identified as the major chemical moieties at low cure temperatures, while biurets were predominant at higher temperature. Bondline chemistry did not change with time when curing at 120 °C. However, curing chemistry at 185 °C did change with time, from mostly biuret to urea. It is believe that urethane formation has been detected under the conditions that cleave biurets. This suggests that urethanes result from the thermal liberation of isocyanate via biuret cleavage. The ¹⁵N technique has proven valuable for the elucidation of this complex cure chemistry.

Holfinger, M. S., et al. [43] studied the difurfuryl diisocyanates which was renewable Ethylidenebis(2.5derived from resource. adhesives new furandivlmethylene)diisocyanate (EDFI) are structurally similar to diphenylmethane diisocyanate (MDI), which has proven to be an excellent adhesive for bonding wood composites. The MDI resin is synthesized from petroleum-derived chemicals; the EDFI resin was synthesized from biomass-derived chemicals. In this study, the mechanical properties of aspen flakeboard bonded with MDI and EDFI were compared. In general, results show that the strength properties of flakeboard bonded with MDI are only marginally better than those bonded with EDFI. Because EDFI was more viscous than is MD!, less than optimum atomization of the EDFI resin during spraying of the flakes is believed to be largely responsible for the differences in strength property values. The dry internal bond strength values of flakeboard bonded with MDI (1.33 MPa) and EDFI (0.97) at 3% resin content are significantly greater than the 0.41 MPa required by the American National Standards Institute (ANSI/A208.1) for type-2 medium density particleboard.

Vick, C.B., et al. [44] studied the structural bonding of acetylated Scandinavian softwoods for exterior lumber laminates. The bonding properties of a phenol-resorcinol-formaldehyde (RF), a resorcinol-formaldehyde crosslinking polyvinyl acetate (PVAx) and an emulsion polymerisocyanate (EPI) adhesive were determined in laminates of acetylated and unmodified Scandinavian pine (Pinus silvestris L.) and spruce (Picea abies Karst.) The effects of different degree of acetylation in adjacent laminae were also examined. The effectiveness of adhesion were determined by measuring delamination after three cycles of vacuumpressure soaking in water and drying, and by measuring shear strength and wood failure in dry and water saturated conditions. Acetylation stabilize laminates so that essentially no stress fracturing developed in wood during severe cyclic delamination tests. Bonds to acetylated and unmodified wood with RF and PRF adhesives resisted delamination well, whether adjacent laminae were of equal or unequal degrees of acetylation. Acetylation affected adhesion of both adhesives as indicated by lower percentage of wood failure after water saturation. The PVAx adhesive also resisted delamination well in acetylated wood so long as individual laminae had equal acetyl content. Acetylated laminates with PVAx effectively resisted stress fracturing near bondlines and within the wood, but the unmodified laminates fractures severely. The EPI adhesive bonded the unmodified laminates so well that no delamination and remarkably little stress fracturing developed during cyclic delamination tests. Acetylation affectes adhesion of the EPI adhesive as indicated by low wood failure in wet shear tests; however, shear strength and wood failure were high in acetylated wood in the dry condition.

Chen, R. and Wu, Q. [45] investigated the modified lignosulfonate as adhesive. Oxidized lignosulfonate (LS-OB) displays a high crosslinking during thermal condensation. When LS-OB was used as a partial substitute of urea-

formaldehyde (UF) in wood adhesive, a positive effect on the curing of resin could be observed. With 30-40% substitution, no detriment in strength properties of particleboard was observed. Polycondensation of lignin and UF could occur between methylol groups in UF resin and hydroxyl and carbonyl groups in lignin, through ether bonds and methylene bridges. A high surface activity of LS-OB would reduce the surface tension of binder solution and facilitate its distribution on wood particles, improving consequently the strength properties of particleboard.

Dix, B. and Marutzky, R. [46] investigated the modification of diisocyanatebased particleboard and plywood glues with natural polymers: polyphenol, carbohydrates, and proteins. The investigations aimed at finding some fast-setting glues for exterior plywood and particleboard based on diisocyanates in combination with compounds from renewable resources like tannins, proteins, and starches revealed the following: The mechanical properties of particleboard bonded with unmodified tannin extracts from spruce (Picea abies) and pine (Pinus sylvestris) were inferior. The fortification of the tannin extracts with nonemulsifiable diisocyanate modified with glutin or maize starch (extender content up to 20%) had exterior grade quality (German standard V100 for flat-pressed boards). Veneer plywood, which is conditionally weatherproof (German standard AW), can be produced by applying diisocyanate together with tannins or starches. The veneer wood species, the glue mixtures, the pressing conditions, and the fillers have to be adjusted to the diisocyanate type and to the extender. Modified, emulsifiable diisocyanate gave plywood with better strength and wood failure than glue formulations with nonemulsifiable diisocyanate.

Yusuf, S., et al. [47] reported on the properties enhancement of LVLs modified with some cross-linking agents. Chemically-modified laminated veneer lumbers (LVLs) were produced and their physical properties and biological resistance were evaluated. For the chemical modification, the vapor-phase formalization and the pad-dry-cure treatment of veneers with some cross-linking agents were employed prior to lamination of the treated veneer. The vapor-phase formalization was conducted for 5, 10 and 24 hours using tetraoxane as a source of formaldehyde, and the pad-dry-cure treatment with glutaraldehyde and dimethyloldihydroxy ethylene

urea (DMDHEU) were made after impregnation of their 2.5, 5 and 10% aqueous solutions. Sulfur dioxide was used as a catalyst in both treatments. Laboratory tests with a brown-rot and a white-rod fungus reveal that decay was almost completely suppressed at the high level of treatment, and fairly eliminated at the low level treatment. The treatment could reduce the weight loss of specimens caused by termite attack, but the effectiveness in resisting it was not as sufficient as was decay resistance. All treated LVLs were very stable to water soaking even in the 2-hour boiling on thickness swelling as well as linear expansion along tangential direction.

Kawasaki, T., Zhang, M. and Kawai, S. [48] investigated the ultra-low density fiberboard and sandwich panel. Low density fiberboards and veneer overlaid fiberboards (sandwich panel), two types of panel products were produced. Low density fiberboard, short fibers were prepared from radiata pine (Pinnus radiata D. Don) and long fibers were prepared from yellow cedar (Chamaecyparis nootkatensis Spach). Foam-type and bond-type polymeric isocyanate were used at 10 and 30% resin content levels. The formed fiber-mat was pressed into density of 0.05-0.5 g/cm³. The veneers were spread with similar resin type at 75 g/cm³, overlaid on the fiber-mat faces. The assembled sandwich panels were then pressed to target densities of 0.35 and 0.45 g/cm³. These fiberboards produced were of good dimensional stability and of high mechanical strength inspite of its low density. These properties were further enhanced by overlaying with veneers. The thickness swelling of sandwich panels were less than 6% after soaking for 24 hours and less than 9% even after the boiling condition. The thermal conductivity of low density fiberboards is very low and almost equivalent to those of thermal insulation material such as polystyrene foam and fiberglass wool.

Sudiyanni, Y., Imamura, Y. and Takahashi, M. [49] studied on the weathering effects on several properties of chemically modified wood. Wood specimens of albizzia (*Paraserianthes falcata* Becker) and sugi (*Cryptomeria japonica* D. Don) were prepared. They were chemically modified by acetic anhydride, propylene oxide, paraformaldehyde, dimethyrol dihydroxy ethylene urea (DMDHEU), and phenol-formaldehyde resins. Half of all specimens were exposed to natural weathering with rainfall for one year. Another half of specimens were subjected to artificial weathering

for total 1,080 hours which was combined with UV-irradiation and water spray. For sugi wood, all modified specimens kept better surface performance and lesser weight loss after natural and artificial weathering than that of untreated controls. Decay resistance of modified sugi wood reduced in all treatments after weathering, particularly by artificial weathering. However, PF-resin treated blocks were most resistant after weathering. While in albizzia wood, acethylated blocks were ranked best in yielding the highest resistance after weathering.

Zhang, M., Kawai, S. and Sasaki, H. [50] studied the production and properties of composite fiberboard. The jute/wood composite fiberboard (JWB) and bamboo/wood composite fiberboard (BWB), the mixing ratios of jute fiber to wood fiber and bamboo fiber to wood fiber were 1/0, 3/1, 1/1, 1/3 and 0/1. The target specific gravity for JWB were 0.45, 0.65, 0.85, 1.00 while 0.60 and 0.80 for BWB were considered. Isocyanate resin was used as binder for both JWB and BWB and the amount of adhesive addition was 10%. For JWB, the effect of mixing ratio was dependent on the specific gravity of the board. At a specific gravity of 0.45, no significant difference was observed on the MOR of the boards of all mixing ratios. However, when the specific gravity of the board was higher than 0.65, the bending strength increased and the high strength properties of jute fiber was realized. Bamboo fiberboard with a specific gravity of 0.60 has similar strength properties as the wood fiberboard of the same specific gravity.

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