EVALUATION OF OIL PALM TRUNK BASED ADHESIVE FOR PARTICLEBOARD

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UNIVERSITI SAINS MALAYSIA

2013

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

July 2013

ACKNOWLEDGEMENT

First of all, thanks to ALLAH S.W.T for his mercy and guidance in giving me full strength to complete this research. A lot of thanks to my supervisor, Professor Rokiah Hashim for all of her support, guidance and advice she has provided throughout my research. I have been lucky to have a supervisor who cared so much about my work. I would also like to thank Professor Othman Sulaiman, Professor Salim Hiziroglu from Oklahoma State University, USA and staffs from School of Industrial Technology for their helping hand. I also need to thank my parents, Sulaiman Amin and Ramlah Ismail, for encouraging me to pursue my study. All the support they have provided me was the greatest gift anyone has ever given me. Also, I need to thank my beloved husband, Mohd Hazim Mohamad Amini, who shows me how to do everything and for spent his time to help me. Finally, I would like to thank Ministry of Higher Education of Malaysia for the MyMaster scholarship and Universiti Sains Malaysia for RU research grant (1001/PTEKIND/815066) and Graduate Assistant scheme, respectively, which allowed me to complete this research.

Thanks.

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LIST OF SYMBOLS AND ABBREVIATIONS

UF	Urea formaldehyde
OPS	Oil palm starch
OD	Oven dry
MOR	Modulus of rupture
MOE	Modulus of elasticity
IB	Internal bond
SEM	Scanning electron microscopy
XRD	X-ray diffractometry
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
NOPS	Native oil palm starch
EMOPS	Epichlorohydrin-modified oil palm starch
EMOPSUF	Epichlorohydrin-modified oil palm starch with UF resin
NRS	Native rice starch
EMRS	Epichlorohydrin-modified rice starch
EMRSUF	Epichlorohydrin-modified rice starch with UF resin

PENILAIAN PEREKAT BERASASKAN BATANG KELAPA SAWIT UNTUK PAPAN SERPAI

ABSTRAK

Projek ini mengkaji potensi kanji yang diekstrak daripada batang kelapa sawit untuk digunakan sebagai perekat komposit kayu. Kanji beras komersial turut digunakan untuk dijadikan sebagai perbandingan. Kanji diubahsuai dengan menggunakan epichlorohydrin untuk memberikan kesan sifat yang lebih baik berbanding sifat kanji dalam bentuk asli. Kanji tersebut kemudiannya digunakan di dalam pembuatan papan serpai yang dihasilkan daripada partikel-partikel kayu getah. Papan serpai yang dihasilkan dengan menggunakan urea formaldehid digunakan sebagai sampel papan serpai kawalan. Ujian fizikal dan mekanikal papan serpai termasuk kandungan lembapan, pembengkakan ketebalan, penyerapan air, kekuatan lenturan dan kekuatan ikatan dalaman dinilai berdasarkan Piawaian Industri Jepun. Papan serpai turut dicirikan dengan menggunakan mikroskop pengimbasan elektron, analisa penguraian sinar X, analisa termogravimeter, dan analisa kalorimeter pengimbas perbezaan.

Sifat fizikal dan mekanikal yang diperolehi melepasi piawaian minimum yang dinyatakan seperti di dalam piawaian ini kecuali bagi sifat pembengkakan ketebalan dan penyerapan air. Analisis daripada pencirian papan serpai menunjukkan bahawa papan serpai yang dihasilkan dengan menggunakan perekat kanji terubahsuai yang dimasukkan dengan perekat urea formaldehid menunjukkan sifat-sifat yang lebih baik. Ini disusuli dengan papan serpai yang dihasilkan dengan menggunakan perekat kanji terubahsuai dan perekat kanji asli. Papan serpai yang dihasilkan dengan menggunakan perekat kanji beras turut menunjukkan sifat-sifat

yang lebih baik berbanding papan serpai yang dihasilkan dengan menggunakan perekat kanji kelapa sawit. Walau bagaimanapun, kanji kelapa sawit masih mempunyai potensi yang baik untuk dikomersialkan sebagai perekat dalam industri papan serpai.

EVALUATION OF OIL PALM TRUNK BASED ADHESIVE FOR PARTICLEBOARD

ABSTRACT

This study investigated the potential of starch extracted from oil palm trunk to be used as wood composite adhesive. Commercial rice starch was used as a comparison. The starch was modified with epichlorohydrin to impart it with better properties than its native form. The starch was then employed in the manufacturing of particleboard made from rubberwood particles. Particleboard manufactured using urea formaldehyde adhesive was used as a control particleboard samples. The physical and mechanical testing which includes moisture content, thickness swelling, water absorption, bending strength and internal bond strength of particleboard were evaluated based on the Japanese Industrial Standards. The particleboard was also characterized by using scanning electron microscopy, X-ray diffractometry analysis, thermogravimetric analysis, and differential scanning calorimetry analysis.

Physical and mechanical properties obtained meet the minimum requirements as stated in this standard except for thickness swelling and water absorption properties. The analysis from characterization of particleboard showed that particleboard bonded with modified starch adhesive impregnated with urea formaldehyde resin possess better properties. This is followed by particleboard bonded with modified starch adhesive and native starch adhesive. Particleboard bonded with rice starch adhesive showed better properties than that of particleboard bonded with oil palm starch adhesive. However, oil palm starch still has a better potential to be commercialized as a binder in particleboard industry.

1.0 INTRODUCTION

The particleboard industry which encompassed in wood-based industry has become one of the main industries that contribute to the economy growth in many countries. Any panel product which is made by utilizing wood particles is a basic explanation for particleboard. These wood particles were bonded with adhesive and pressed at a specific pressures and temperatures. The problem associated with high cost in using logs and lumber has been solved as particleboard industry emerges. Besides, particleboard was found to have a great number of advantages such as better resistance towards bacteria, fungi and insects attack. Their properties can be engineered and special properties can be made such as low thermal conductivity, fire resistance, or improving their surfaces for decorative purposes.

1.1 Problem statement

The particleboard industry associates with several problems. One of the main problems is the formaldehyde release which can cause a bad health effect to human. This problem arises as the main binder used in particleboard industry is urea formaldehyde (UF) resin. The exterior uses were irrelevant since the UF resin is not weather resistant. Therefore, the usage of UF resin was concentrated on the interior uses. Yet, the formaldehyde release problem has restricted the quantity of interior uses since there are regulations which limit the maximum of formaldehyde in the air. Thus, another alternative that can be applied is by using natural based adhesive as a binder instead of UF resin (Thoemen et al., 2010).

Natural based adhesive can be derived from many natural sources such as protein, blood and starch. Starch has been seen as one of the natural sources which have a great potential to be utilized as a binder in manufacturing of particleboard.

Starch is relatively abundance, can be obtained at low cost (Huber and BeMiller, 2010) and easy to be isolated in a pure form (Robyt, 2008). However, starch in its natural form possesses numerous deficiencies in order for it to be exploited in industry. These deficiencies include high proneness to retrodegradation, deficiency in process tolerance and high viscosity at low solids content which results in handling problem (Huber and BeMiller, 2010). Thus, starch need to be modified either through chemical modification or physical modification to overcome these defects. Modification process will alter the properties of native starch by altering the functionality of starch. The most common starch modification process was completed chemically. This includes oxidation, esterification and etherification. The starch modified chemically results in starch with high stability against acidic, mechanical shearing, high temperature hydrolysis and decreasing in retrogradation rate (Xie et al., 2005).

There are four chemical reagents that are most widely used namely adipic and acetic mixed anhydrides, phosphorus oxychloride, sodium trimetaphosphate and epichlorohydrin. Nevertheless, epichlorohydrin is the most common chemical reagents which have been used in polysaccharide chemistry (Ačkar et al., 2010). According to Jyothi et al. (2006), the modification of starch with the use of epichlorohydrin as reagents results in formation of distarch glycerols. This leads to the formation of ether linkages between the cross-links and the hydroxyl groups in starch granules. The resulting starch was found to be more resistant to mechanical shear and pH.

Oil palm tree (*Elaeis guineensis*) is one type of plant which provides many other useful applications from its different parts of tree other than production of oil from its fruits. Most of these parts were treated as wastes and were left to decay or burned. One of the parts from oil palm tree which contribute to a large number of wastes and can be utilized into other valuable product as well is the oil palm trunk. Oil palm trunk can be used to produce plywood (Mokhtar et al., 2011) or serve as a source for starch extraction. Tomimura (1992) reported that oil palm trunk parenchyma consists of 55.5% starch while Noor et al. (1999) stated that the oil palm trunk contains of 7.15% starch. The relatively high starch content in the oil palm trunk make the extraction of starch was possible to be carried out.

Numerous researches had been carried out investigating on starch modification to be utilized as a binder in particleboard manufacturing. Cheng et al. (2004) had done a research on the utilization of modified soybean flour in wheat straw particleboard. This was done to improve the mechanical properties and water resistance of resulting particleboard panels. The results showed that panel manufactured using soybean flour modified with urea and N-(n-butyl) thiophosphoric triamide had better mechanical properties while the panel bonded by boric acid treated soybean flour had better water resistance. The mechanical properties of particleboard bonded with corn starch-tannin adhesives had been investigated by Moubarik et al. (2010a). According to their study, the resulting particleboard had comparable mechanical properties to the panel manufactured by using urea formaldehyde (UF) resin.

Most researchers had carried out investigation on the modified starch characteristics to be used as adhesive. However, research based on the utilization of oil palm starch as a raw material to produce natural based adhesive in particleboard manufacturing has not been done yet. Therefore, this study was carried out to study the properties of epichlorohydrin-modified oil palm starch as well as its potential to be utilized as a natural binder in particleboard manufacturing.

1.2 Objectives

The objectives of this study are:

1) To study the properties of modified oil palm starch as compared to their native starch properties.
2) To compare the properties of oil palm starch with properties of commercial rice starch.
3) To investigate the properties of particleboard bonded with native and modified starch adhesive as well as modified starch adhesive impregnated with urea formaldehyde resin.

2.0 LITERATURE REVIEW

2.1 Wood-based industry

Wood-based industry has been one of the most important resource-based industries and export earner that led to the economy growth in Malaysia (Malaysian Investment Development Authority, 2012). The wood-based industry comprises of four sectors which are primary wood processing, secondary wood processing, tertiary wood processing as well as pulp and paper products. The sawn timber, veneer and plywood are categorized under the primary wood processing. Products such as reconstituted panel products (particleboards, medium density fibreboards (MDF), laminated veneer lumber (LVL)) in addition to builder's joinery and carpentry (BJC) and mouldings were categorized under the secondary wood processing. The tertiary wood processing comprises of product such as furniture and furniture components (Teischinger, 2012).

The wood-based industry in Malaysia comprising of almost 5,870 manufacturing establishments which make this industry was classified as one of the largest industry in Malaysia. Among them, about 80-90% is considered as SME which stand for small or medium enterprises and only a small amount of them are regarded as big companies. A capacity of 9.5 million cubic meters per year was covered by more than 1, 200 sawmill mills in Malaysia. These mills have a workforce of 5, 500 employers as well (Anonymous, 2012).

The state of Sabah and Sarawak in Malaysia locates most of the larger sawmills, veneer mills and plywood mills. The plywood mills accounted for more than 45 per cent while the mouldings mills accounted for about 60 per cent. The tropical wood species were consumed for the manufacturing of sawn timber, veneer, plywood and other veneered panel products by mills in Sabah and Sarawak. The downstream processing mills for the secondary and tertiary wood processing sectors are primarily located in Peninsular Malaysia. The rubberwood from sustainable plantations is the source that was utilized by mills in Peninsular Malaysia in order to produce the reconstituted panel products, builders' joinery and carpentry products (BJC), mouldings, furniture and furniture products (Malaysian Investment Development Authority, 2012).

2.1.1 Utilization of rubberwood in a wood-based industry

The Amazon forest of Brazil is the native habitat of rubber tree. The introduction of rubber tree from its native habitat to the South East Asia was credited to Henry Wickham (Ciullo and Hewitt, 1999). Then, the rubber seeds were shipped by him to the United Kingdom in 1876. Among all, a total of 2,700 seeds were successfully germinated. This was followed by the planting of rubber seeds in the Botanical Gardens, Sri Lanka in the same year. One year afterward, fifty of these seedlings were shipped to the Singapore Botanical Gardens. However, another 22 plants were sent as the earlier seedlings were not survived. Finally, the rubber tree was introduced in Malaysia as nine of these plants were then shipped to Kuala Kangsar, Perak. Further shipments of seed were then made directly from Brazil to Java, Indonesia in later years (Hong and Sim, 1994).

The demanding for rubberwood by the different sectors comprises in the wood-based industry is increasing. Normally, the rubber trees are cut down and replanted after 25-30 years when they are uneconomical for latex tapping. Then, the wood is harvested and become a raw material to be used in the wood-based industry. Formerly, the rubberwood was regarded as a waste. At that moment, the rubberwood was commonly utilized as a fuel wood or just burnt away (Ratnasingam et al., 2011). The commercial utilization of rubberwood in Malaysia was only started in the late of 1970. Forest Research institute Malaysia (FRIM) was the first organization that conducts numerous researches to determine the potential use of rubberwood and its application in the manufacturing of products such as fibreboard, wood pulp and other. However, these attempts were almost ignored as at that time because the supplies of wood sources were abundance and can be obtained at low prices. Year by year, as the forests area available for logging decreases, the logs were always supplied in smaller size. The labour costs were increasing as well which make the rubberwood arises as an important raw material to be utilized in a wood-based industry especially in a furniture manufacturing (Hong and Sim, 1994).

Nowadays, the rubberwood is known as one of the major sources for wood-based industry in Malaysia which is easy to machine, cut and durable. It was also recognized as a plantation species that is environmental friendly. Therefore, the rubberwood was often utilized in the local furniture industry. The rubberwood furniture products in Malaysia accounted for roughly 80% of the overall export value of wooden furniture (Ratnasingam et al., 2011). The Malaysian rubberwood furniture products were exported to the other country such as USA, Japan and the West Asia (Malaysian Timber Industry Board, 2012). The rubberwood in Malaysia was used in the manufacturing of panel products such as plywood and laminated veneer lumber (LVL) as well. Rubberwood in the form of off-cuts, edges, slabs and branches were utilized in the medium density fibreboard (MDF), particleboard and wood cement board (Ratnasingam et al., 2011).

Despite Malaysia, India was acknowledged as the first country to use rubberwood as a raw material in a wood-based industry. However, Malaysia could claim to be the first to success in rubberwood export in the late 1970. The first country which imports the rubberwood and rubberwood products from Malaysia was Japan. At present, other countries such as Thailand and Indonesia follow the same path as Malaysia by actively evolving the processing and export of rubberwood. Since, the rubberwood was acknowledged as environmental friendly species as it is grown in renewable plantations, the acceptance of rubberwood products is very high especially in countries which has sensibility towards “green movement” (Hong and Sim, 1994).

2.2 Particleboard

Particleboard is a composite product made by compressing the mixture of discrete wood particles and resin or other appropriate binder under heat and pressure. Particleboard also is known by other names such as flakeboard, chipboard, waferboard or shavings board (Wilcox et al., 1991). These names indicate the particle’s size and shape used in the manufacturing process. The wood particles used in particleboard manufacturing usually derived from waste materials of sawmills and plywood and woodworking plants. The manufacturing of particleboard mostly involves the pressing process in flat-platen presses. However, there is a small amount which was extruded through a long, wide and thin heated die. The particleboard can be produced in a single layer or multilayer with a higher density top and bottom surfaces. The main structural use of particleboard is in the manufacturing of horizontal and vertical diaphragms. The uniform building code now permits particleboard to be used as lateral-force-resisting diaphragms. The other structural uses of particleboard also were found in the manufacturing of subflooring and roof sheathing (Stalnaker and Harris, 1997).

Particleboard is one of the engineered wood products which were categorized under the non-structural wood products. The other product that belongs to the same category is medium density fibreboard (MDF) (Kirby and Kelsey, 1996). Another category of engineered wood products is known as structural wood products which comprises of products such as structural plywood, oriented strandboard (OSB), structural composite materials, glue laminated timber (Glulam), laminated veneer lumber (LVL) and strand lumber (parallel or oriented) . Nowadays, particleboard has been one of the products that manufactured more by Malaysian wood manufactures in addition to other products such as structural plywood, LVL, and MDF. This fact is due to the need to maximise the utilisation of wood resources. Currently, there are 32 mills that are manufacturing particleboard available in Malaysia (Malaysian Investment Development Authority, 2012).

2.2.1 History of particleboard

The history of particleboard manufacturing was started in the late 1940 in Germany (Salthammer et al., 2010). This wood-based product was then introduced to Australia in 1957. The processing of particleboard is started by removing the log's bark. It was then converted into thin flakes and dried. The process was continued by mixing the flakes with urea formaldehyde resin (Kües, 2007). A heated die was used to extrude the mixture constantly. Years later, in 1960, Pyneboard Pty. Ltd. built a second plant at Oberon, New South Wales. This plant utilized the process which was improved by forming the board on an endless steel wire mesh. The board was then cut into a specific length before they were pressed between the heated platens (Algar, 2009). More new plants were built afterwards since the economy of the 1960 was expanding coupled with other factors such as the availability of raw material increases and the product gain a high acceptability. In the 1970, this tapered off as building industry activity slackened but new plants sustained to be built, so that by 1978, capacity utilization was down to around 60 per cent. The industry has been innovative in process and product as well as raw material, mainly by adapting overseas developments to local environments. It has made broad use of sawmill residues, which amount to above 50 per cent of its raw material (Kües, 2007; Algar, 2009).

The introduction of wood-veneered particleboard was accomplished in 1961, by Westralian Forest Industries. The improvement in particleboard product was carried out in the early 1970 by applying plastic laminates on the surfaces of the manufactured particleboard. The particleboard manufacturing was facing another modification in the mid of 1970 by utilizing water-resistant phenol- or tannin-formaldehyde resin instead of urea formaldehyde resin. This improvement contributes ideas to the wood-based industry to develop other potential structural applications. This improvement was carried out with support and help from the Wood Technology Division of the New South Wales Forestry Commission and the Capricornia Institute of Advanced Education (Algar, 2009).

The other type of modified particleboard which utilizes elongated particles is acknowledged as oriented strandboard (OSB). Pyneboard’s plant located at Tumut, New South Wales, Australia, was the first to introduce and manufacture this type of particleboard (Anonymous, 1967). The overall economics of softwood plantation forestry was said to be influenced by the particleboard industry. This fact is due to the usage of thinning, tops and sawmills residues in the particleboard manufacturing. The emerging of particleboard industry also led to the reducing demand for solid wood and plywood (Andersson, 2003).

2.2.2 Particleboard manufacturing process

The process flow of particleboard manufacturing was illustrated as in Figure 2.1.

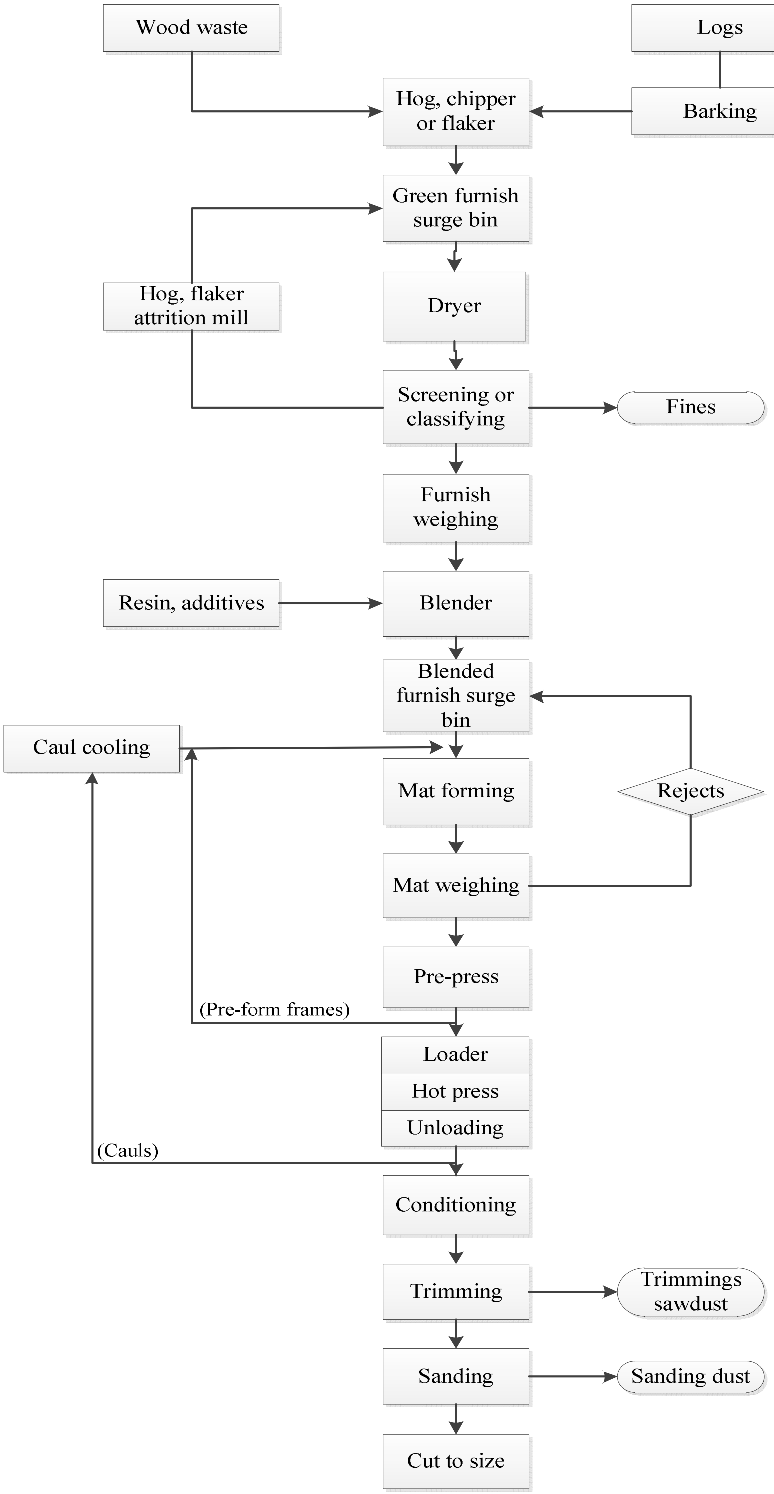

Figure 2.1: A process flow of particleboard manufacturing (FAO, 1990)

Practically, most of the particleboard manufacturing in industry involves a process flow as illustrated in Figure 2.1. The main processes comprise in particleboard manufacturing are particle preparation, particle drying and screening, blending and mat forming, pressing and board finishing. Each process needs different types and different amounts of energy.

A lignocellulosic raw material utilized in the manufacturing of particleboard can be derived from many sources. The particleboard manufacturers are required to use low grade residues such as hogged mill waste, planner shavings and sawdust as increasing in competition for solid wood and solid wood residues happens. The raw materials need to be segregated according to size and if possible the raw materials need to be segregated according to their type as well (FAO, 1990; Environmental Protection Agency, 1995). Bark removal need to be done so as to avoid blunting chipper knives or other reduction equipment. The core and surface layers of the particleboard requires particles with different size and geometry. This can be completed by using various reductions equipment which matched to the range and size of wood and wood residues used. Some common equipments used in the industry are chippers, knife-ring flakers, hammer mills and disc refiners. Each of this equipment is operating either by using knives, hammer bars or grooved disc plates (FAO, 1990).

The particles were then dried to a moisture content of about three to eight per cent. This was carried out for the purpose of particles bonding with resin. In industry, the particles drying were done by exposing them to hot gases or heat using rotating horizontal dryers. These hot gases or heat were emitted from the tube bundles which carry hot water, steam or thermic oil (United States Department of Agriculture, 2007). The particle drying is also known as continuous process. An alternative to rotary dryers is known as flash drying which requires quite lower drying temperatures compared to rotary dryers. The particles drying process was followed by particles screening process as moist particles tend to stick together. This will lower the overall efficiency of the screening process as the stick particles will plug the screen plates. This process was carried out in a vibrating or gyrating screens, or by way of air classification. In this process, the particles were screened based on their size. This fact is due to the different particle size was used for the face and core layers of the particleboard. The fines developed in this process were screened out while the oversized particles need to be recycled again for further reduction. This can avoid a disproportionate amount of resin consumed (FAO, 1990).

Synthetic resins like urea, phenol and melamine formaldehyde are the most type of binders used to bind the particles together. The application of resin in the industry was in the range of three to ten per cent. Most particleboard was manufactured with the addition of additive to impart properties such as fire resistance. The mixture of particles, resin and additives are blended in batches or as a continuous operation under controlled conditions. Slow speed are required if the blending process takes place in a large vat. Higher speed was utilized if the blending takes place in a small blender and this usually required shorter blending times (Akovali, 2005).

The older formers required manual equalizing in mat formation process compared to the mat forming process in modern particleboard plants which is a wholly mechanical process. There are wide variation of former existed nowadays. Though, the basic principles between them are still similar. The uniform flow of particles from a surge bin is fed to the former (Shrivastava, 2005). The forming heads of the formers may be fitted as either single or multiple and either stationary or moving. This forming head is designed so that the coarser particles are delivered to the core layer of the mat while the finest particles form the surface layer. The formation of evenly distributed mat with desired weight is crucial. The mats which do not fit in with the set standard are rejected and recycled (Shukla and Singh, 1994).

The cauls or metal plates are used to transport the mat to the pre-press and hot press after the mat formation. The cauls are then transferred manually or mechanically wheeled to the press. In the case of caulless systems, flexible metal webs, plastic belts and trays are responsible for the transportation of mat to the hot press (Akovali, 2005). Pre-press is a common process prior to the hot pressing process due to the consolidation and decreasing in mat width. This fact allows easy handling and reduces pressing time since the narrower openings in the hot press can be utilized. The condition of pre-press can be either hot or cold, differ from the main press which often heated and the temperature is depending on the type of press and resin used (FAO, 1990).

After the hot press process, the board forms are separated from the cauls by hand, turning devices or chains. Then, the cauls are returned to the forming station on push carts. The other way to return the cauls is by transporting them mechanically on a fixed return line after being stacked and cooled. The boards form are cooled and conditioned to avoid resin degradation. The edge of the boards are trimmed by trimming saws and cut using the same equipment (FAO, 1990; Environmental Protection Agency, 1995). The edge trimmings are being recycled or used for fuel. A knife planer and belt or drum may be used to meet the set standards of thickness and surface quality. Then, the boards were cut to size along their width and length by using a combination of saw, based on the dictates of the markets. The normal size of particleboard was 1220 x 2440 mm with the thickness in the range of 3-35 mm. The normal density of particleboard was in the range of 400-800 kg/cm^3 which is categorized as a medium-density board (FAO, 1990).

2.3 Wood adhesives

A main chemical ingredient in all formulations of wood adhesives is an organic polymer that is derived from either natural or synthetic origin (United States Department of Agriculture, 2007). The wood adhesives are set by cooling or elimination of excess moisture by means of pressure, heat or absorption into the wood (Pinto, 1981). There are various adhesion theories available that are chemical bonding, diffusion, adsorption, van der Waals interactions, molecular interactions and mechanical interlocking. Wood adhesion could involve several of these adhesion theories, depends on the structure of the wood and type of adhesive being employed (Kurjatko and Kúdela, 2002).

In 1930, the wood adhesives based on synthetic origin were produced commercially. This marked the starting of fundamental changes in the formulation of wood adhesives from natural to synthetic origin. The production of synthetic based adhesives in this year has marked the beginning of reduction in the utilization of natural based adhesives as well. This is due to the properties of synthetic based adhesives which are stronger, rigid, and durable accompanied by high water resistance property than natural based adhesives (United States Department of Agriculture, 2007).

Condensation resins based on formaldehyde were the largest employed material within the wood adhesives industry. These resins are formed by reacting formaldehyde with one or more chemicals like urea, melamine, phenol or resorcinol or with combinations of these substances. These adhesive resins are used in liquid form and consist of primarily linear or branched oligomeric and polymeric molecules in an aqueous solution. During curing of the resin, they were converted to insoluble and non-melting three-dimensionally crosslinked networks with the hardening conditions whether acidic (aminoplastic resins), highly alkaline (phenolic resins) or neutral to light alkaline (resorcinol resins, tannins). Isocyanates were also a popular wood adhesive but did not involve formaldehyde in its formulation (Dunky and Pizzi, 2002).

On the natural side, tannin, lignin, animal glue, protein glue and starch based vegetable glue were the most popular type of binders used in wood bonding. Tannin is a binder that is obtained from tree extract. Hydrolysable tannin and condensed tannin are two main types of tannin. Hydrolyzable tannin is made up of simple phenols such as ellagic acid and pyrogallol. However, condensed tannin is the most used binder which constitutes more than 90% of the total world production of commercial tannins due to its abundance in various tree barks. Acacia (mimosa bark extract), Tsuga (hemlock bark extract), Schinopsis (quebracho wood extract), Rhus (sumach extract) species and various Pinus bark extract species are some of trees that could be extracted to get tannin (Pizzi, 1982). An example of tannin structure is shown in Figure 2.2.

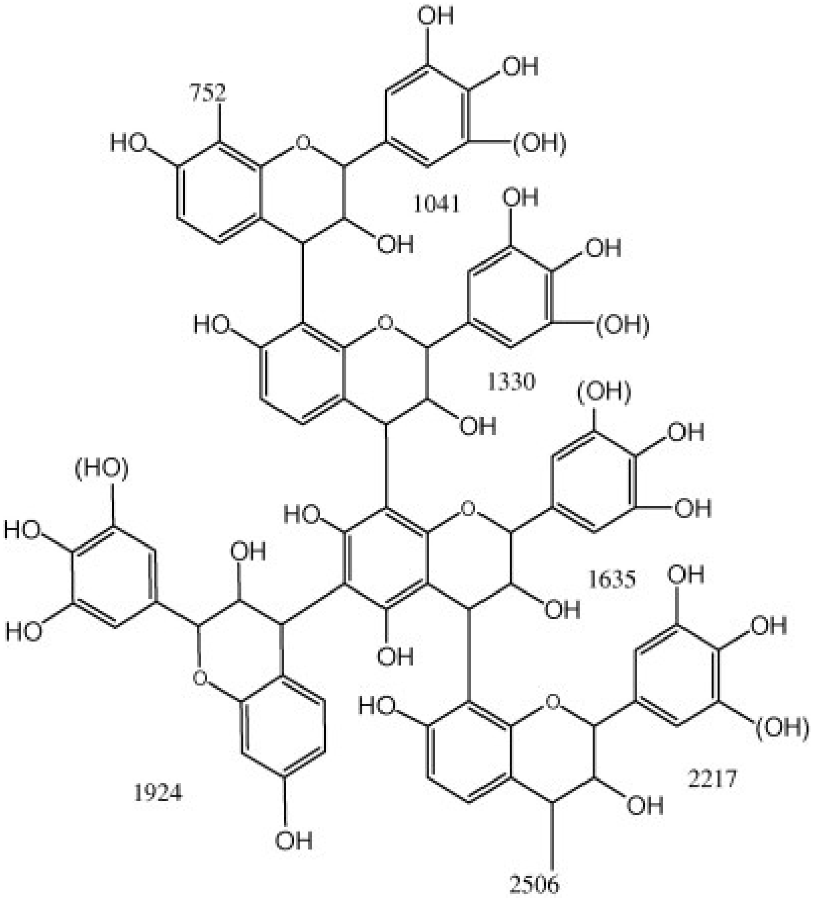

Figure 2.2: *Acacia mangium* tannin (Hoong et al., 2010)

Lignin is a source of natural phenolic adhesive. Lignin is a polyphenolic substance with amorphous structure. They were built up from three basic units that are p-hydroxyphenyl, guaiacyl and syringyl structures connected with carbon atoms in phenylpropanoid units. Lignin is a major component of plants which usually obtained as by-product of pulping process (Hatakeyama and Hatakeyama, 2004). Lignin was used solely as a binder or as addition to phenolic resins. The function of addition of lignins to phenolic resins can be as an extender or to chemically modify the resin. Using lignin alone as adhesive has several drawbacks. The hardening process is slower as compared to phenol due to the low reactivity because of lower number of reactive sites in the molecule. This will further cause increased press times for curing. Next is the concern of chemical variation in the feedstock where the chemical structure of lignin is very complex with non-fixed structures (Dunky and Pizzi, 2002). An example structure of lignin is shown in Figure 2.3.

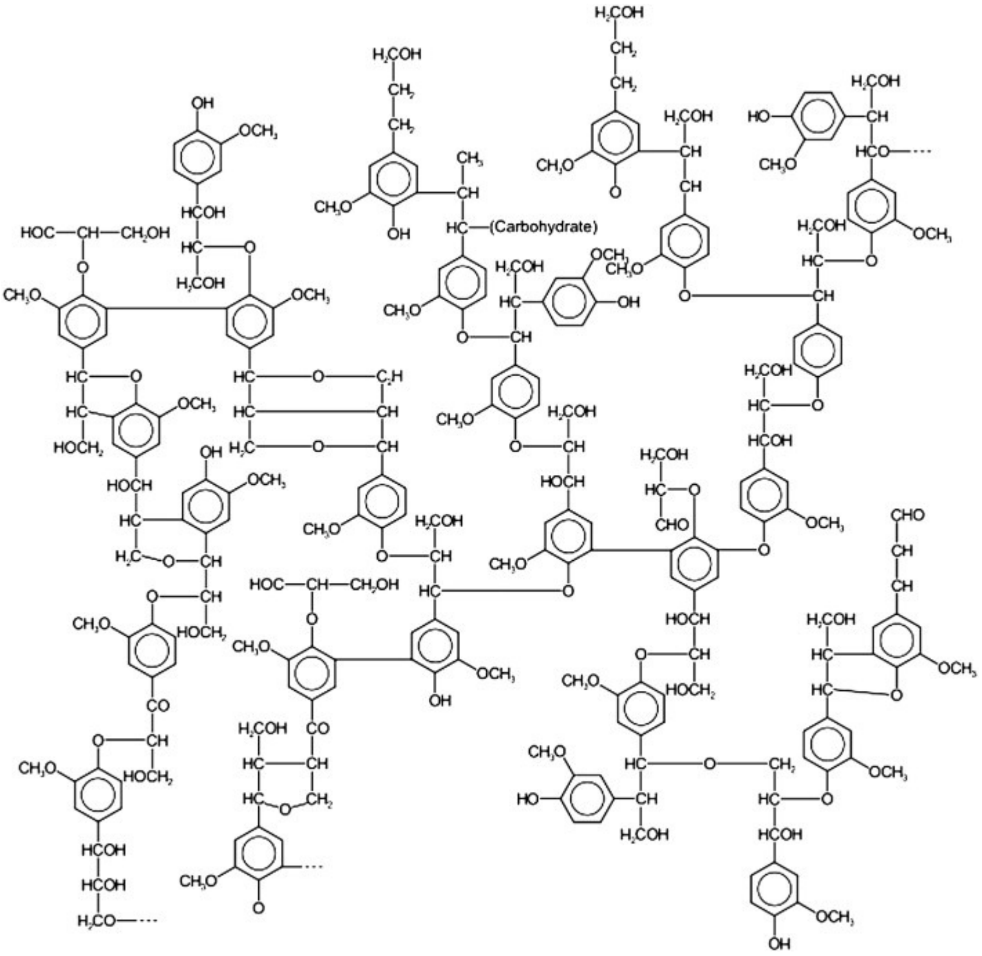

Figure 2.3: An example structure of lignin (Sakagami et al., 2010)

Animal glue was typically made from the bones and hides of cattle, horses and sheep. This animal glue was frequently classified as either hide or bone glue. Adhesive from fish was also grouped under this type of adhesive. Animal glues were obtained in powder, as beads or as a jelly. Solid form of animal glue was soaked in water, heated up to 60 ºC to reduce their viscosity to a level it can be applied onto wood. Fish glue was usually available readily in liquid form which was easier to use. Animal glues take time to dry and develop full strength. Furthermore, they have low moisture resistance, susceptible to attacked by molds and fungi, making them inconvenient to use. They must be applied at the proper temperature besides they are relatively expensive (Eckelman, 2012).

Soybean glue, casein glue and blood glue are classified under protein type. Soybean is a protein based vegetable glue which was manufactured from soybean meal. Soybean glue lacks of water resistance when compared to casein glue. Other characteristics are almost the same. Soy bean glue was used alone or mixed with blood glue to bind wood with the help of hot press. In older days it was used to bond softwood plywood for interior use but now had been largely replaced by phenolic resins (da Silva et al., 2011).

Close to soybean glue is the casein glue. The casein curd which was obtained from precipitation of skim milk or buttermilk was used to prepare the casein glue. In order to obtain this casein curd, the milk was allowed to sour naturally or with the help of acid. The preparation of glue needs the curds to be dissolved in an aqueous alkaline solvent for instance lime water. Most casein glue is sold in dry powder form. Thus, it must be dissolved in water prior to use. Once mixed with water, casein will have a shorter pot life. Casein glues were important in the older days because of their superior moisture resistance compared to animal and soybean glues (Carvill, 1994). However, there are several characteristics which limit their usefulness. First, they are likely to stain wood species which are rich in tannic acid such as the oaks which is a highly unwanted characteristic for furniture industry. Secondly, they caused woodworking tools to dull rapidly and are attacked by moulds and fungi. Furthermore, casein glue had recently becoming more expensive as the demand of milk, which is the raw material for casein adhesive making was increasing due to the increment in world human population (Eckelman, 2012).

Blood glue is another type of protein based adhesive which was manufactured from whole blood which is a by-product of slaughter house operations. Serum from fresh whole blood was evaporated to turn it into powder form. Dried blood powder was mixed with water and other chemicals such as lime and caustic soda to yield blood-albumin glue. Hot pressing is required to cure it in application. Blood-albumin glues have less strength than the casein glues but their advantage is they are much superior in moisture resistance. They are moderately resistant to water and damp atmosphere (da Silva et al., 2011).

Starch based vegetable glue is another type of natural wood adhesive. Starch could be extracted from corn, potatoes, rice, cassava and many more. Vegetable glues were usually sold in powdered form and must be mixed with water. Starch was mixed with chemicals such as alum to improve their properties. These mixtures are heated before used. Starch glue is relatively cheap with a long pot life. They were cured by removing the moisture which required heat or longer time clamp. However they lack of moisture resistance and could be attacked by micro-organisms. Starch glues were usually used in plywood making in the older time (Eckelman, 2012). Detailed information about starch will be described in chapter 2.4.

2.4 Starch

Starch is a naturally occurring polysaccharide, with abundance rivalling cellulose in the amount found on the Earth. Most plant contains starch. Starch is created by photosynthesis process and serves as the chemical storage. Starch provides high percentage of the energy to other organisms. Wheat, potatoes, rice, maize, barley, rye, beans, peas, sorghum, tapioca (or cassava), sweet potatoes, avocados, arrowroot, taro, bananas, mango, pineapple, sago (palm starch) and many others contain a lot of starch (Radley, 1976).

Besides as a source of food, wheat starch was also used to give body and the ability to hold ink to papyrus, a thin bark that was the earliest material used for writing long time ago. Starch was also used to give body to the paper and to hold ink on the paper in China, around 100 A.D. and it continues today to be used in paper sizing. The Romans used starch to whiten cloth and to powder hair as well as to stiffen cloth and was often mixed with dyes to colour the cloth (Robyt, 1998).

2.4.1 Isolation of Starch Granules

Starch granules are water insoluble. Therefore they are relatively easy to isolate from their plant sources. First, seeds from for example maize, wheat, barley, rice, beans, and so forth are first soaked in water for 10 to 15 h at 50 °C. This process is done to soften the outer parts of the seeds so the starch inside is easier to be obtained. The soaked material is then ground, milled, or blended to give a white insoluble suspension of starch that is filtered to remove fibrous non-starch substances. The suspension was left for some time to let the starch to settle and the water is poured off. Fresh water is added and the starch is washed two or three times to remove impurities. The starch is centrifuged or filtered and allowed to air dry at 20 °C, followed by grinding into a fine powder (Robyt, 1998).

2.4.2 Physical and chemical properties of starch

Starch is made up of small granules. The alternated amorphous and crystalline shells made up most of starch granules. These structures are between 100 and 400 nm thick and was known as growth rings. Starches that were isolated from different botanical sources showed different characteristic of granule morphology. Starch granules have various shapes, including spherical, oval, polygonal, disk (lenticular), elongated and kidney shapes as shown in Figure 2.4. The sizes are ranging from 1 µm to 100 µm in diameter. Diameters of starch granules vary from the smallest in amaranth and small pigweed submicron, to more than 100 µm of canna starch (BeMiller and Whistler, 2009).

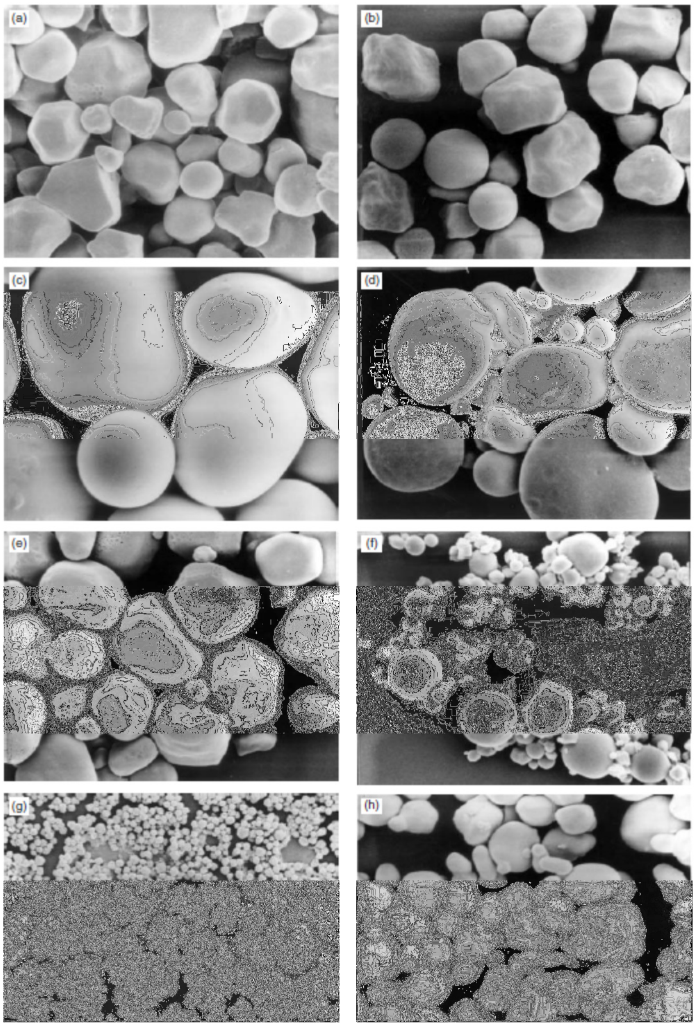

Figure 2.4: Scanning electron micrographs of starches (a) normal maize, (b) waxy maize, (c) potato, (d) wheat, (e) sorghum, (f) sweet corn, (g) amaranth, (h) high-amylose maize (BeMiller and Whistler, 2009)

Starch is chemically composed of two kinds of polysaccharides. First is the amylose which is a linear α-(1→4) linked glucan and second is amylopectin which is an α-(1→4) linked glucan with 4.2 to 5.9% α-(1→6) branch linkages. Figure 2.5 and Figure 2.6 showed the structure of amylose and amylopectin. The ratios of amylose to amylopectin are different, depending on the source of the starch. It ranges from 17 % to 70 % amylose and a corresponding 83 % to 30 % amylopectin (Robyt, 1998).

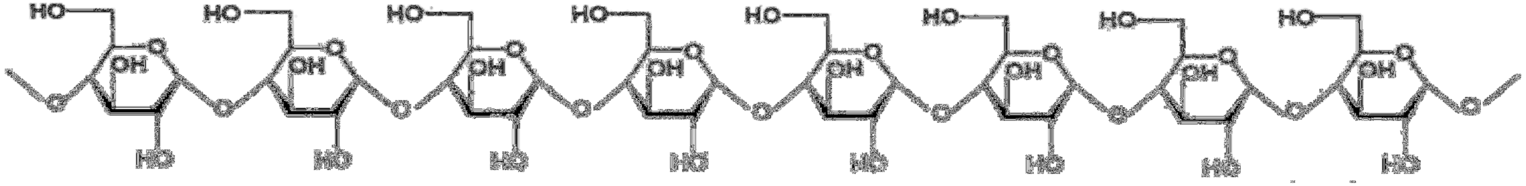

Figure 2.5: Segment of an amylose molecule (Robyt, 2008)

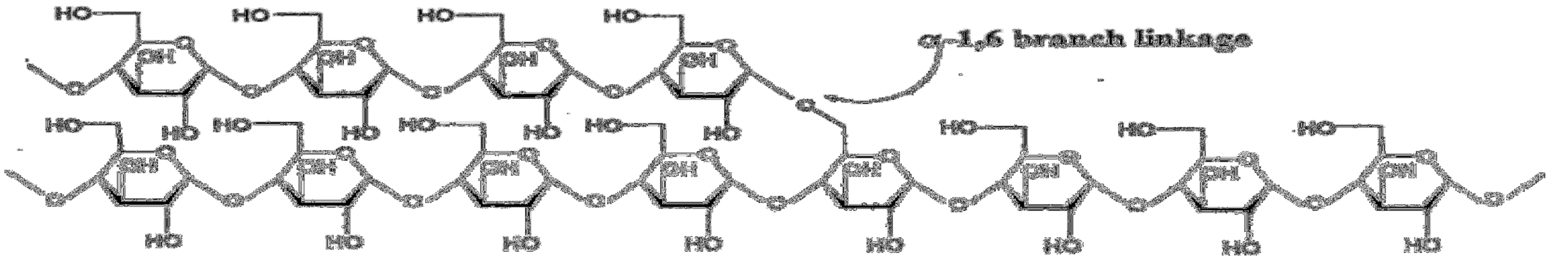

Figure 2.6: Segment of an amylopectin molecule (Robyt, 2008)

2.4.3 Product from starch

This chapter describes various products that were derived from starch. Products of starch modification will be covered in the next sub-chapter. First product is the sweetener. Starch will undergo acid-catalyzed hydrolysis, degrades it into dextrose, other saccharides and polysaccharides which is called as glucose syrups. Glucose syrups of the 1800s and early 1900s were produced in liquid forms and dehydrated to produce glucose in solid form (Horton, 2012).

Next is the ethanol. From glucose syrup, they can be fermented using yeast to produce ethanol. Because of beverage ethanol has been produced from many sources of sugar and starch for many centuries, large scale production of fuel-grade ethanol by fermentation is specially made for combustible motor fuel additives. Ethanol offered a cheaper fuel compared to gasoline. At present, most ethanol is made from corn starch. Starch was separated from corn by wet milling, thinned with alpha-amylase and saccharified with amyloglucosidase. Sugar solution will be obtained and the next step is fermentation by Saccharomyces yeast to produce ethanol. Latest ethanol plants use simultaneous saccharification, yeast propagation and fermentation. Most fuel-grade ethanol nowadays is produced by continuous fermentation. The advantages of continuous fermentation over batch fermentation are lower capital cost for fermenters, improved microbiological control and ease of automating control of the process. Approximately 14.5 kg of corn starch could produce approximately 9.5 litres of ethanol (BeMiller and Whistler, 2009).

Polyols is another product produced from starch. Starch was hydrolysed, followed by hydrogenation of the resulting sugars which produces a class of