PARTICLEBOARD MADE FROM MODIFIED CROSSLINKED CARBOXYMETHYL STARCH FROM OIL PALM TRUNK AS BIO-ADHESIVES

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by

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LIST OF SYMBOL AND ABBREVIATIONS

g/cm^3	gram per centimeter cubic
cm	centimeter
g	gram
%	percentage
˚C	degree Celcius
OPT	oil palm trunk
FTIR	Fourier transform infra red
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
IB	Internal bond
MOR	Modulus of rupture
MOE	Modulus of elasticity
MPa	Mega pascal
pH	Hydrogen ion concentration
rpm	revolution per minute
ASTM	American Society for Testing and Materials
JIS	Japanese Industrial Standard
UV-VIS	Ultraviolet/visible spectrometry
PF	Phenol formaldehyde

MF	Melamine formaldehyde
UF	Urea formaldehyde
WA	Water absorption
TS	Thickness swelling

BOD PARTIKEL DIPERBUAT DARIPADA KANJI TERUBAHSUAI KARBOKSIMETIL TERPAUT SILANG DARIPADA BATANG KELAPA SAWIT SEBAGAI BIO-PEREKAT

ABSTRAK

Kesesuaian kanji batang kelapa sawit modifikasi silang paut karboksimetil sebagai perekat baru berasaskan sumber semulajadi untuk komposit berasaskan kayu dilakukan melalui beberapa ujian seperti analisis proksimat, sifat fizikal dan mekanikal. Kanji diekstrak daripada batang kelapa sawit yang berusia melebihi 25 tahun yang mana buahnya telah berkurangan dan proses penuaian yang sukar. Kanji yang diekstrak disilang paut menggunakan natrium kloroasetat ($C_2H_2ClNaO_2$) diikuti dengan penambahan fosforil klorida ($POCl_3$) menghasilkan kanji bersilang paut karboksimetil. Bod partikel dihasilkan berdasarkan dua sasaran ketumpatan (0.60 g/cm^3 and 0.80 g/cm^3) dengan menggunakan 4 jenis perekat yang berbeza iaitu urea formaldehid (UF) sebagai sampel kawalan, kanji asli batang kelapa sawit, kanji batang kelapa sawit modifikasi silang paut karboksimetil, dan perekat campuran yang terdiri daripada kanji batang kelapa sawit termodifikasi silang paut karboksimetil dan 2% urea formaldehid. Berdasarkan ujian fizikal dan mekanikal yang telah dijalankan, bod partikel yang menggunakan kanji termodifikasi menunjukkan penambahbaikan berbanding bod partikel yang menggunakan kanji asli daripada batang kelapa sawit. Penambahan 2% urea formaldehid (UF) dan 13% kanji batang kelapa sawit modifikasi silang paut karboksimetil menunjukkan penambahbaikan dari segi sifat fizikal bod partikel terutama dari segi penurunan nilai pembengkakan ketebalan dan penyerapan air. Bagi sifat mekanikal pula, penambahan 2% urea formaldehid menunjukkan ianya sudah cukup untuk mencapai nilai minimum bagi modulus kepecahan dan modulus kekenyalan bertepatan dengan piawaian “Japanese Industrial Standard (JIS A 5908)” bagi bod partikel Jenis 8.

Untuk kekuatan ikatan dalaman pula, kesemua bod partikel yang dihasilkan menggunakan 4 jenis perekat berbeza berjaya mencapai tahap yang telah ditetapkan dalam piawaian JIS bagi bod partikel Jenis 8, Jenis 13 dan Jenis 18. Bagi ujian pembebasan formaldehid, seperti dijangka bod partikel yang dihasilkan menggunakan perekat campuran menunjukkan pembebasan formaldehid yang jauh lebih rendah berbanding sampel kawalan yang menggunakan urea formaldehid. Berdasarkan keseluruhan data yang diperolehi, ternyata bahawa kanji modifikasi berasaskan batang kelapa sawit mempunyai potensi untuk dijadikan alternatif, malah boleh dikomersilkan sebagai perekat dalam pembuatan bod partikel dan pada masa yang sama mengurangkan pergantungan terhadap perekat berasaskan formaldehid bagi aplikasi tertentu.

PARTICLEBOARD MADE FROM MODIFIED CROSSLINKED CARBOXYMETHYL STARCH FROM OIL PALM TRUNK AS BIO-ADHESIVES

ABSTRACT

The compatibility of modified crosslinked carboxymethyl oil palm trunk starch as the new natural based adhesive for wood-based composite was studied through a numbers tests such as proximate analysis, physical and mechanical test. The starch was extracted from oil palm trunks which are more than 25 years old oil palm trees due to the decreased fruits yield and the difficulty for harvesting process. The extracted starch were crosslinked using sodium choloroacetate ($C_2H_2ClNaO_2$) followed by the addition of phosphoryl chloride ($POCl_3$) to produced highly branched carboxymethyl starch. The particleboards were produced based on two different target densities (0.60 g/cm^3 and 0.80 g/cm^3) made up by using 4 different types of adhesive namely urea formaldehyde (control sample), native oil palm trunk starch, modified crosslinked carboxymehtyl oil palm trunk starch and mixed adhesives consisting of modified crosslinked carboxymethyl oil palm trunk starch mixed with 2% urea formaldehyde. Based on the physical and mechanical test, the particleboard bonded using modified starch showed improvement in properties compared to the particleboard bonded with native starch based on oil palm trunk. The addition of 2% urea formaldehyde with 13% modified crosslinked carboxymethyl oil palm trunk starch improved the physical properties especially the reduction of thickness swelling (TS) and water absorption (WA). For mechnical properties, it was shown that the addition of 2% urea formaldehyde is good enough to meet the minimum value specified for modulus of rupture (MOR) and modulus of elasticity (MOE) conforming to the Japanese Industrial Standard (JIS A5908) for Type 8 particleboard. For internal bond (IB) strength, all the particleboard bonded using 4 different types of adhesives successfully satisfied the JIS requirements for Type 8, Type 13 and Type 18 particleboard. For formaldehyde release test, as expected the particleboard produced with mixed adhesives exhibited much lower formaldehyde release compared to the control sample that using urea formaldehdye. Based on this study, it showed that the modified starch based on oil palm trunk has a potential to be use as an alternative adhesive and later commercialize in the particleboard making and at the same time reduce the dependant on formaldehdye based adhesives for some application.

1 INTRODUCTION

1.1 Research background

Malaysia is known as one of the major countries that produce and export wood-based panels products such as wooden furniture and panel products including particleboard in Asia. The wood-based panels industry is the main contributor to the value added, export earnings and employment in the manufacturing sector. Besides that, these industries give a large impact towards the economic growth and had undergone a number of major changes in order to maintain its significant value to the country. Since these manufacturing sector give a large influence to the economic growth, Malaysia had stopped being one of exporter of unprocessed wood (Market Watch, 2011). During the Second Industrial Master Plan (IMP2) period the fastest growing segment in this industry is the rubberwood furniture and starting from 2000, the main contributor to the country exports was overtaken by the plywood (Ministry of International Trade and Industry, 2006). In the period 2006- 2020 (Third Industrial Master Plan, IMP3) wood-based panels industry will continue to be the export driven to Malaysia. Various steps had been taken to improve the quality of the products and minimization of waste through research and development.

Over the past few decades, urea formaldehyde (UF) was used as the main adhesive in the wood based panels industry especially in the particleboard manufacturing. The urea formaldehyde was chosen due to its excellent properties such as hardness, good thermal properties, initial water solubility, and short curing time (Pizzi et al., 2003). This excellent properties allow this resin to be used as the main adhesive to produce particleboard with good mechanical and physical properties that can fulfill all the requirement needed in a standard such as American

Society for Testing and Materials (ASTM) and Japanese Industrial Standard (JIS). Although Malaysia wood-based panel industry had undergone a great successful years, this industry had its own disadvantages to the environment. The disadvantages of the wood-based panels industry is related to the formaldehyde release from the panels that were bonded by formaldehyde based adhesives. This usually occurs during the curing of formaldehyde based adhesives, the formaldehyde gases will be released to the atmosphere that is dangerous to human health (Bosetti, et al., 2008). Through the volatile organic compounds (VOCs) test, the released of formaldehyde lead to indoor air contamination (Brown, 1999). The long term exposure which normally occurred by staying in a room that was contaminated with this hazardous gases may cause irritation to the eyes, nose and upper respiratory tract (Conner, 1996). Due to the environmental consideration, a lot of research and development regarding the formaldehyde emission have been done in order to produce a good wood-based panel adhesive that is not hazardous to human health. For example, the introduction of E_1 type particleboard to reduce the formaldehyde release without affected the physical and mechanical properties of the panels (Hosseini and Fdaei, 2013). In addition of that, many researchers focus on the substitution of formaldehyde-based adhesives with a new natural-based adhesives or bio-adhesives in the wood-based composite panels.

Bio-adhesive is the synthesis adhesives that was obtained from natural resources that has its own potential to be used as wood-based panel adhesive such as lignin, tannin and carbohydrate. Generally, bio-adhesive owns a numbers of properties that make it differs from the artificial adhesives such as sensitivity towards moisture and ability to form strong bonds under water (Suárez, 2011). To ensure the natural based adhesive had a comparable performance with synthetic adhesive such as urea formaldehyde (UF), phenol formaldehyde (PF) and melamine formaldehyde (MF), this raw materials should undergo a numbers of chemical modification process to improve its properties based on its applications. The previous work by Pan et al. (2006) showed that particleboard bonded with rice bran and polymeric methylene diphenyl diisocyanate adhesives had a comparable performance with panel that was bonded using conventional adhesives. In this study, the starch extracted from the oil palm trunk (OPT) will be chemically modified to produce modified crosslinked carboxymethyl oil palm trunk starch as a new adhesive for a particleboard. In previous work (Kim and Lim, 1999), they synthesized crosslinked carboxymethyl by using corn starch for the removal of heavy metal ions presence in the water. However, there is no study on the application of this modified starch on a wood-based composite as the new bio-adhesive.

1.2 Research Objective

1) To carry out the characterization of extracted starch from oil palm trunk for further modification.

2) To determine the compatibility of modified starch (CMS) from oil palm trunk as a new bio-adhesive for particleboard manufacturing.

3) To determine the effects of starch modification on physical and mechanical properties of wood composite panels bonded with modified crosslinked carboxymethyl starch (CMS) as compared to panels bonded with native starch (NS).

2 LITERATURE REVIEW

2.1 Wood-based industry

Over the last two decades, wood-based panel industry has become as part of the main contributer to the Malaysia economic growth (MITI, 2006). In 2011, this industry has earned RM5.2 billion from the exports of unprocessed logs and timber where most of these raw materials were exported to Japan, Republic of Singapore, Thailand and Netherlands (Market watch, 2011). Within the same year, the export of panel product such as veneer and plywood has succesfully earned RM5.1 billion and make Malaysia as the main producer and exporter of tropical particleboard in the whole world. According to Malaysia Investment Development Authority (2012), approximately 5,870 wood-based product manufacturers in Malaysia. The large numbers of wood-based manufacturers in Malaysia is good enough to show that this industry is one of the major industry in Malaysia.

Wood-based panel industries were included among with the other small numbers of other industries that able to convert raw materials into the finished products that succesfully reached the global market. Generally, wood-based industry is characterized by two different systems which are upstream and downstream activities. The upstream activities including the systematic and well-manage of natural forest utilization as well as replanting of the forest (Market watch, 2011). The downstream activities represent the sectors that are involve in processing of logs to the manufacturing either in a form of semi-finished or finished wood products. The downstream activities consist of four different types of sector which are primary wood processing, secondary wood processing, tertiary wood processing and finally pulp and paper products manufacturing. Primary wood processing is referred to the sector that focussed on the production of sawn timber, plywood and veneer. The secondary wood processing sector, is the sector that generally produced fully processed wood-based product which are mouldings, builder‘s joinery and carpentry (BJC) and reconstitued panel products such as particleboards and medium density fiberboards (MDF). The processing mills that produced furniture and its components was known as the tertiary wood processing mills (Teischinger, 2012).

2.2 Rubberwood as raw materials in wood-based industry in Malaysia

Over a few decades, the main objective of rubber tree plantation is only for the latex production which is suitable for various application (Hong et al., 1995). Rubber trees were introduced in Malaysia in 1879 where the first rubber tree seed were transported from Singapore and firstly planted in Kuala Kangsar, Perak (Ratnasingam et al., 2000). Normally, to reach a mature stage rubber tree will grow up to 20-30 m height and the diameter of the tree may reach up to 30 cm (Balsiger et al., 2000). According to Lim et al. (2003), generally rubberwood tree have a clear bole start from 3 m up to 10 m depending on the location of growth and the clones. Rubberwood is a bright-colored wood with medium density and homogenous raw materials that make it suitable to produce high quality particleboard with undeniable physical and mechanical properties. Figure 2.1 shows the example of a rubber tree plantation in Malaysia.

Figure 2.1 Rubber tree plantation in Kelantan, Malaysia

Nowadays, the utilization of rubber tree for wood-based industry is rapidly increasing in order to reduce the dependence on the other wood species which are more expensive for the production of low cost furniture and other wood-based products. In selecting the rubber tree that is suitable to be cut down for the utilization of wood-based industry, the rubber tree that are more than 25 years of age were selected (Hong et al., 1995). This is because the rubber tree that had reached 25 to 30 years old, the latex production normally decreases and no longer economical for latex tapping. Previously, the felled trees were considered as waste and low commercial value which commonly used as fuelwood. The restriction of Malaysian government on the logging activities between 1980 to 1990 are due to the decreased of wood supplies and this had made rubberwood as the new alternative source raw material for a wood-based industry (Ratnasingam et al., 2000). Today rubberwood has become an important source of wood for Malaysia timber industry and in addition, this industry is the major source of revenue for Malaysia (Hong et al., 1995). Rubber tree (*Hevea brasiliensis*) has been widely exploited in Malaysia as the main raw materials in the wood-based industry to produce furniture and partitioning inputs. The wood-based panels produced using rubberwood are widely accepted across the Asia due to its properties which succesfully satisfied various standard requirement (Izran et al., 2011).

2.3 Particleboard

In 1940's, an engineered wood product called particleboard was first introduced in the building and construction industry. Particleboard is a composite material which is made by hot-pressing of small particles made from saw dust, wood shavings, wood flakes, splinters or even wood chips with the additional of suitable binding agent such as synthetic adhesives and sizing agents depending on its applications (Moubarik and Pizzi, et al., 2010).

The introduction of this industry helps the wood based industries to dispose and convert a large quantities of mills residues such as sawdust and wood chips into something more valuable. A wood waste from urban construction sites and logging residues also can be used as the main raw materials to produce particleboard since these sites has to deal with abundant of wood waste (Carll and Charles, 1986). The usage of paper sludge in the particleboard making has been carried out to produce the panels with comparable physical and mechanical properties (Taramian et al., 2007). The application of paper sludge as the part of raw materials in board making not only reduce the depending on wood based raw materials but also helps to convert the paper waste into a value added product.

In industrial particleboard manufacturing (Figure 2.2), the first step in the board making is the selection of raw materials. The raw materials can be in the form of logs, branches and even collected wood residue or side product from the other wood-based industry. In Malaysia, rubberwood is the most frequently used raw material in the wood-based panels manufacturing. The raw materials will be chipped and flaked to reduce the size of the particles into desired length and thickness (FAO, 1990). The right particle length and thickness are important in order to produce panels with optimum strength and smooth surface finishing.

Next, the particles with desired length and thickness must be dried through a hot gas air to control the moisture content of the particles. The moisture content of the particles must be controlled in the range of 3% to 8% in order to produce good quality panels. According to United States Department of Agriculture (2007), the hot gases used for drying the particles were released either from the tube bundles containing thermic oil or hot water. The dried particles will be screen to separate each particle according to its length and size.

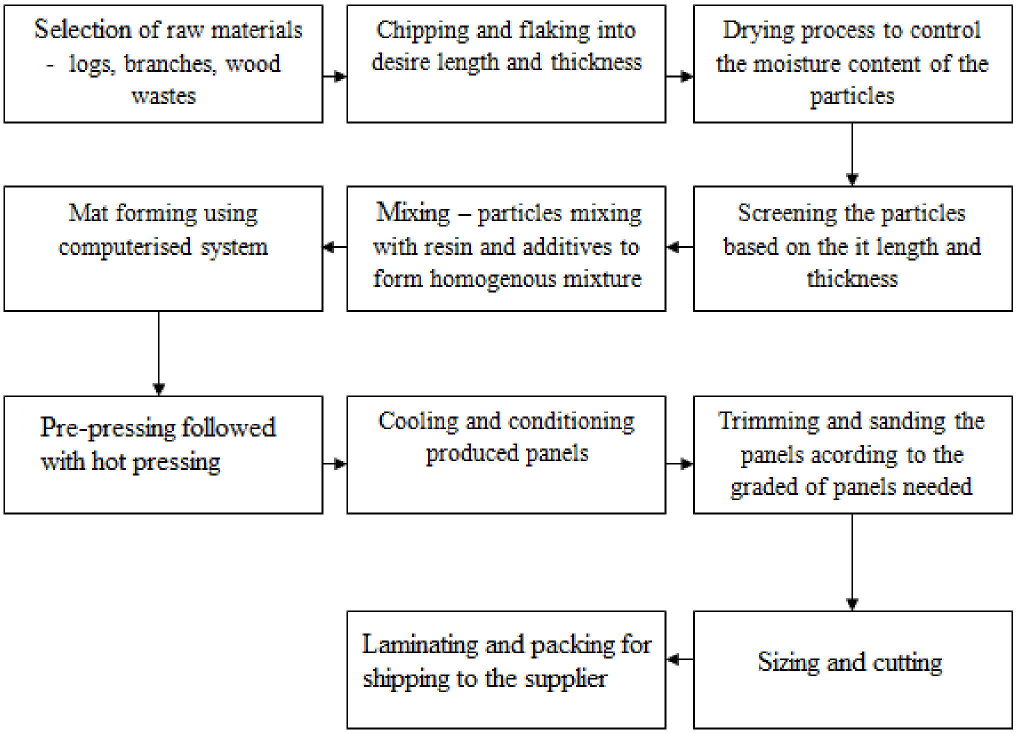

Figure 2.2 A process flow of industrial scale particleboard manufacturing (FAO, 1990)

Once screening process has completed, the particles are mixed with the resin such as urea formaldehyde (UF), phenol formaldehyde (PF) and additives into the blender. In the particleboard making process, the addition of resins normally is in the range of 3% to 10% depending on it end uses. The objective of this process is to form homogenous mixture between the particles, resin and additives. Homogenous mixture of particles, resin and additives play an important role to form a strong bonding between the particles and resin in a particleboard. The addition of additives like sizing agent depends on the types of board application. There are various types of sizing agents which help to improve the properties of the particleboard such as wax, rosin and asphalt (Stark et al., 2010). For some application, small amount of fire retardants such as zinc borate and preservative was added to improve the thermal and durability of the board (Haque et al., 2013).

To ensure the mixture reached the homogenous state, the speed of the blender need to be controlled. High speed of blending process normally used for a small scale blender for shorter blending time while the slow speed usually take place on the large blender (Avokali, 2005). The mixture of 3 different raw materials were placed into the mould which controlled by the computerised system to form a mat. The mat was subjected to cold pressing or pre-pressing followed by the hot pressing where the pressure and heat are required. The presence of pressure and heat during hot pressing will form a bonding between the particles and the resin to create a solid panel. The total press time for the particleboard making is generally 2.5 minutes and up to 6 minutes for single-opening presses and multi-opening presses respectively (Stark et al., 2010).

After that, the board produced will be cooled and conditioned to prevent resin degradation. Before the board arrives to the supplier, the edge of the board was trimmed by using a pairs of trimming saw and the trimmed parts will be recycled as a fuel (FAO, 1990). The finishing operation such as laminating was also applied on the board to ensure the final product has an attractive appearance. The laboratory scale particleboard making is generally almost similar with the industrial scale in term of the procedure and the raw materials use but the major difference between these two is the end product where the laboratory scale end products are smaller than the industrial scale.

Nowadays, particleboard is widely used in the production of furniture and construction industry due to its low cost and easily to work with. In the production of particleboard, there are 3 major factors that differentiate and give significant effect on the properties of particleboard namely the geometry and the size of particles used, total amount of adhesive, and the target density of the board (Abdul Khalil and Rozman, 2004). These factors enable the manufacturer to control the particleboard properties that suits with its applications and to ensure the particleboard produced reach the specification needed, a numbers of standard can be referred such as Japanese Industrial Standard (JIS), British Standard (BS), European Standard (EN) and American Standard of Testing Materials (ASTM). The particleboard classification varies among these standards. The classification technique not only depends on the mechanical properties such as bending strength of the panels but other factors such as incombustibility, types of adhesive, quantity of formaldehyde emission and the condition of the face and back of the particleboard become the factors that classisfied the particleboard produced (JIS, 2003). In Japanese Industrial Standard for example, the bending strength of the particleboard is also considered as one of the factors for the classification of particleboard. The classification of the particleboard based on the bending strength is shown in the Table 2.1.

Table 2.1 Classification of particleboard based on the bending strength (JIS, 2003)

Classification		Symbol	Bending Strength
Base particleboard and decorative particleboard	Type 18	18	The bending strength must be 18.0 MPa or more both lengthwise and widthwise
	Type 13	13	The bending strength must be 13.0 MPa or more both lengthwise and widthwise
	Type 8	8	The bending strength must be 8.0 MPa or more both lengthwise and widthwise
Base particleboard	Type 24-10	24-10	The bending strength must be 24.0 MPa or more lengthwise and 10.0 MPa or over widthwise
	Type 17.5-10.5	17.5-10.5	The bending strength must be 17.5 MPa or more lengthwise and 10.5 MPa or over widthwise
Veneered particleboard	Type 30-15	30-15	The bending strength must be 30.0 MPa or more lengthwise and 15.0 MPa or over widthwise

The example of synthetic resins that are commercially used in the wood based products industry especially in particleboard are urea formaldehyde (UF), phenol formaldehyde (PF) and melamine formaldehyde (MF) (Abdul Khalil and Hashim, 2004). All these common adhesives are petroleum based products. Over the last few decades, the reduction of this valuable resource had caused the drastic change on its price. The price of the petroleum based product became suddenly increase and the comprehensive research should be done to overcome this problem. The increase of this raw material cost had turn the researcher to focus on the natural based raw materials with some chemical modification to reduce the dependant on the current commercial adhesive (Papadopoulou et al., 2008). Natural based raw material was chosen due to its availability which is abundant and cheap. Numerous research and development of this composite regarding the adhesive matter had been done to improve the properties, quality and make it more sustainable including the raw materials used in its production. A particleboard bonded with rice bran and polymeric methylene diisocyanate adhesives (Pan et al., 2006) is the example work done by researchers to replace the commercial synthetic resin.

2.3.1 Applications of particleboard

Particleboard was first introduced for the building and construction industry and most of these engineered product was being used for interior application. Inexpensive home furnishing such as desks, shelves and storage cupboard are the examples of product made from particleboard. The outstanding mechanical properties and versatility of this wood based panels that easily can be decorated either using paint or wood veneers make it become the most preferred products by the customers comparing to the furniture that was made from solid wood (McNatt, 1973). In the industrial scale particleboard production, each panel produce comes with different grades depending on environmental condition and its uses are varying from domestic up to industrial application (Anonymous, 2013b). For industrial uses, normally the high grades panels were used in industrial storage systems. For structural use, the mechanical strength of the panels is the most crucial part since its application will expose the product to the high load.

Instead for structural panels, particleboard were also being used in the application for nonstructural panels. Example of nonstructural panel is an underlayment where its uses can be either as subflooring or underlayment on timber joists (Carll and Charless, 1986). For this application, the panels were laid on the top joists wood floor which attached to the metal‘s chassis of the mobile home. Besides that, it also can be used as underlayment in a floating floor system. In Taiwan for example, the government introduced the regulations where the wood waste must be reuse to produce non structural panels such as ceiling, decorations and flooring in order to sustain the utilization of new raw materials (Wang et al., 2007).

2.3.2 Types of particles

Generally, particleboard comprises of 3 main components which are wood, adhesive and wax (Haque et al., 2013). The primary difference between the wood based products is the main material used in its manufacturing such as the types of particles used (Abdul Khalil and Rozman, 2004). Wood flakes, chips, granules, fibers, strands and wood excelsior are the examples of commonly use raw materials in particleboad making (Abdul Khalil and Hashim, 2004). Selecting the right wood species is an important step to ensure the panels produced do not face a lot of problem once it reached to the customers. Wood density and extractive content in the wood are the factors that need to be considered in selecting the right wood particles for the particleboard making. Low density wood species are the best compared to the higher density in most of the wood based panel productions. The characteristics of low density woods are having density below than 540 kg/m^3 and easily dent when a load is applied on it. The examples of low density woods are Douglas Fir, Cedar, Redwood and Rubberwood. Low density wood are preferred for particleboard manufacturing due to the high content of wood particles per kg, enable to provide better contact between glue and particles and enable to reduce the uneven density within the panels (Zhou et al., 2007).

In this study, rubberwood was chosen for the particleboard making in laboratory scale. The rubberwood had a basic density between 450-550kg/m^3 which is classifed as a low density wood species (Zhou et al., 2007). Wood species with high extractive content are not favourable because it will result in some problems during resin curing. Generally, the particles used are the side products taken from the furniture factory such as wood flakes, fibers strand, excelsior, saw dust, sawmill shaving, and wood chips but in some factory they produced the particles specially for particleboard making (Abdul Khalil and Hashim, 2004), (Izekor and Kali, 2008). Hammermills, refiners and flakers are the example of machinary involved in the preparations of particles. The physical and mechanical properties of the particleboard can be controlled by using various size of wood particles and the geometry of the wood particles in the surface and core of the panels (Haque et al., 2013). The mechanical strength including the internal bond (IB) strength, flexural strength and tensile strength that will determine whether the particleboard produced meet the standard or vice versa (JIS, 2003).

In the particleboard manufacturing, the fine particles such as granules are normally used to produce smooth surface since smaller size particles enable to fulfill the void presence. The application of longer particles instead of fine particles on the surface of the panels will result in uneven and rough surface on the finished product. A smooth surface panels usually is needed in the furniture production where the aesthetic value are the first priority. The longer particles were specialized for the core of the panels in most of 3 layer particleboard making since it increased the bending strength of the panels (Haque et al., 2013). The longer particles is more preferable because the longer particles enable to form a better bonding between the particles (Abdul Khalil and Hashim et al., 2004). For the finished products such as structural boards, the longer particles are the most suitable to increase the percentage of overlap between the particles.

2.3.3 Adhesives

Adhesives in wood-based panel industry is defined as a thermoset resin that being use as the subject that hold the wood particles together to form a wood based panels. The definition of adhesive strength is the force required to pull apart the substrates that are bind together (Frihart et al., 2005). Adhesive for wood bonding was discovered more than 3,000 years ago by the Egyptians (Skeist and Miron, 1990) and undergone a lot of changes to improve its use in various application. Wood based composite adhesives can be divided into two main groups which are synthetic adhesives and natural based adhesives.

2.3.3.1 Synthetic adhesives for wood based composite

Synthetic adhesives for wood based composite generally are a petroleum based adhesives. Urea formaldehyde (UF), phenol formaldehyde (PF) and melamine formaldehyde (MF) are the examples of synthetic adhesives that enable to provide a better perfomance for wood based composite. Each of this formaldehyde based adhesives have its own characteristic that made it differ between one another for different applications (Pizzi and Mittal, 2003).

2.3.4.1.1 Urea Formaldehyde

Urea formaldehyde (UF) resins or amino resin adhesives are the most commonly used adhesives in the production of particleboard. The amino resins are used as the main adhesive for bonding not only for particleboard but also being used in the production of plywood and medium density fiberboard (MDF) as well (Frihart et al., 2005). UF resins is commercially available in two forms which is in liquid and powder forms. UF resins are commonly known as the most outstanding thermosetting resins in the amino resin groups and it also covered 80% of the amino resin production in the entire world (Conner, 1996). Other than for forest products industries, urea formaldehyde resins are widely used in the textile industry to impart permanent properties, paper production as a wet end additive and automobile tires to enhance the bonding between the rubber and tire band. These resins were synthesised by the reaction between urea and formaline (Figure 2.3).

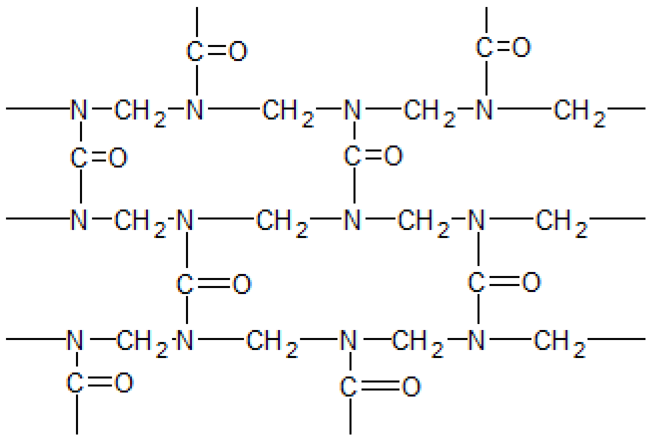

Figure 2.3 Urea formaldehyde molecular structure (Frihart et al., 2005)

The application of amino resins or UF resin as an adhesive in the particleboard making is due to its characteristics that are low cost, lack of color after cure, hardness, non-flammable, good thermal properties and easily curing conditions (Pizzi and Mittal, 2003). In particleboard making, the usage of UF resins alone does not enough since it also has its own weaknesses. The disadvantages of UF resin compared to other wood adhesives are low resistance towards water and moisture and these weaknesses is getting worst with the presence of heat. These problems make UF resin is only suitable for indoor use rather than outdoor applications where the possibility of the products expose to water and heat is too high. Long term exposure to water and moisture will cause bond deterioration and the release of formaldehyde which is dangerous to human health (Conner, 1996).

Small amount of hardener is needed in order to improve the properties of UF resin in the particleboard making. The addition of hardener such as ammonium phosphate, $(NH_4)_3PO_4$ is the best technique to overcome the UF resin weaknesses. The major property that may greatly effected after the addition of hardener is the solubility of the resins (Pizzi and Mittal, 2003). Although hardener has been added to improve the properties of the resins, the pungent smell caused by the release of formaldehyde which is carcinogenic.

2.3.3.1.2 Phenol Formaldehyde

Phenol formaldehyde (PF) which is also known as phenolic resin were synthesized by the condensation reaction between phenol and formaldehyde in aqueous sodium hydroxide (Figure 2.4) and has been commercially used since the beginning of 20^{th} century (Detlefsen, 2002). The reaction between both important materials will produce thermosetting polymers known as resole (Athanassiadou et al., 2010). The synthesis of resole resin was carried out with the mixture ratio 1:3 for formaldehyde and phenol respectively under controlled pH between 4 to 7 (Kendall and Trethewey, 2013). PF resin represent the second largest adhesive consumption after the amino resin in term of volume (Athanassiadou et al., 2010). This phenolic resin are normally used for the applications as coatings, wood based panels and wood laminating due to its positive attributes such as the ability to perform better bonding on wood, highly stability and high durability (Frihart et al., 2005). The properties of PF resin that is water resistant is the main advantage of this resin and made it suitable for external use (Athanassiadou et al., 2010).

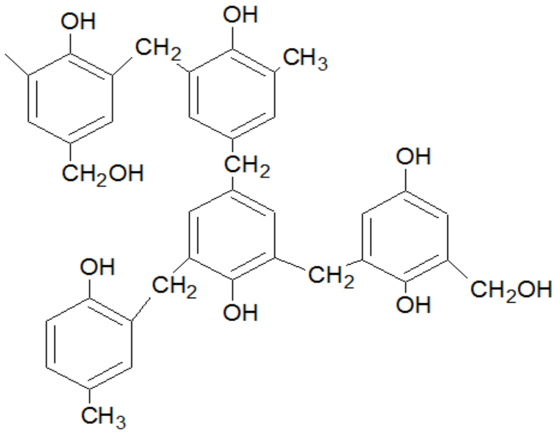

Figure 2.4 Phenol formaldehyde (Pizzi and Mittal, 2003)

The main objective of PF resin being introduced into the wood based panels industry is to improve the weaknesses of UF resin with some better properties such as improving the curing time, decreasing the formaldehyde release and reducing the production cost of the resins (He and Reidl, 2003). Besides that, PF resin application was specialized for the particleboard that its application subjected to the high temperature exposure (Haque et al., 2013). The durability of this resin made it as the most favourable adhesives for a wood based panels production. However, PF resin also has its own drawback where its application is limited only for the panels that required an extra durability because the price of this adhesives is higher compared to other formaldehyde based adhesives (Pizzi and Mittal, 2003).

2.3.3.1.3 Melamine Formaldehyde

Melamine formaldehyde (MF) is one of the formaldehyde based resins that is produced from the chemical reaction between melamine and formaldehyde (Figure 2.5) to produce the resin which are highly resistance towards water, heat, stain, and electricity (Pizzi and Mittal, 2003). The most important characteristic of MF resin that made it differ than any other formaldehyde based resins is the bright color of MF resin that make it suitable for decoration purpose (Frihart et al., 2005). In particleboard making, MF resins normally used for semi-exterior and exterior grade particleboard.

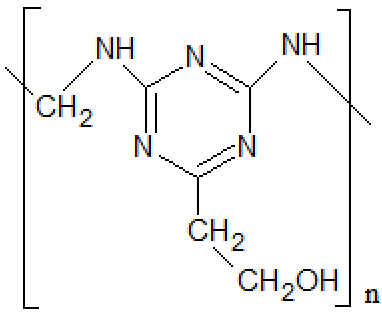

Figure 2.5 Melamine formaldehyde molecular structure (Frihart et al., 2005)

Although the application of MF resin is to produce particleboard that meet the standard requirement, the high cost of melamine has became the main disadvatage of MF resin and led to the introduction of melamine-urea-formaldehyde (MUF) resin (Frihart et al., 2005). The MUF resin exhibit the similar water resistance properties like MF resin yet at lower cost.

2.3.3.1.4 Formaldehyde emission

Wood based panels industry was known as the biggest formaldehyde based adhesives consumer due to the resin ability to produce panels with the best mechanical and physical properties as well as high resilience. The main problem with these adhesive is the formaldehyde emission that is dangerous to human health especially for the interior building panels applications (Wang et al., 2007). This event normally occurred from the panels that are using urea formaldehyde (UF), phenol formaldehyde (PF) and melamine formaldehyde (MF) where the formaldehdye emission took part during the curing and the degradation of the adhesives. This issue started in the mid-1970s where the application of urea formaldehyde resins increased rapidly especially for the indoor application. The public awareness about this issue also led to the introduction of new standard regarding the content of urea formaldehyde resins in the wood product notably particleboard (Papadopoulou et al., 2008).

The formaldehyde emission is known as the main contributor to the indoor air pollution which is also known as volatile organic compounds (VOCs) (Baumann et al., 2000). The VOCs are the gases release either from solids or liquid form. Generally, the gases release comprise of various types of chemicals that significantly gives negative effect for both short and long term exposure. The examples of health problem arise from the short term emission of formaldehdye are coughing, nausea and skin irritation. The long term effect resulting from the formaldehyde exposure is the potential to cause cancer since formaldehyde was known as carcinogen to human health (National Cancer Institute, 2011). The highly possible cancer cause by excess formaldehyde inhalation is nasopharyngeal cancer (Bosetti et al., 2008). A number of test can be used in laboratory to determine the amount of formaldehyde release such as desiccator method (JIS A 1460, 2001) and flask method (BS EN:717-3, 1996).

To overcome these problems, various researches have been done extensively in order to reduce the amount of formaldehyde emission without neglecting the physical and mechanical performance of the panels. In Europe for example, the concern of formaldehyde emission had led to the introduction of the famous E_1 Type Particleboard for limiting formaldehyde emissions from particleboard (Hosseini and Fdaei, 2002). Other than that, the addition of polymeric 4,4'-methylenediphenyl isocyanate (PMDI) in the core of 3 layer particleboard is one of the method to produce low formaldehyde emission particleboard with comparable perfomance to the panels bonded using urea formaldehyde resins alone (Wang et al., 2007). The substitution of formaldehdye based adhesive with natural based materials are found to be the possible alternatives to minimize the usage of petroleum source adhesive in particleboard making. The production of particleboard bonded with a mixture between corn starch-mimosa tannin-urea formaldehyde resins (Moubarik et al., 2010) is also an effort to develop a new adhesives based on natural origin. In present study, the starch extracted from oil palm trunk will be modified to create crosslinked carboxymethyl starch that will be used as the new adhesive and to reduce the dependence on petroleum based adhesives.

2.3.3.2 Natural-based adhesives for wood-based composite

Natural-based adhesive is an adhesive derived from the natural resources usually acquired from plant. Tannin, lignin and carbohydrate are the examples of natural based adhesive derived from various types of plant but the percentage varies among the species. In wood-based composite industry, the application of natural based adhesive is not something new. According to Valenzuela et al. (2012), the usage of tannins as the main adhesive in the particleboard making have been used industrially in Concepcion, Chile and produced the particleboard with excellent quality.

The objectives of natural-based adhesive applications in particleboard making is to reduce the dependence on petroleum-based adhesive and at the same time to eliminate the exposure towards the formaldehyde gases (Huang and Li, 2008). Besides that, the depletion of petroleum source significantly increase the price of petroleum based adhesive and natural-based adhesive are found to be the best alternative to overcome such problem.

2.3.3.2.1 Tannin

Tannins are phenolic compound that were extracted from various species of plant but the percentage of tannins content differ among the wood species (Frihart et al., 2005). Normally, large concentrations of tannins were extracted from the wood bark (Bertaud et al., 2012) and it was known as renewable source that is widely used in the adhesive production that are suitable for various industrial applications (Pizzi & Mittal, 2003). Previous study by Bertaud et al. (2012), showed that the tannins extracted from *Pinus radiata*, containing tannin possessed naturally high degree of polymerization that make it highly reactive. The large concentration of tannin from