CHARACTERIZATION AND UTILIZATION OF EXTRACTED STARCH AND PARTICLES FROM OIL PALM TRUNK FOR PARTICLEBOARD MANUFACTURING

by

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

December 2014

ACKNOWLEDGEMENT

First, I want to dedicate my special thanks to merciful ALLAH S.W.T for His guidance along this journey by giving me strength, trust, and hope to fulfil my ambitions and complete this research. Secondly, I would like to appreciate my supervisor, for all her patience, knowledge, ideas, and words of support, I can never thank her, Professor Rokiah Hashim, enough. She attributes her presence by transforming me in all aspects, despite my weakness and fragility in completing this work, I have been indebted for all what you had given to me and I truly embolden your gentle encouragement throughout this work. I am honoured to thank to Professor Othman Sulaiman, and staffs from School of Industrial Technology. I have been fortunate to be surround with great friends by helping me throughout this work by giving me support and thank you for being my best companions along this journey. I also want to thank to my beloved mom, Noliah Umar, I would not have made it without her prayers, trust, encouragements, and words of wisdom that she gave to me. I have the greatest family ever, who repudiate to let me be anything but my best: Azian, Norzarira, Mohd Hapiz, Khalid, and my sweet little angle, Zanariah. Finally, I would not have made it this far without Universiti Sains Malaysia for the Fellowship and grant 1001/PTEKIND/815066 provided throughout this research.

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LIST OF SYMBOLS AND ABBREVIATIONS

UF	Urea formaldehyde
OD	Oven-dry
OPT	Oil palm trunk
OPP	Oil palm particles
OPS	Oil palm starch
RWP	Rubberwood particles
WS	Wheat starch
POPS	Oil palm starch modified with polyvinyl alcohol
UOPS	Urea formaldehyde + oil palm starch
PWS	Wheat starch modified with polyvinyl alcohol
UWS	Urea formaldehyde + wheat starch
PVOH	Polyvinyl alcohol
MC	Moisture content
TS	Thickness swelling
WA	Water absorption
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

LIST OF PUBLICATION

1. Salleh, K. M., Hashim, R., Sulaiman, O., Hiziroglu, Salim., Nadhari, W. N. A. W, Karim, N. A., Jumhuri, N., Ang, L. Z. P. “““Evaluation of properties of “starch based adhesives” and particleboard manufactured from them.””” Paper accepted to Journal of Adhesion Science and Technology.

PENCIRIAN DAN PENGGUNAAN KANJI YANG TEREKSTRAK DAN SERPIH DARIPADA BATANG KELAPA SAWIT UNTUK PENGHASILAN PAPAN SERPAI

ABSTRAK

Kajian ini mengkaji potensi kanji yang diekstrak dan serpih kelapa sawit yang dihasilkan daripada batang kelapa sawit. Serpih kayu getah dan kanji gandum komersial digunakan sebagai perbandingan. Kanji batang kelapa sawit dan kanji gandum dimodifikasikan dengan polivinil alkohol untuk menambahbaikkan potensi kanji-kanji ini sebagai bahan perekat. Ciri-ciri asas bahan mentah dikaji terlebih dahulu untuk meramal sifat akhir produk yang dihasilkan. Pencirian bahan mentah juga dijalankan menggunakan mikroskop pengimbasan elektron, analisa penguraian sinar X, analisa termogravimeter, dan analisa kalorimeter pengimbas perbezaan. Perbandingan dilakukan antara papan serpih dan papan serpih yang direkat dengan urea formaldehid digunakan sebagai kawalan.

Sifat fizikal dan mekanikal produk diuji berdasarkan Piawaian Industri Jepun, antaranya ialah ketumpatan, kandungan lembapan, ujian kestabilan dimensi, dan kekuatan mekanikal. Kesemua sifat mekanikal papan serpai yang dihasilkan memenuhi kehendak piawaian, namun tidak satu pun sifat fizikal yang memenuhi piawaian melainkan kandungan lembapan. Papan serpai yang direkat daripada serpih batang kelapa sawit dan papan serpai yang direkat dengan kanji kelapa sawit mempunyai sifat mekanikal yang lebih baik namun mempunyai sifat fizikal yang kurang memuaskan berbanding papan serpai yang diperbuat daripada serpih pokok getah dan papan serpai yang terekat dengan kanji gandum. Papan serpai yang direkat dengan kanji yang dimodifikasi menunjukkan peningkatan yang ketara pada sifat fizikal dan mekanikal berbanding dengan kanji yang asal, selain mempunyai

kestabilan dimensi yang setanding dengan papan serpai kawalan. Serpih batang kelapa sawit dan kanji batang kelapa sawit mempunyai potensi untuk digunakan dalam industri pembuatan papan serpai.

CHARACTERIZATION AND UTILIZATION OF EXTRACTED STARCH AND PARTICLES FROM OIL PALM TRUNK FOR PARTICLEBOARD MANUFACTURING

ABSTRACT

This study investigated the potential of the oil palm particles and oil palm starch produced and extracted from the oil palm trunk. Commercial rubberwood particles and wheat starch were used as a comparison. The starches were modified with polyvinyl alcohol to change its properties for better performance. Basic properties of raw materials were determined for their final properties of the boards. The raw materials were also characterized using scanning electron microscopy, X-ray diffractometry analysis, thermogravimetric analysis, and differential scanning calorimetry analysis. Comparisons were made between boards and panels bonded with urea formaldehyde were used as a control board.

The physical and mechanical testing carried out based on Japanese Industrial Standard A5908, which include density, moisture content, dimensional stability testing, and mechanical strength. All mechanical properties met the requirements, but none of the physical properties met the requirements except for moisture content. The panels made using the oil palm particles and bonded with the oil palm starch showed better mechanical properties, but poor dimensional stability compared to those panels made with the rubberwood particles, and panels bonded with the wheat starch. The panels bonded with the modified starches showed a good increment on its physical and mechanical properties compared to its natives. It also has comparable dimensional stability with the control panels. Oil palm particles and oil palm starch have the potential to be used in particleboard making industry.

1. INTRODUCTION

1.1 Research background

Particleboard making industry is largely influenced by the availability of wood or non-wood and type of adhesives used. Different countries will have different types of wood resources. For Malaysia, which is known having billion of ringgit for natural resources still cannot provide a sufficient wood resource which needs to import wood and non-wood from other country (Loh et al., 2010). Furthermore, with the increasing of demand in wood products, the wood consumption rapidly increased year after year. These problems seem do not have a solution indeed there is no newfangled discovery. Eventually, our government has exhorted researchers to surmount these problems by providing research grant and facilities to ameliorate as well as to devise a long-term economy plan (Loh et al., 2010, Aljuboori, 2013).

Other than the wood shortage problem, one of the most common problems in particleboard making industry is formaldehyde emission. The formaldehyde-based adhesives were introduced due to its low price, easy to be produced, and particleboard blended with this adhesive will have a good strength and acceptable physical stability compared to other adhesives (Conner, 1996, Chew et al., 1988). Since the emission of formaldehyde gas is dangerous, green product, and zero emissions of formaldehyde are the main concerns in particleboard making industry nowadays. That is why carbohydrate based adhesive namely starch was introduced to replace or at least reduce the use of the formaldehyde-based adhesive in particleboard making (Chiu and Solarek, 2009).

The most probable new resources to produce a new type of particles and new green adhesive are from oil palm industry. When this plant was planted in this country around 30 years ago, our government gained so much profit from this industry due to the properties of oil palm tree itself, and it takes millions of hectares to plant this tree (Aljuboori, 2013). However, after 30 years, this tree is unable to produce a significant amount of fruit for oil palm production. Thus, it needs to be cut and re-plantation. The problems' encounter as this waste was not fully utilized with often mismanagement by throwing away this valuable waste for open burning and natural degradation (Sheil et al., 2009). There are two plausible products that can be produced are a new type of particle and a new type of adhesive, which is made and extracted from the oil palm trunk waste.

The idea of using the oil palm trunk in particleboard making is due to its two main constituents comprising the strand and parenchyma. The oil palm strand is surrounded by parenchyma elongate from bottom to the top of the tree. The distributions of both constituents are differed from bottom to top whereas the bottom consisting higher percentage of oil palm strand with a lower percentage of parenchyma and vice versa. Usually the whole trunk composed of 55% of the parenchyma while the remaining 45% made from the oil palm strand (Abe et al., 2013, Mhd Ramle et al., 2012).

There are various works that had been done by using oil palm trunk in particleboard making (Baskaran et al., 2012, Hashim et al., 2010, Hashim et al., 2011b). By using the oil palm strand with different size to determine the effects of particle geometry, particleboard made with the oil palm strand can be used in particleboard since it has promising mechanical properties for particleboard making (Hashim et al., 2010). From another study, by using different types of polyhydroxyalkanoates reported that particleboard made with oil palm trunk had promising properties and with proper utilizations (Baskaran et al., 2012). These advantages can be a divine opportunity for industry to utilize this natural resource in particleboard making. Copious researchers used carbohydrate based adhesive in particleboard making. Since the oil palm trunk is a waste after 25 years, this hidden valuable material for adhesive making was investigated by numerous researchers. Killmann and Lim reported that one oil palm trunk contained at least 24% of oil palm starch. Tomimura reported starch content could be up to 55.5% from the whole trunk followed by Noor et al. reported that parenchyma of the oil palm trunk consisting approximately 7.15% of starch (Killmann and Lim, 1985, Tomimura, 1992, Noor et al., 1999).

Evaluation of starch properties to enhance its performance comprising its ability to form bonding and reducing their absorbing properties, researchers have gone through with many possible ways, for example, a modification process. The modification process is usually going through with a chemical process, which includes esterification, etherification, and oxidation process (Huber and BeMiller, 2010). The modified starches have dissimilar end properties depending on chemical reagents used such as epichlorohydrin, polyvinyl alcohol, and acetic mixed anhydrides; conditions of the reaction such as temperature, pH, the time interval, and so forth (Chiu and Solarek, 2009, Chung and Lai, 2006).

1.2 Problem statements

From the previous study, the polyvinyl alcohol was used to form partially gelatinized natural adhesives of corn starch with improved moisture resistance, and higher with favourable viscosity of the adhesive for particleboard making (Imam et al., 1999). Nevertheless, full characterizations of this modification technique with other starches were not done yet. Thus, the combination of the oil palm starch and polyvinyl alcohol is expected to have good properties for starch based adhesives' production. The modification process usually will result in high stability of starch, good adhesion, higher thermal stability, less sensitive to moisture, and the lower retrogradation rate (Chiu and Solarek, 2009, Huber and BeMiller, 2010, Baldwin et al., 2009, Bertolini, 2009, Maningat et al., 2009).

Other researchers had done the investigations of oil palm strand and oil palm starch, but the combination of both this raw materials in particleboard making has not been done yet (Abe et al., 2013, Baskaran et al., 2012, Hashim et al., 2011a, Hashim et al., 2010, Hashim et al., 2011b). Other than that, oil palm starch-modified with the polyvinyl alcohol also has not been done yet; therefore, this study will cope the idea of using natural resources to produce a new green particleboard in the wood industry.

1.3 Objectives

The objectives of the studies are:

1) To study the characteristics of particles and extracted starch produced from oil palm trunk for particleboard making.

2) To determine the potential and suitability of particles and starch for particleboard making.

3) To determine the effect of starch modification on physical and mechanical properties of particleboard.

2. LITERATURE REVIEW

2.1 Wood-based industry

As a tropical country, Malaysia is well known with its wood –based industry. Due to the abundance of this resource lead to the creation of various types of wood industry which comprises from logging, wood processing, wood preserving, wood manufacturing, and to the production of high-end wood products. There are many products produced from this industry with various classifications in Malaysia; the wood-based industry comprises of two major sectors, which are solid wood and bio-composite. For solid wood, it can be divided into four main sub-sectors. The first one is sawn timber veneer, panel products, and reconstituted panel products. The second sub-sector is Mouldings and Builders' Joinery and Carpentry (BJC). Furniture is the third while the last sub-sectors is furniture component. For bio-composite sector there are two sub-sectors, which are conventional composite and advance composite (Teischinger, 2012).

Based on National Timber Industry Policy (NATIP) of Malaysia the annual growth targeted for the wood industry from 2009-2020 is 6.5% annually with the exports' value of the RM 53 billion (Loh et al., 2010). This long-term target was evaluated due to the potentials and the availability of wood products from our forest as it will generate money, creating new job opportunities as well as fully utilized our wood resources.

In Malaysia, there are 5,870 of manufacturing establishment and around 80-90% are considered as small or medium enterprise (SME) while the remaining 10-20% considered as big companies. The number of this wood-based manufacturing company is increased year after year. These companies are mostly located in the eastern part of

Malaysia, which is referring to the states of Sarawak and Sabah. Both states had the largest land area with small inhabitants compared to the peninsula of Malaysia, where here the wood resources are more abundance with various wood species for production of wood-based products (Zaidon et al., 2007, Mokhtar et al., 2011).

Wood industry continuously emerging year after year as the introduction of the agricultural trees such as rubberwood tree and oil palm tree also has been giving emphasis as it additionally can be an alternative material for wood-based industry. It is expected the wood-based industry will remain as the major contribution to Malaysia economy for the next 50 years (Aljuboori, 2013, Mokhtar et al., 2011).

2.2 Particleboard

Manufactured panels from dry wood particles that have been sprayed, dusted or manually blended with a binder is known as particleboard (Carll, 1986). There are various parameters of making the particleboard that must be controlled started with types of raw materials, conditions, which comprises its size, pH, types of treatments, etc. Other than that, types of adhesives, which include the chemical properties, percentage of formaldehyde emission, effect towards the environment, adhesive's efficiency, etc. Lastly, manufacturing processes such as the pressing conditions, which comprehend the temperature level and pressing time (Halligan, 1970). All these parameters usually used and controlled to gain good end products, which met acceptable quality for manufactured board.

The particleboard can be a single or multiple layers depend on the end use of the products. Some of the particleboards will have high resistance with moisture but poor mechanical properties; some of it will have excellent fire resistance, pleasurable mechanical properties but poor physical stability, and it all depends on the end use of the products (Loh et al., 2010, Medved et al., 2011, Nemli, 2002).

One of the advantages of using particleboard is cost effective. The particleboard usually used wood residues and even at-large scale of production the total cost is still lower compared to other manufacturing industries. The main reason of the cost effective is due to the process throughout particleboard making is cheap, and energy consumption is low even though fuel was used for the heating process (Amini et al., 2013). This particleboard usually not weather and moisture resistance but it is applicable and pleasantly suitable for plastic lamination and to make its look more like solid timber it also can be laminated with a thin layers of veneer. The particleboard commonly a green product but it depends on the type of adhesives used. If the adhesives contain carcinogenic chemical such as formaldehyde, it might be harmful to human health and cannot be considered as a green product (Dunky, 1998, Park and Jeong, 2011, Pendlebury et al., 2010).

The downside of using particleboard is it still unable to compete with the properties of solid timber. Nevertheless, this disadvantage can be diminished by mixing with suitable adhesives and embark with high-end finish processes. Other than that, the particleboard is not available in very thick sizes. If the thickness of the panels is high; it might not fully cook, and it also increases the energy consumption, so it is not cost effective (Liiri et al., 1980).

2.2.1 Particleboard manufacturing process

Typical manufacturing process for particleboard making in industry was shown in Figure 2.1.

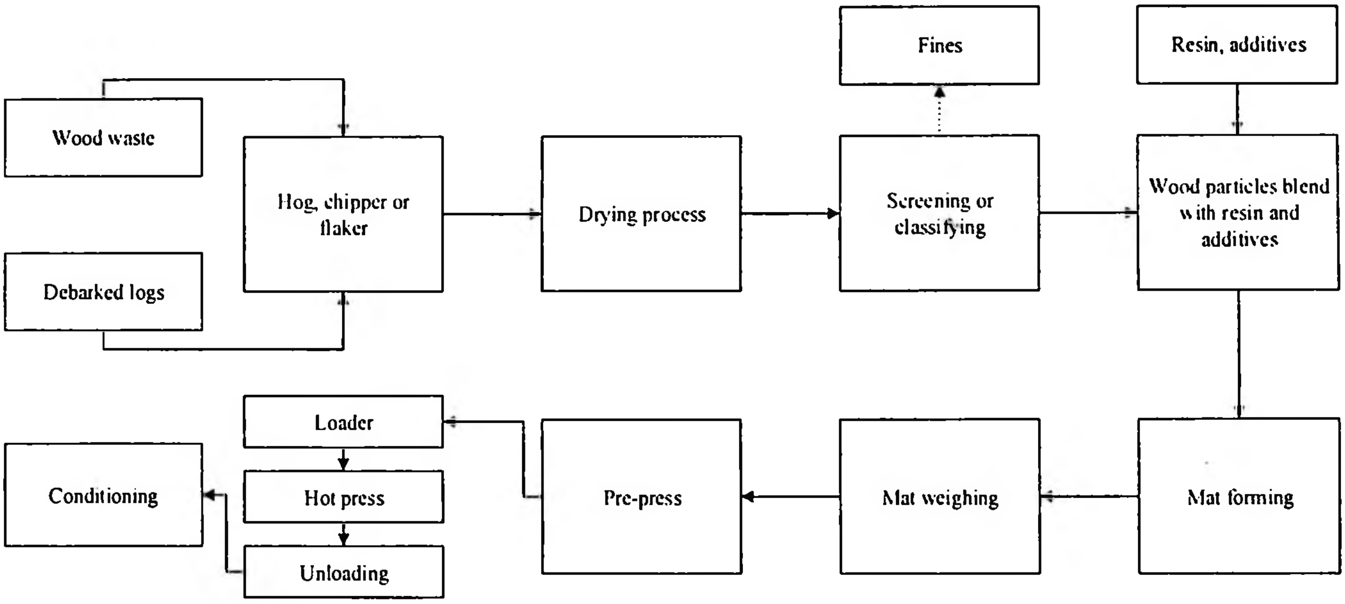

Figure 2.1 Particleboard manufacturing process flow (FAO, 1990)

Figure 2.1 showed the typical process flow for particleboard making practiced by industries. The main processes for particleboard manufacturing encompass the particles preparation, drying, and screening, then followed by blending, mat-forming, pressing and conditioning. Particleboard manufacturing is different depending on industrial practice. The process flow was designed based on the end product. All the materials, conditions, and conditioning process were examined to suits the target end product.

First process is choosing the types of lignocellulosic materials. For particleboard manufacturing, low-grade residues often used such as hogged mill waste, sawdust, and planer shavings. Then these raw materials were delivered to the mill yard after that proceed with segregation of particles based on size, and species. To prevent blunting chipper knives, damage to the equipment and ignition due to hot engines, bark was removed from logs (Cai et al., 2009, FAO, 1990). Reduction equipment which capable of process various sizes of wood and wood residues was used to produce a particle with different size and geometry (Cai et al., 2009, Nemli et al., 2007).

Then the particles will proceed with drying and screening process. The particles were dried, and the moisture content of the particles were controlled between 3-8%, which enable particles to form bonding with liquid resins (Medved et al., 2011, Wong, 1999). The particles were dried continuously in rotating horizontal dryers. The heat in the dryers generates by combustion of oil, gas or process residues via exposure towards hot gases or heat emitted from tube bundles. Other than that, flash drying as an alternative was also used to rotary dryers, and this method only requires low drying temperatures (FAO, 1990).

After that, the particles were screened for different sizes via vibrating or gyrating screens. This process conducted after drying because if the screening process takes place before drying, the particles are very moist and stick together, which difficult the screening process to take place (Liiri et al., 1980). Then, different sizes of particles were graded while the oversized particles were recycled for further reduction (FAO, 1990). There are so many types of particles such as flakes, granules, chips, excelsior, fibers, and strands (Carll, 1986).

Next, after forming the particles into desired shape and size, blending between particles and adhesives were taken place. The most popular and commonly used adhesives in particleboard making are the formaldehyde-based adhesives such as melamine formaldehyde, phenol and urea formaldehyde (Pendlebury et al., 2010, Xing et al., 2007, Conner, 1996). The particles and the adhesives with percentage of 3-10%

together with additives were mixed with considerable quantities under controlled conditions into a loose mat. This process can be done in continuous or as a batches' operation (FAO, 1990).

After blending process, formation of the mat is taken place. Usually, particleboard manufacturing is a wholly mechanical process, but the mat formation techniques are still the same. The mixed particles were uniformly flow and fed to the surge bin, and distributed evenly from layer to layer into a frame on moving belt. The mats were then weighed and followed with pre-press process (Hashim et al., 2011b, Wong, 1999). The forming mats were transferred on metal plates, called cauls, for the pre-press and hot press process. The pre-press process can either be hot or cold. This step was taken place to reduce the mat thickness for better handling and reduce the pressing time (FAO, 1990).

After the particles and adhesives were well blended and formed into the mat by pre-press, the process was followed by pressing process. The particleboard, which density depends partly on the amount of adhesives, less pressure and heat were required and vice versa (Gu et al., 2012, Nemli, 2002). Depending on the type of resin and press, the temperature within the range of 140-400 °C was used (FAO, 1990). After the particleboard was removed from the pressing machine, the finished product was conditioned. The finished product was cut with desired shapes. Then, it was stored before distributing for selling (Carll, 1986).

For laboratory scale, the process flow for particleboard is almost similar but different number of scale, size of end products, and conditioning process. For laboratory purposes, the board was conditioned based on standards such as Japanese Industrial Standard (JIS) A5908, American Society for Testing and Materials (ASTM)

D1037, and British Standard (BS) 5669-1: 1989. For example, the Japanese Industrial Standard A 5908, the board is required to be stored under air-dry condition at the temperature of 20 ± 2 °C with the humidity of 65 ± 5% (JIS, 2003).

2.2.2 Types of adhesive

2.2.2.1 Synthetic adhesive

2.2.2.1.1 Urea formaldehyde

The urea formaldehyde (UF) is commonly used in the wood based panels industry because of its high reactivity, good performance of end product, and low price compared to other synthetic adhesives. The drawback of using this adhesive lacks in water resistance resulted to the reversibility of the aminomethylene link and susceptibility to hydrolysis (Dunky, 1998). This resin is used around 61% for particleboard manufacturing as a bonding agent; 27% for medium density fibreboard, 5% for hardwood production, 7% for bonding of laminating adhesive (Conner, 1996).

The production of UF involving the reaction between manifold of two monomers, namely urea and formaldehyde, with molar ratios of between 1 and 1.2 or 1 and 2.0. The formaldehyde emission can be minimized by lowering the formaldehyde ratios. Even though this technique was more favourable, but it had inferior strength and water resistance with slower curing (Ferra et al., 2011, Hematabadi et al., 2012). Anyhow, recent formulations at some extent have overcome these drawbacks. The most common curing agent used to cure the adhesives at elevated temperatures is ammonium chloride, NH_4Cl (Packham, 2006).

The productions of UF mainly differ based on a broad variety of possible reactions and structures, which can be explained at the molecular level by their high reactivity, their water solubility, and the reversibility of aminomethylene link, which enables it to against water and moisture absorptions (Dunky, 1998, Risholm-Sundman et al., 2007). To date, this adhesive is still extensively produced. This adhesive falls into aminoplastics resin, which comprise 80% or worldwide production based on its class (Conner, 1996, Dunky, 1998).

The most typical use of UF in boards making is for interior wood products due to its limitation to resist water as the presence of moisture undergo UF to hydrolytic degradation particularly at temperature above 40 °C (Packham, 2006). The main advantages of using UF in particleboard making industry are its low price as it is relatively inexpensive compared to other synthetic adhesives. It is also non-flammable due to its high-nitrogen content thus it is only burning with support of flame (Biswas et al., 2011, Buyuksari et al., 2010, Hematabadi et al., 2012). The UF also well known for its synergic effects with other adhesives as it can be simultaneously combined with other adhesives to complement each other. This adhesive also has high reactivity and low-press time, including full hardening to thus decrease the manufacturing cost (Dunky, 1998, Salem et al., 2011).

Aside with no water and weather resistance, the main disadvantages of using UF in particleboard making is the emission of formaldehyde. The formaldehyde gas is a well-known carcinogenic chemical that emits from boards bonded with formaldehyde-based adhesives (Conner, 1996, Dunky, 1998, Ferra et al., 2011, Jiang et al., 2010). There are several formulations that were introduced to diminish these drawbacks or at least to reduce the emission of formaldehyde in UF based adhesive. One of the techniques proposed were changing the formulation of UF adhesive resin. First, by adding formaldehyde-scavenging materials directly to the UF adhesive resin. Second, separately adding formaldehyde-scavenging materials to wood finishes.

Third, treating panels after their manufacture either with a formaldehyde-scavenger or by application of coatings or laminates. Lastly, changing the entirely different adhesive resin system by using non-formaldehyde based adhesives (Conner, 1996).

For particleboard making, the amount of UF is around 8 g of solid resin per 100 g of parched chips whilst for the medium fibre board is 12 g of solid resin per 100 g dry fibres (Packham, 2006). Properties of typical UF disclosed in Table 2.1.

Table 2.1 Basic properties of urea formaldehyde (Packham, 2006)

Properties	Urea formaldehyde, UF
pH at 30 °C	8.15
Viscosity at 30 °C	150 cPs
Specific gravity at 30 °C	1.272
Solid content	64.5%
Gel time at 100 °C	180 min
Free foam	0.26%

2.2.2.1.2 Melamine formaldehyde

The melamine formaldehyde (MF) is also one of the most common synthetic adhesives in wood-based industry, which is also well-known as melamine resin. For commercial purposes it has numerous trade names such as Melit, Melsir, Cellobond, Melmex, Isomin, Epok, Plenco, Melolam and Melopas (Pendlebury et al., 2010). This adhesive formed in white color, tasteless, odorless, and exhibits great chemical and heat resistance. The price of melamine formaldehyde is quite expensive compared to UF. The melamine content in MF adhesive is decreasing at the same time maintaining the high performance of the adhesives by improving the resin formulation (Pendlebury et al., 2010, Hematabadi et al., 2012).

The difference between UF and MF, the MF rarely used even though it have better performance in terms of strength and weather resistance. These two adhesives often combine together as melamine-urea-formaldehyde (MUF), either by mixing or preferably produced as a co-condensate, as it gives a very good impact to the durability of formaldehyde-based adhesives (Packham, 2006, Han et al., 1998). These adhesives of MUF have similar water resistance like MF but at lower cost. The MF is a member of the aminoplastics family together with UF and phenol formaldehyde (Dunky, 1998). Aside from using in wood panels, it is also used in many household goods, in various electrical applications, in bonding and coatings. The melamine itself offers acute hardness, admirable color ability and arc-resistant non-tracking characteristics. By the condensation reaction of formaldehyde, HCHO and melamine, $C_3N_3(NH_2)_3$, thermosetting resins formed (Risholm-Sundman et al., 2007, Salem et al., 2011, Xing et al., 2007). The MF is analogous based on its chemistry to that UF, except the presence of three amino groups of melamine provides more possibilities for cross-linking. This enables them to be highly reactive, and all six-hydrogen atoms of melamine will react, forming the hexamethyl compound (Pendlebury et al., 2010).

These resins also used to meet certain green building standards for productions of composite panels, such as particleboard, medium density fiberboard, and hardboard. Other than a high price of the melamine, other disadvantages of this adhesive are it easily affected by alkalis and concentrated acids, for example, sulphuric acid, H_2SO_4 and oxalic acid, $H_2C_2O_4$. Similar to the UF, the main disadvantages of the MF is the emission of formaldehyde (Buyuksari et al., 2010, Li et al., 2013, Pendlebury et al., 2010).

2.2.2.1.3 Phenol formaldehyde

The phenol-formaldehyde (PF) is also known as phenolic resin. Phenol is an aromatic alcohol derived from benzene react with formaldehyde, which a reactive gas derived from methane will form a synthetic resin known as phenol formaldehyde. This adhesive extensively used in plywood and particleboard making (Packham, 2006). The PF adhesive is yellow to brown or amber in colours. This adhesive fall into high polymers' synthetics. By the reaction between phenol and substituted phenol together with formaldehyde, this adhesive combined and formed into networks of permanently interlinked. These adhesives have many forms, from liquid to solid, differ by crosslinking process (Salem et al., 2011, Xing et al., 2007). Depend on the end uses of the adhesives, via polycondensation the adhesives no longer soluble but can be swelled by organic solvents. Particleboard made with PF will form a smooth and lustrous surface whereas this adhesive can be combined with various types of fillers depending on the nature of adhesive (Han et al., 1998, Salem et al., 2011, Packham, 2006).

For industrial practice, there are two basic methods to produce this polymer. The first method is an excess of formaldehyde with the presence of base catalyst is reacted with phenol in water solution to yield a pre-polymer resole with low-molecular-weight. The resole, usually in solution or liquid form, can be cured to a solid thermosetting network polymer by, for instance, sandwiching it between layers of wood veneer. Then, heating the assembly under pressure to form plywood. The second method is the reaction of formaldehyde with the presence of an acid catalyst react with an excess of phenol to produce a pre-polymer called as novolac. This pre-polymer has lower molecular weight compared to resole (Packham, 2006).

The phenol-formaldehyde can form chemical bonds with the phenol-like lignin, which make it excellent as wood adhesives for particleboard and plywood manufacturing (Nemli and Öztürk, 2006, Pendlebury et al., 2010). Owing to their good moisture resistance, the PF usually desirable for exterior plywood and particleboard. Other than using in particleboard making, the PF also used as appliance handles, distributor caps, and so forth. The main advantages of using PF in particleboard making are excellent flame resistance, high strength and modulus properties, and pleasant dimensional properties. The disadvantages of using PF are emissions of formaldehyde same as urea and melamine formaldehyde (Salem et al., 2011, Packham, 2006).

2.2.2.2 Natural adhesive

2.2.2.2.1 Starch

Starch is a major energy reserve consisting macro-constituent of many foods. It is loosely defined as a polymer occurs with the interactions with other constituents, particularly water and lipids, varies greatly within botanical species (Copeland et al., 2009, Stoddard, 2004). Starch is insoluble in water because of the polysaccharide or also known as alpha-glucan mainly consists of amylose with a linear $\alpha - (1 \rightarrow 4)$ linked glucan and amylopectin with an $\alpha - (1 \rightarrow 4)$ linked glucan with 4.2 to 5.9% $\alpha - (1 \rightarrow 6)$ branch linkages (Robyt, 2008, Tester et al., 2004). Segments of both polysaccharides are showed in Fig 2.2 and Fig 2.3 can vary substantially between different starches about placement and length of branches. The percentages between this two polysaccharide are different. It ranges from 17-70% of amylose and the remaining 83-30% of amylopectin.

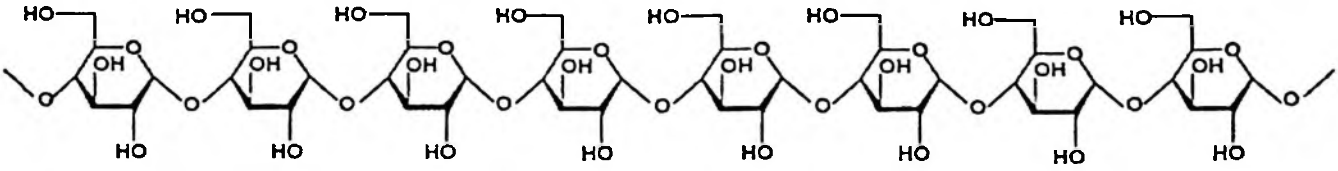

Figure 2.2 Segment of an amylose molecule (Robyt, 2008)

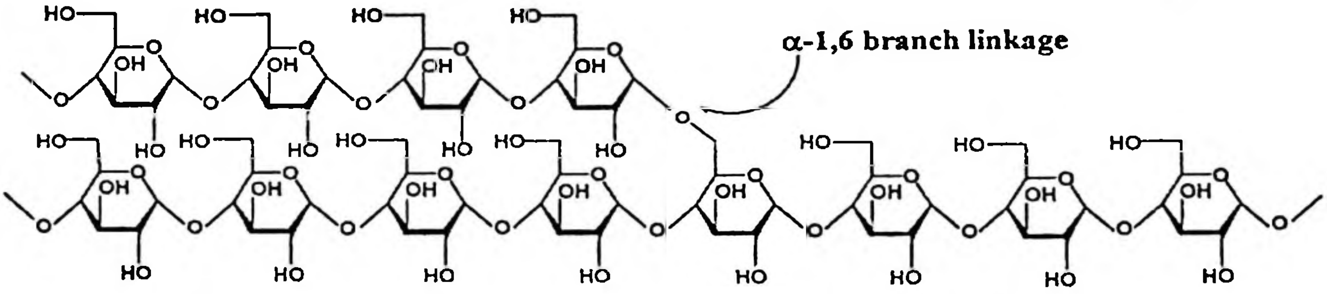

Figure 2.3 Segment of an amylopectin molecule with different linkage (Robyt, 2008)

The amylopectin is a much larger polymer compared to amylose due to its branch-like-structure, with molecular weight about 10^8 and a degree of polymerization (DP) exceed one million. The amylopectin is one of the largest natural polymers known (Baldwin et al., 2009). The polymer chains' molecules can possess into three populations, which can be classified into short chains having ($12 < DP < 20$), long chains having ($30 < DP < 45$), and a very long chain having $DP > 60$. The branches of the amylopectin further classified into three types based on their patterns of substitution (Biliaderis, 2009, Buléon et al., 1998). The first one known as A-chains are defined as unsubstituted, followed by B-chains are substituted by other chains, and lastly C-chains as single chains carries the reducing glucose (Copeland et al., 2009, Baldwin et al., 2009). The amylopectin α – (1→6) branch linkages are believed to eventuate in the amorphous regions of the granule. With clustered-like-structure, the branched amylopectin was contained several chains of 15-20 glucose residues from the cluster, intertwined into double helices, contributing to the crystallinity (Robyt, 2008, Copeland et al., 2009, Jackson, 2003, Mitsui et al., 2010).

The amylose with linear structure usually has molecular weight range approximately 10^5-10^6, with degree polymerization around 1000-10000 of glucose units. The presence of glucose units in amylose α – (1→6) linkages are less than amylopectin with less than 0.5%, resulting to a low degree of branching (Copeland et al., 2009, Ačkar et al., 2010, Stoddard, 2004, Tester et al., 2004). The amylose chains can exist in both single and double helices for non-complexed amylose chains such as cereal starches (Robyt, 2008, Bertolini, 2009, Tester et al., 2004, Zeng et al., 2014). Granular-bound starch synthase synthesizes the amylose whilst amylopectin synthesized by the soluble starch synthase (Jane, 2006). Calorimetric test can determine the presence of starch giving a blue color due to the inclusion complexes of amylose helices with polyiodide (Copeland et al., 2009). The nature of starch granules is relied on the percentage of amylose and amylopectin of the starch as these two components largely affected the physical, chemical, and thermal properties of the starch granules.

Table 2.2 show the percentage of polysaccharides of amylose and amylopectin make up 98-99% of total dry-weight while the remainder is comprising the small amount of lipids, protein, and phosphate content of different sources of starch (Robyt, 2008, Copeland et al., 2009). The polysaccharide has many monosaccharides attached together with repeating units. The bonds assemble the starch are firm to break and difficult to dissolve in the liquid medium.

Table 2.2 Percentage of chemical compositions of starch from different sources of starch (Robyt, 2008)

Starch	Amylose, %	Amylopectin, %	Lipid, %	Protein, %	Phosphate, %
Maize	25	75	0.80	0.35	0.090
Waxy Maize	0	100	0.20	0.25	0.024
Potato	22	78	0.01	0.10	0.210
Wheat	23	77	0.90	0.40	0.180
Rice	19	81	0.59	0.30	0.090
Tapioca	17	83	0.02	0.10	0.009
Banana	20	80	0.48	0.32	0.060
Shoti	30	70	0.01	0.20	0.630

The behaviour of starch granules mostly affected by the percentage of amylose and amylopectin. Eventually, the remaining 1-2% of lipid, protein, and minerals also play an important role by affecting the moisture sensitivity, thermal, and rheological properties of starch-water pastes (Baldwin et al., 2009). The presence of lipid, for example, evidently will affect the hydrophobicity of starch granules. The existence of protein makes the starch capable of rapid swelling upon hydration. These two organic materials indirectly will attribute the characteristics of starch granules (Juhani and Chokyun, 1978, Robyt, 2008).

The presence of protein in starch granules were due to the protein partially covered the granules, which explain why the existence of protein in starch granules (Juhani and Chokyun, 1978). However, the percentage of protein depends greatly on extraction methods (Stoddard, 2004). The percentage of lipid content is correlated with the concentration of amylose of the starch. The amylose-lipid relationship occurs as the lipid is bound in the loose helical structure of the amylose, which usually known as free fatty acids (commonly linoleic) or lysophospholipids (Stoddard, 2004, Robyt, 2008). The presence of protein and lipid are by far the most copious minor components of the starch.

The starch granules are semi-crystalline, alternating amorphous and crystalline shells between 100-400 nm thick, which referring to the growth ring of the starch granules (Baldwin et al., 2009, Bertolini, 2009, Buléon et al., 1998). Understanding the starch granules characteristic is important since the size, shape, chemical compositions, chemical sensitivity, ability to swell, and so forth are different from various sources.

The starch granules are known with polymodal characteristics for some types of starch, which referring to variations of starch granules in terms of size. The size of starch granules can be divided into three types, which are A-granule, B-granule, and C-granule. Roughly, the A-granule is > 15 µm, B-granule is between 5-15 µm and C-granule is < 5 µm (Wilson et al., 2006). Sometimes to differentiate these starch granules it is difficult as many researchers view small G-granules as a distinct C-granule type (Stoddard, 2004). Wheat starch consists all types of sizes while the other starches only have one to two types only. In maize, the starch granules are more to the spherical shape. The A-type granules of barley and wheat have a similar shape as rounder. Rice and oat have compound like structure. Legume starch granules are ovoid or elliptical whilst tuber and root starches have round to ovoid like structure (Stoddard, 2004). Figure 2.4 showed the scanning electron microscopic (SEM) of the starch granules from different type of sources.

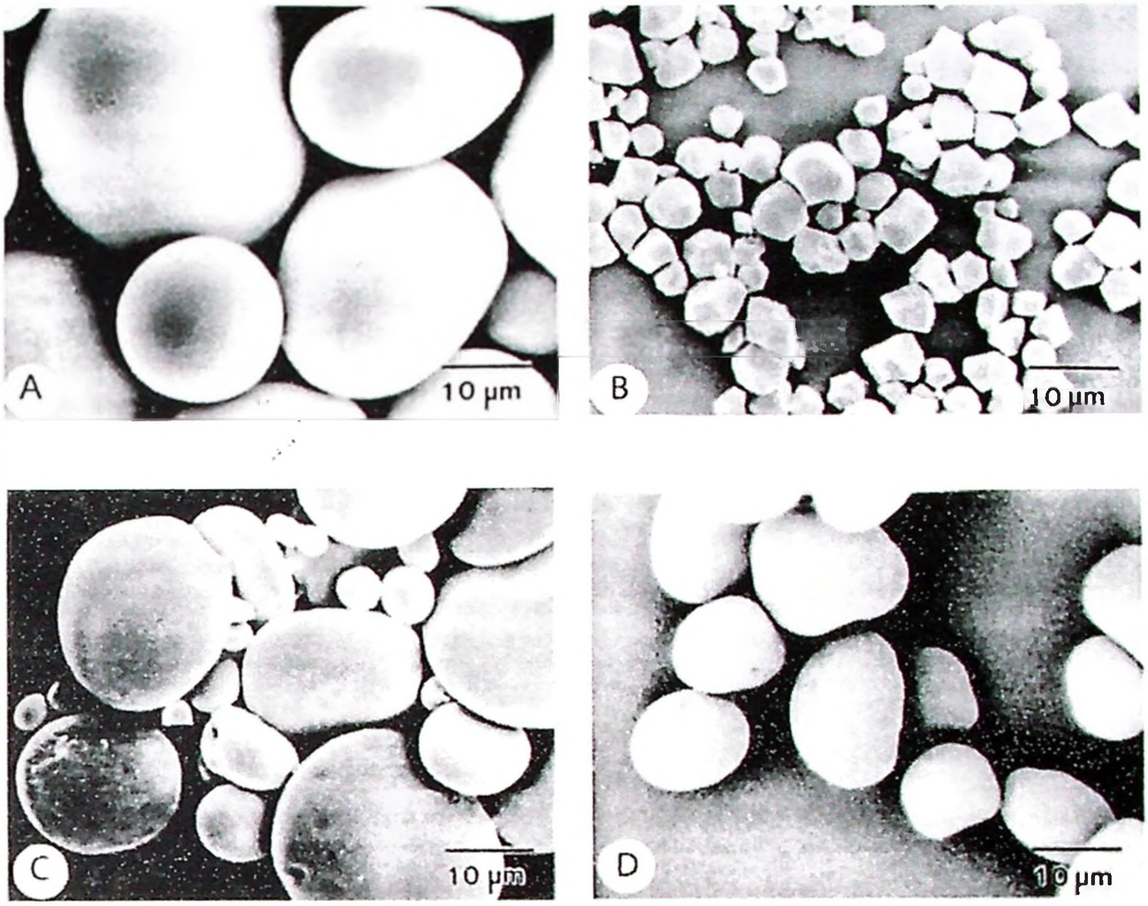

Figure 2.4 Scanning electron microscopic of starches (a) potato (b) rice (c) wheat (d) mung bean (Robyt, 2008)

The size of the starch granules sometimes interchangeable from C-type and B-type to A-type. This could happen after the starch granules were exposed to the heat-moisture treatment, for B-type with constant exposure of 30 °C heats-moisture treatment, the structure would change to A-type whilst C-type require ~ 50 °C to change (Robyt, 2008, Baldwin et al., 2009, Patel and Seetharaman, 2006, Ratnayake and Jackson, 2008). This occurrence due to deformation of intermolecular bonds and re-crystallization occurred after cooling process. The A-type also interchangeable with other forms of crystalline by the destruction of the original structure to allowed re-crystallize occurs (Ratnayake and Jackson, 2008).

The structure and smoothness of the surface of the starch granules from different sources could be determined by looking into their microscopic view through SEM analysis. Size range of starch granules usually between 1-100 µm in diameter, which vary greatly depending upon the structure and organization of the amylose and amylopectin molecules (Copeland et al., 2009). Starch from maize, waxy maize, oats, and sorghum usually have a smaller diameter around 15-25 µm, with the exclusion of rice starch having starch granules with an average diameter of 3-5 µm. Starches from bean and peas having 10-45 µm, and some of the starches are extremely small, such as Chinese taro having 1-4 µm, amaranth having 0.5-2 µm and parsnip having 1-3 µm (Robyt, 2008, Biliaderis, 2009, Chung and Lai, 2006, Zeng et al., 2014).

Starch granules are water insoluble materials for practical purposes, but the interaction of water and starch did occur (Juhani and Chokyun, 1978). The hydrogen bonds and hydrophobic bonds were formed from the amylose and amylopectin intermolecularly and intramolecularly interactions. The varying degrees that hold the molecules amylose and amylopectin, giving a water-insoluble granule (Ačkar et al., 2010, Maningat and Seib, 2010, Neelam et al., 2012). The arrangement and quantity of these bonds signify the differences of granule's properties by having a variation in the amount of the crystalline region. The regions indicate the degrees of crystallinity of the starch granules. Other than that, because of these occurrences, the gelatinization temperature and susceptibility to enzyme hydrolysis were also affected (Robyt, 2008).

2.2.2.2.2 Isolation of starch granules

The water-insolubility of starch granules makes it possible to isolate from different sources such as wheat, rice, maize, beans, and so forth. First, the seeds soaked in water for 10 to 15 hours at 50 °C. This steeping process was done to soften the outer parts of the seeds, which enables to extract the starch inside the seed plants. The protein that encircles, the starch granules, were removed by soaking them in 1.63 g of sodium sulphite, Na_2SO_3 (Mitsui et al., 2010, Robyt, 2008, Samuel, 2006).

Then, the soaked materials ground, milled or blended until white suspension extracted from the seed. After that, the white suspension filtered through six layers of cheese cloth, then filtered again through eight layers of cheese cloth to remove the remaining fibrous non-starch substances. Then, the extracted starch was washed two to three times with distilled. After that, the extracted starch centrifuged or filtered followed by air dry at 20 °C before grinding into a fine powder (Robyt, 2008, Mitsui et al., 2010, Samuel, 2006).

2.2.2.2.3 Products from starch

For centuries, starch was used for many purposes for industrial productions. From the food to bio-degradable products, the applications of this raw material vastly change through time. Starch is well known for its low cost, availability, and ability to impart a broad range of functional properties to food and non-food products. The uses of starch far-reaching to the most sophisticated end products as shown in Fig 2.5 (Koch and Röper, 1988).

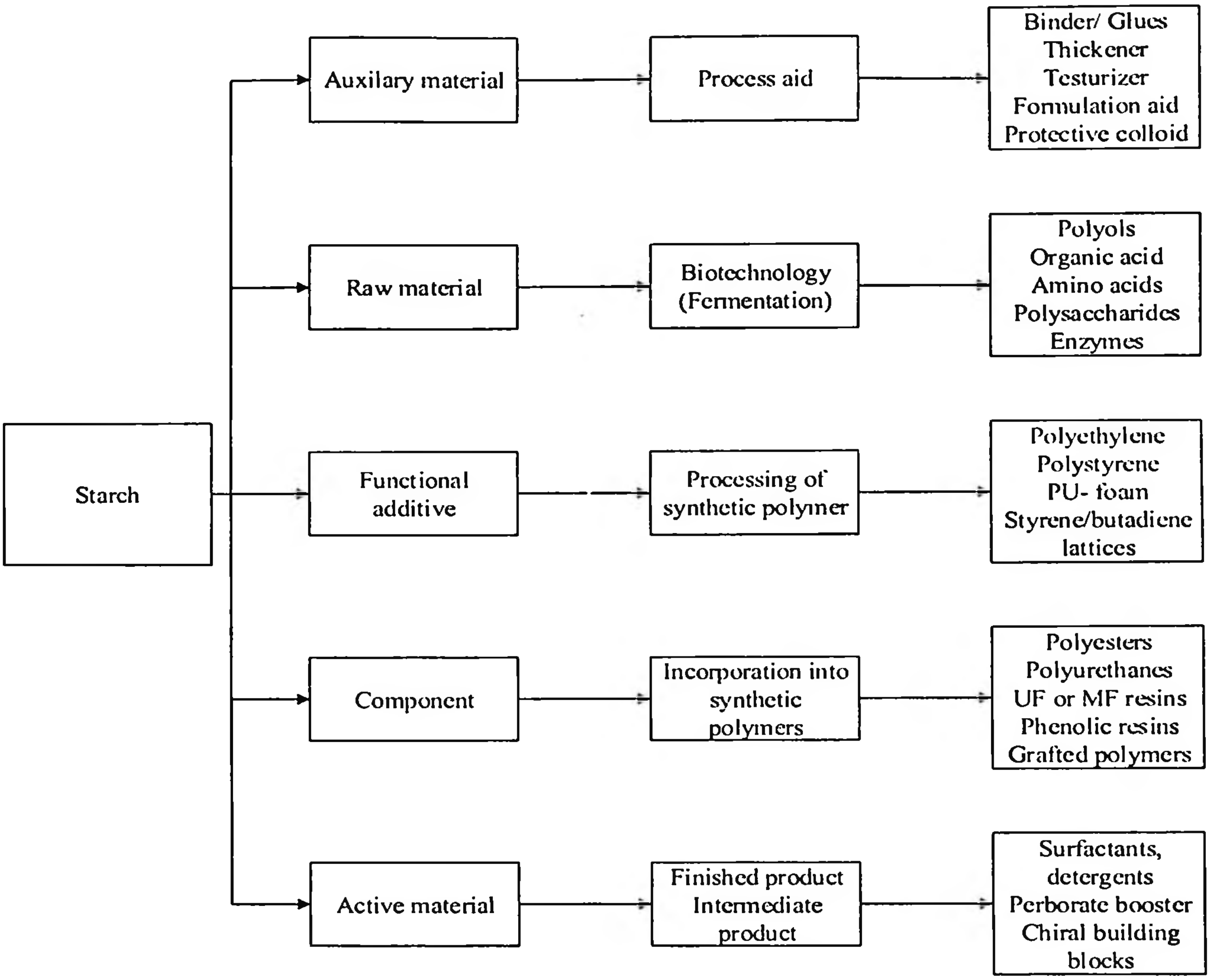

Figure 2.5 Starch functions, applications and products (Koch and Röper, 1988)

The versatilities of starch compared to other carbohydrates were due to the capabilities of native starch to be physically and chemically modified with relatively simple process and technologies. The starch granule is dispersible in cold water and exhibits a higher reactivity than the highly polymeric cellulose (Baldwin et al., 2009, Biliaderis, 2009). By using acids and enzymes, the starch granules were very susceptible to partial or total hydrolytic degradation composing monomeric or oligomeric products, which can be additionally modified or derivatives. These derivatives were cannot be fabricated from cellulose or sucrose as raw material.