OPTIMIZATION AND CHARACTERIZATION OF MELAMINE UREA FORMALDEHYDE (MUF) BASED ADHESIVE USING NATURAL FILLERS FOR PLYWOOD

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Thesis submitted fulfilment of the requirements for the award of the degree of Master of Engineering (Chemical)

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Dedicated to my parents and friends

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ABSTRACT

In this research, Palm Kernel Meal (PKM) and Palm Shell (PS) were studied as a filler for wood adhesive formulation and compared with present industrial filler (IF), wheat flour. Melamine Urea Formaldehyde (MUF) resin was selected as the resin for formulating the wood adhesive. The effects of natural filler on shear strength and formaldehyde emission of plywood were studied. The response surface methodology (RSM) was used to identify the optimum hot press temperature and press time for plywood process. The experimental results showed that the optimum hot press temperature and time of PKM, IF and PS were 129.5 ^{o}C; 133.7 ^{o}C; 130.7 ^{o}C and 170 sec; 159 sec; 186 sec respectively. The physico-chemical interaction between veneer and adhesive was investigated using Fourier Transform Infrared Spectroscopy (FTIR) technique. The FTIR spectrum of PKM showed blue shift which indicated that the functional groups (such as C=O, -OH and NH) become more free in the heat treatment samples. In the PKM-MUF blend bonding interactions, red shift occurred on C=O and N-H groups were observed. Red shift of C=O and N-H groups stretching in PKM-MUF-Wood blend was observed which suggests the interaction of these functional groups occur through hydrogen bonding. In addition, PKM-Wood-MUF with different amount of PKM, the bonding interaction between C=O (PKM) with O-H and N-H groups effectively involved more as the amount of PKM increase. Plywood bonded with PKM exhibited the highest shear strength comparitively with others. The formaldehdye emission of plywood bonded with PS was higher than PKM and IF respectively. At 13 % PKM concentration shows maximum shear strength. Experimental results showed that formaldehyde emission was minimum (environmental standard) at 18 % of PKM. This research concluded that, PKM based MUF adhesive resins exhibited potential application in production of plywood in Malaysia.

ABSTRAK

Dalam kajian ini, isirong sawit serbuk (PKM) dan tempurung kelapa sawit serbuk (PS) telah dikaji sebagai pengisi untuk penggubalan pelekat kayu dan berbanding dengan pengisi sekarang guna di industri (IF). Melamine Urea Formaldehyde resin (MUF) telah dipilih sebagai resin untuk merumuskan pelekat kayu. Kesan pengisi semulajadi pada kekuatan ricih dan pelepasan formaldehid papan lapis telah dikaji. Kaedah respons permukaan (RSM) telah digunakan untuk mengenal pasti suhu penekan panas dan penekan masa optimum untuk proses papan lapis. Keputusan pengajiaan menunjukkan bahawa optimum suhu penekan panas dan masa PKM, IF dan PS adalah 129.5 ^{o}C; 133.7 ^{o}C; 130.7 ^{o}C dan 170 sec; 159 sec; 186 sec masing-masing. Interaksi fiziko-kimia antara venir dan pelekat telah dikaji dengan menggunakan Spektroskopi inframerah transformasi Fourier (FTIR) teknik. Spektrum FTIR PKM menunjukkan anjakan biru yang menunjukkan bahawa kumpulan berfungsi (seperti C=O,-OH dan NH) menjadi lebih bebas dalam sampel selepas rawatan haba. Dalam PKM-MUF ikatan interaksi campuran, anjakan merah berlaku pada C=O dan kumpulan NH telah dipatuhi. Anjakan merah C=O dan kumpulan NH menjadi regang dalam PKM-MUF-Kayu campuran yang mencadangkan interaksi kumpulan berfungsi ini berlaku melalui ikatan hidrogen. Di samping itu, PKM-Kayu-MUF dengan kepekatan PKM yang berbeza, interaksi ikatan antara C=O (PKM) dengan OH dan kumpulan NH yang berkesan melibatkan lebih dengan jumlah PKM meningkat. Papan lapis yang terikat dengan PKM mempamerkan kekuatan ricih tertinggi berbanding dengan lain-lain. Pelepasan formaldehdye papan lapis yang terikat dengan PS adalah lebih tinggi daripada PKM dan IF. Pada 13 % PKM menunjukkan kekuatan ricih maksimum.Keputusan penyelidik menunjukkan bahawa pelepasan formaldehid adalah minimum (standard alam sekitar) pada 18 % daripada PKM. Kajian ini menyimpulkan bahawa, PKM berasaskan perekat resin MUF mempamirkan potensi dalam pengeluaran papan lapis di Malaysia.

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C	Formaldehyde concentration of test pieces
A_d	Absorbance of a sample solution
A_b	Absorbance of blank test
F	Inclination of calibration curve
x_1	Temperature
x_2	Pressing Time
x_3	PKM, PS, IF
Y_1	Shear Strength
Y_2	Formaldehyde Emission

LIST OF ABBREVIATIONS

ABES	Automated bonding evaluation system
ANOVA	Analysis of variance
BWT	Boiling water test
CA	Curing agent
CF	CNSL-formaldehyde
CNSL	Cashew nut shell liquid
CP	Crude protein
CPF	Control phenol formaldehyde
CV	Coefficient of variation
DKL	Demethylated kraft lignin
ECH	Epichlorohydrin
EFB	Empty fruit bunches
EVA	Ethylene vinyl acetate
F	Formalin
FLEC	Field and laboratory emission cell
FTIR	Fourier Transform Infrared Red
GA	Glutaraldehyde
GO	Glyoxal
IARC	International Agency for Research
IB	Internal bond strength
IF	Industrial wheat flour
JAS	Japanese Agriculture Standard
LPF	Lignin phenol formaldehyde

MA	Maleic anhydride
MDI	Diphenylmethane-4.4-discocyanate
MF	Melamine Formaldehyde
MOE	Modulus of elasticity
MOR	Modulus of rupture
MSPI	MA-modified SPI
MUF	Melamine Urea Formaldehyde
NaOH	Sodium hydroxide
NMR	Nuclear magnatic resonance
OSB	Oriented strandboard
PEI	Polyethylenimine
PET	Polyethylene terephthalate
PF	Phenol Formaldehyde
PFO	Phenol formaldehyde oligomer
PKC	Palm kernel cake
PKM	Palm kernel meal
PKS	Palm kernel shell
p-MDI	Polymeric methylene biphenyl diisocyanate oligomer
POME	Palm oil mill effluent
PPF	Palm press fiber
PRF	Phenol Resorcinol Formaldehyde
PS	Palm shell
PTF	Phenol tannin formaldehyde
PU	Polyurethane
PUF	Phenol urea formaldehyde resin

PUR	Polyurethane powder
PVAc	Polyvinyl acetate
PVOH	Polyvinyl alcohol
RF	Resorcinol Formaldehyde
RSM	Response Surface Methodology
SBR	Styrene butadiene rubber
SC	Sludge cake
SEM	Scanning Electron Microscope
SF	Soy flour
SPI	Soy protein isolate
SPI-K	SPI-kymene
SYP	Southern yellow pine
U_1	$Urea_1$
U_2	$Urea_2$
UF	Urea Formaldehyde
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

In this chapter, information about wood adhesive, resin and filler was provided. Apart from that, formaldehyde emission issue and bonding interaction of the adhesive were also discussed. In wood adhesive section, knowledge about wood adhesive was provided. The types of resin, background of filler, formaldehyde emission issue and bonding interaction will be discussed further in section 1.2, 1.3, 1.4 and 1.5 respectively. Research objective, research problem statement, research scope and rationale and significant will be proposed in section 1.6, 1.7, 1.8 and 1.9 respectively.

1.1 Wood Adhesive

Malaysia is one of the largest ten wood suppliers of wood-based products in the world region, especially to Europe, Japan, Taiwan, Singapore and Middle East. Malaysia is the leader of production and export of tropics wood log and main export country in tropics plywood, veneer and wood mold. Total exports of wood-based products from Malaysia amounted to RM14.89 billion in 2011(Malaysian Timber Board Industry, 2011). Wood industry exports in Malaysia rised nearly 40 % when compared to the exports 10 years ago. Other than that, total plywood exports from Malaysia amounted to RM3.83 billion in 2011 (Malaysian Timber Board Industry, 2011). Most of the plywood adhesive is formaldehyde based adhesive which is not environmental friendly because formaldehyde is a human carcinogen (International Agency for Research on Cancer, 2004). Plywood export to Europe and US was reduced due to the environmental issues. As the wood-based product is an important international player in the global market, so the quality of timber and timber products uphold and supply must be consistent.

The statistics showed that Malaysia has a wide range of market of wood industry. The important material for this industry is adhesive used for wood products production. During the last decades, there were many researches and development in wood-based industry and adhesive industry which have shown successful result. On the other hand, many industrial requirements still need noticeable developments in this area. Adhesives play a central role in wood-based panel production (Pizzi, 1994). The bonding quality and properties of the wood-based panel determined mainly by the adhesive types and quality. Development in wood-based panel is always linked to the development in adhesives and resins.

Wood adhesives are polymeric materials that are capable of interacting physically or chemically, or both, with the surface of wood in such a manner that stresses are transferred between bonded materials. Adhesives must be applied in the form of liquid, to spread over and wet the surface of the wood. Adhesive pre-polymers can be applied directly if they are liquids or can be applied as solutions, usually in water solutions. They are widely classed as either synthetic or natural as shown in Table 1.1 (Sellers, 1998). Adhesives are basically compounded by resin, filler and hardener. Therefore, resin and filler will be discussed in section 1.2 and 1.3 respectively.

Table 1.1: Classification of wood adhesives

Class	**Resin type**	**Typical adhesive system**
Synthetic		
Thermosetting	Amino	Urea-formaldehyde (UF) Melamine-formaldehyde (MF) Melamine-urea-formaldehyde (MUF)
	Phenolic	Phenol-formaldehyde (PF) Resorcinol-formaldehyde (RF) Phenol-resorcinol-formaldehyde (PRF)
	Isocyanate	Diphenylmethane-4.4-discocyanate (MDI)
	Epoxy	Bisphenol A-based epoxy resins
	Elastomeric	Styrene butadiene rubber (SBR)
Thermoplastic	Vinyl	Polyvinyl acetate (PVAc) Polyvinyl alcohol (PVA)
	Hot-melts	Ethylene vinyl acetate (EVA)
Natural		
	Protein	Casein Soybean Blood Animal

(Source: Seller, 1998)

1.2 Resin

Resin can be classified into two major classes which are synthetic resin and natural resin. According to Seller (1998), there are various types of resin such as amino, phenolic, isocyanate, epoxy, elastomeric, vinyl and hot-melts resin. The famous type of resin that is applied in the plywood industry is amino and phenolic resin. Therefore, the production of amino types resin and phenolic type resin especially PF, MF, UF and MUF will be briefly explained in the section 1.2.1; 1.2.2; 1.2.3 and 1.2.4 respectively.

1.2.1 Production of PF resin

The main material used to produce PF resin were phenol, sodium hydroxide and formaldehyde. The phenol was mixed with 40 % sodium hydroxide solution and formaldehyde in a three-neck reactor equipped with a stirrer, a thermometer and a reflux condenser. Stir the solution for 20 min at 40 ^{o}C. Then the reaction mixture was heated to reflux (90 ^{o}C) over a period of 30 min at constant temperature. Formaldehyde and the appropriate amount of distilled water were added to the reactor. The temperature was kept at 85 ^{o}C until the Gardner-Holdt viscosity (measured at 20 ^{o}C) of the resin was reached between 300 - 500 mPa.s. The resin was cooled to 30-40 ^{o}C (Fan et al., 2009).

1.2.2 Production of MF resin

Initially, Melamine, Formalin (37 %) and water are mixed in a three-neck reactor equipped with a stirrer, a thermometer and a reflux condenser. The pH of the mixture was adjusted to 9.0 with 20 % sodium hydroxide solution and refluxed at temperature 100 ^{o}C. The melamine was added for final formaldehyde to melamine mole ratio of 2:1. The temperature of the mixture was dropped to 90 ^{o}C when the melamine was added. After the melamine was completely dissolved in the mixture, it was heated 10 min and then cooled to room temperature. Final miscibility was about water to resin ratio of 1:1 at 25 ^{o}C (US patent 3470134, 1969).

1.2.3 Production of UF resin

The one-step process as described by Barminas and Osemeahon (2007) was used in the preparation of trimethylol urea by reacting one mole of urea with three moles of 37 % (w/v) formaldehyde by using sodium dihydrogen phosphate (Chen et al., 2001). The pH of the solution was adjusted to 6 using 0.5 M H_2SO_4 and 1.0 M NaOH solutions. The solution was heated in thermostatically controlled water bath at 70 ^{o}C. The reaction was allowed for 2 hours after which the sample was removed and kept at 30 ^{o}C (Osemeahon et al., 2007).

1.2.4 Production of MUF resin

The main materials used to produce MUF resin were formaldehyde, melamine, urea and sorbitol as additive. The MUF resin synthesis process is carried out in three reaction stages. In the first stage, formalin (37 %) is poured into a three-necked flask, followed by melamine, urea1 and sorbitol. The speed for the rotator is set to 7. The initial temperature of the mixture is 65 ℃. Several drops of sodium hydroxide (NaOH) with 40 wt% concentration of solution are added to adjust the pH of the mixture to 8.5-9.0. Then, the pH of the mixture is monitored. In the second stage of the resin synthesis, the temperature of the mixture is raised to 80 ^oC. Refluxing is continued until the end point is reached. The end point can be determined by dropping the mixture in water at 30 ^oC for every 5 minutes. If the mixture droplet is diluted in the water without any trace, it means the end point has not yet been reached. Upon achieving the end point, the pH of the mixture is adjusted to 8.5-9.0 by adding NaOH solution. Finally in stage three of resin synthesis, urea2 is added upon achieving 60 ^oC. The resin was cooled down to an ambient temperature and transferred to a plastic container for further testing (Bono et al., 2003, Bono et al., 2006, Bono et al., 2007 and Bono et al., 2008).

1.3 Background of Filler

Generally, adhesive is made from a combination of 5 main compositions. These include resin, extender, filler, pigment and solute. Each of composition gives different contribution in the formulation for producing the desired adhesive. In the Table 1.2 below, application of each composition in adhesive is summarized. Each type of composition is purposed to make sure adhesive can be adopted for various applications (Jackson, 1976).

Table 1.2: Composition material in adhesive

Material	**Function**
Resins	Main and most important component in adhesive where it gives the characteristics of adhesive.
Filler	Chemical material that is added to adhesive to decrease the adhesive cost and lower the resins dissipated into the wood. It also fills up tiny hole on the board surface to avoid weak bonding.
Extender	Glucose source, which become gelatin under alkaline condition, where gelatinized starch gives sticky characteristic and increase viscosity of adhesive. Besides that, extender is also used to control the adhesive when it is use.
Pigment	Chemical agent, which gives color for adhesive.
Solute	Chemical agent, which is added to the adhesive to change viscosity and adhesive gelation.

(Source: Jackson, 1976)

Filler used to lower the resins dissipated into the wood as well as to control the production cost. It also fills up the tiny hole on the board surface to avoid weak bonding. Therefore, the adhesive that is used in the industries consists of resin,hardener and filler (Pizzi, 1994; Ebewele and Koutsky, 1986). However, the shear strength performance of adhesive with filler was weak than without. In order to overcome these phenomena, there are many other types of fillers that are proposed such as wheat flour, soybean, tapioca flour, corn starch flour and so on.

In Malaysia, wood industry uses filler to increase the solid content and reduce the production cost. One of Malaysia's largest wood producers, Shin Yang Chemical Sdn. Bhd. Used wheat flour (industrial flour) as the filler for wood product. The reason of Shin Yang Chemical choosing wheat flour as their filler is due to the protein content of the wheat flour. Wheat flour consists of a large amount of protein and this protein content would enhance the bonding formation between the adhesive and wood surface. However, the price of wheat flour is high and it is the edible one which can used in food sector. Therefore, in this research, Palm Kernel Meal (PKM) and Palm Shell (PS) were proposed as the substitution for the wheat flour. The reason to choose PKM and PS as the filler is due to Malaysia is the world second largest export in palm oil. Malaysia has plenty of palm oil mills, where, PKM and PS was the by-product of the palm oil mill. Besides that, the chemical properties and content of PKM have the similarity with industrial wheat flour. The major component in the PKM is the protein compound. PKM, PS and Wheat flour will be discussed further in section 1.3.1; 1.3.2 and 1.3.3 respectively.

1.3.1 Palm Kernel Meal (PKM)

Palm oil is one of the major agro-industries in Malaysia, but the by-product contribute from the palm oil mill include the empty fruit bunches (EFB), palm press fiber (PPF), palm kernel cake (PKC), palm kernel shell (PKS), sludge cake (SC) and palm oil mill effluent (POME). Only EFB, PPF, PKS and POME appear in large quantities and are considered as wastes. The others can be sold for animal feed or fertilizer. Average percentage of the FFB composition found from the survey (28 % EFB, 12 % PPF and 8 % PKS) (Prasetsan et al., 1996). The solid wastes from palm oil mills are classified into shell (3.25 %), fiber (11.79 %), empty fruit bunch (51.36 %), and kernel (33.6 %). Shell, fiber and empty fruit bunch mainly consist of lignin, cellulose and hemi-cellulose. Thermo-chemical conversion, especially pyrolysis, of these three chemicals produce a liquid mixture of several valuable hydrocarbons (e.g. alcohols, aldehydes, ketones, carboxylic acids, phenol and its derivatives) (Yan et al., 2005). The chemical properties of PKM was shown in Table 1.3.

PKM is a by-product of palm kernel oil extraction from the nut of the palm tree, Elaeisguineensis (Perez et al., 2000). Palm Kernel Meal (PKM) contains biomaterials such as protein, cellulose and organic acids. The transformation of this by-product into new and non-conventional source of proteins is of great interest because of it crude protein content (≈ 14 - 20 %) and the resourcefulness of this material (Iluyemi et al., 2006) in Malaysia.

PKM can be extracted and purified to be used as animal feed supplement in animal feed industry. It supplied valuable dietary sources of protein, energy and fiber (Iluyemi et al., 2006). According to Boateng et al. (2008), PKM also has been found that to reduce the cost of animal’s diet. Besides that, PKM contains proteins were well known to be used as cattle feed concentrates in dairy cows to increase milk fat. However, PKM is more suitable consumed by ruminants (cattle, sheep) but limited to use as feedstuff for monogastric animals such like chicken, swine, fish and others. It is because PKM contains high fiber (cellulose, hemicellulose), low digestibility.

According to Malaysian Palm Oil Board (2008), Malaysia produced around 2,358,732 tons of by-products Palm Kernel Meal (PKM) from palm oil (15,823,745 tons). Malaysia has been the largest Palm Kernel Meal (PKM) exporter in the world, the current global leader in the oil palm industry, with the European Union countries importing more than 85 % of Malaysian Palm Kernel Meal (PKM) annually with low price. The other importers are the Netherlands, United Kingdom, Germany, Ireland, and Asian countries like South Korea and Japan (Subbarao et al., 2008). Palm Kernel Meal (PKM) is obtained through either mechanical (expeller) or solvent process. The global production of Palm Kernel Meal (PKM) was ever increasing due to the tremendous growth of the oil palm industry in many parts of Asia and Africa. Therefore, Palm

Kernel Meal (PKM) is a readily and suitable raw material to be used for plant protein source.

Table 1.3: Chemical Properties of PKM

Fraction	**Composition**
Dry matter, %	94
Crude protein, %	14 – 21
Crude fibre, %	21 -23
Ash, %	3 – 6
Gross energy, Kcal/kg	4,998

(Sources: Boateng et al., 2008)

1.3.2 Palm Shell (PS)

There was 3.25 % of palm shell produced from the palm oil mill and treated as waste. Shell mainly consists of lignin, cellulose, and hemi-cellulose and trace amount of protein (≈0 %) (Yan et al, 2005) (Islam et al, 1999). PS was the most difficult waste to decompose. The shell size was uniform and not as bulky as the EFB. They were usually left unused in the factory or disposed of in the land-fill. In terms of energy, PS was an energy intensive substance. Local industries that require process heat (or steam) generally have furnaces (or boilers) designed for firewood or fuel oil. However, substantial modification of the furnaces is needed if the conventional fuel were to be replaced by PS. Therefore, many factories are still reluctant to use PS as fuel unless they were economically forced to do so.

There is a possibility that the PS can be used for activated carbon productions (Daud and Hamid, 1990) (Hamid et. al., 1992) or charcoal (Kirkaldy and Sutanto, 1976). PKS contains 20.3 % of fixed carbon and is physically similar to the coconut shell, which has been used to produce the activated carbon successfully. It was anticipated that the stringent environment control measures will increase the demand for activated carbon in the future. It is possible that activated carbon can be applied for the decolorization of the unacceptably dark-colored effluent of the palm oil mills (Prasetsan et al., 1996). The chemical properties of PS was shown in Table 1.4.

Table 1.4: Chemical Properties of PS

Fraction	**Composition**
Hemicellulose, %	≈22.7
Cellulose, %	≈20.8
Lignin, %	≈50.7
Crude protein, %	≈ 0

(Sources: Aziz et al, 2012)

1.3.3 Industrial Wheat flour (IF)

Wheat was the leading cereal grain produced in the world, with a production of nearly 600 million metric tons (MMT) in 2000 (USDA/NASS, 2001). It is used worldwide for food (67 %), feed (20 %), and seed (7 %). The wet-milling of wheat flour to produce starch and vital gluten as the major co-products has been reported to account for 6 % of total production (Oleson, 1994). Hard and soft wheat flours with a high protein content (>11 %) are preferred in wet-milling to co-produce vital wheat gluten and wheat starch (Sayaslan, 2004).

There are many types of wheat flour, which differ in characteristics according to factors, such as the variety of wheat, growing conditions, planting and harvesting times. Wheat flour is sold in three main forms – wholemeal, brown or white.

Gluten-free flour complies with the international gluten-free standard and is most commonly used in products specifically manufactured for people with coeliac disease. It is made from wheat flour, which has had most of the proteins, including the gluten, removed. Malted wheat grain flour is brown or wholemeal flour with added malted grains. Plain flour contains 10 % protein and is suitable for a variety of uses such as biscuits and sauces. Strong flour contains a maximum of 17 % protein and is used for yeast doughs and for flaky, puff and choux pastry. Weak/soft flour contains 8 % protein and is suitable for cakes. Wheat germ flour is brown flour, which contains at least 10% added wheat germ (the embryo of the wheat seed which is usually discarded when wheat is milled to white flour) (British Nutrition Foundation, 2004). Besides that, industrial wheat flour as the by-product of the wheat flour milling industry, the protein content with less than 8 % (Perry, 1944). The chemical properties of IF was shown in Table 1.5.

Table 1.5: Chemical Properties of IF

Fraction	**Composition**
Crude protein, %	≈7.11
Ash, %	≈0.36
Wet gluten, %	≈2.05
Dry gluten, %	≈0.70

(Sources: Chiang et al, 2006)

Apart from that, environmental and health issue will be discussed in the following section. Besides that, in section 1.5 will discuss bonding interaction of adhesive and wood.

1.4 Formaldehyde emission issue

Formaldehyde, one of the key ingredients in currently used wood adhesives such as PF, MF, UF and MUF. The wood based panels and flooring materials have gained great attention from the wood industries and the general public. Currently, inexpensive formaldehyde based thermosetting resin such as phenol formaldehyde, urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde adhesive was commercially used in wood industry. However, formaldehyde has become well known as a toxic air contaminant and carcinogenic agent. World Health Organization (WHO) intergovernmental agency, International Agency for Research on Cancer (IARC) reclassified formaldehyde from “probably carcinogenic to humans (Group 2A)” to “carcinogenic to humans (Group 1)” in June 2004 (IARC, 2004).

1.5 Bonding interaction

Plywood shear strength performance evaluation was based on Japanese Agriculture Standard (JAS, 2003). Automated bonding evaluation system (ABES) was the common method to determine the shear strength of the adhesive and testing for the bond strength development during the curing time. There is many researches done to determine the bonding interaction of adhesive. Several instruments were proposed in investigating the bonding interaction such as 13^{C} Nuclear magnetic resonance (13^{C} NMR), Fourier Transform Infrared Red (FTIR) spectroscopy and other (khan et al., 2004; Soto et al., 2005; Liu and Li, 2006; Mansouri and Pizzi, 2007; Mishra and Sinha, 2010; Li et al., 2010; Kong et al., 2011). However, there are limited researches done in analyses the bonding interaction between resin, filler and plywood. Therefore in this study, we proposed Fourier Transform Infrared Red (FTIR) spectroscopy and Scanning Electron Microscope technique in bonding interaction study.

Hence, objective of this research is to study the suitability of Palm Kernel Meal as the filler. Besides that, comparison of the adoption of Palm Kernel Meal (PKM) with currently used filler such as wheat flour and palm shell (PS) in Melamine Urea Formaldehyde (MUF) resin based adhesive production. The comparison of effect is bonding strength (shear strength) and formaldehyde emission of plywood bonded with adhesive with a different type of filler. The reason of choosing PKM is due to the similar characteristic with industry wheat flour. The main component in the PKM is protein. Apart from that, FTIR and SEM techniques were used to investigate the bonding interaction between MUF resin, filler and wood.

1.6 Research problem statement

The problem statements for this research can divide into three part; wheat flour is the industrial common used filler, whereas Palm kernel Meal (PKM) as the by-product of the oil palm industry can be replace the existing wheat flour. PKM is available in abundance in Malaysia and, it is cheap. The research work indirectly leads to converting waste to wealth. Besides that, formaldehyde emission from the wood composite poses a hazard to human health because it is a human carcinogen. The PKM applied as proteinaceous filler for adhesive in wood composite can lower the formaldehyde emission. Besides that, PKM can reduce the usage of MUF resin in adhesive and, it directly reduces the amount of formaldehyde emission from wood composite. Other than that, very limited work has been conducted on the mechanism of bonding between resin, filler and veneer surface. The proper understanding in mechanism will help to find the optimum process parameter.

1.7 Research Objective

There is few objectives for this research, the first obejective is to study the applicability of different natural fillers in adhesive formulation. After that, optimization of MUF adhesive with different processing parameter (pressing time and temperatue) also will studied. The physico-chemical interaction between veneer and adhesive will studied. Lastly, shear strength and formadlehyde emission of plywood with different natural fillers also will studied.

1.8 Research Scope

The scope of this research is to formulate the MUF adhesive and to enhance the applicability of different natural fillers. Apart from that the optimization of the adhesive formulation and the processing condition (pressing time and temperature) and study the formaldehyde emission of the plywood will also be done.

1.9 Rationale and Significance

A formulated new eco-friendly Melamine Urea Formaldehyde based wood adhesive proves with better performance and will be used in wood industry.

1.10 Organization of Research

In this research, it was organized into a few chapters in order to make sure readers read and understand easily. There are five main chapters which are introduction, literature review, methodology, result and discussion, and conclusion and future work.

In the introduction part, the background of wood adhesive, importance of PKM protein, why PKM has high potential in becoming alternative source to act as filler for wood adhesive production was mentioned. Besides that, the objective and scope for this research were stated in this chapter. Throughout this research, reader would understand the purpose of this research to be carried out and how the problem to be solved. In literature review part, researches, theories and data which had been published before was review. It is discussed the background of MUF resins, chemistry of Melamine Urea Formaldehyde (MUF) resins. Also, explains about the application of various types of filler, formaldehyde emission issue and interaction studied. The reader would get a picture and knowledge on wood adhesive production with a different type of filler in the literature review part.

In the methodology section, study on experimental methods used for this research is done. Basically, it contains the list of all the chemicals and equipment that have been used; detailed information for all the experiments and analysis procedures. Besides that, experimental design for optimization was carried out by using Response Surface Methodology (RSM). As for the result and discussion section, it included results of the experiments, analysis of the results by using RSM and discussion about the relationship of variables on the results. Besides that optimization, of temperature and, pressing time are also shown in this chapter. Apart from that, effect of formaldehyde emission and physico chemical interaction also included in this chapter.

Lastly, Chapter 7 concluded and summarized all the results in the research. It also contains some recommendation for future work, in order to improve the understanding of type of filler and resins.

CHAPTER 2

LITERATURE REVIEW

In this chapter, literature review about resin and filler was provided. Apart from that, formaldehyde emission issue and bonding interaction of the adhesive were also discussed. In the resin section, knowledge about amino resin and wood adhesive was provided. Resin, amino resin, melamine urea formaldehyde (MUF) resin, modification of wood adhesive with various types of fillers, formaldehyde emission and bonding interaction will be discussed further in section 2.1, 2.2, 2.3, 2.4, 2.5 and 2.6 respectively.

2.1 Resin

In international standard ISO 472 and ISO 4618/3 (Strong, 2000), resins are defined as solid, semi-solid or pseudo-solid organic compound. Besides that, resins have an indefinite and often high relative molecular mass that generally soften or melt over a range of temperature on heating.

The adhesives commonly used for exterior and semi-exterior wood panel are melamine formaldehyde (MF), urea formaldehyde (UF), phenol formaldehyde (PF) and melamine urea formaldehyde (MUF). Other than that, MF, UF, and MUF resins were also used as adhesive for preparation and bonding of low and high-pressure paper laminating and overlays. Amino resin will be discussed in section 2.2.

2.2 Amino resin

Amino resin is a thermosetting resin which hardens and coagulates when temperature was applied. The hardness of resin is eternal although temperature is increased. Thermosetting resin is more stable at high temperature or around the heat instability environment (International Patent Classification: C08L 61/28, 31/04). Bruice (1998) reported that amino resin after thermoset coagulated, it cannot re-melt.

Amino resin is either in solid or liquid form. These resins built up from a mixture of the amino group (-NH_2) solution with aldehyde (Mukherjee and Subrata, 1996). Although other aldehyde has investigated while, formaldehyde was used almost in all the wood industry because the production cost for formaldehyde based resin was cheap when compared to other materials. Normally, the raw materials for amino resin are phenol, melamine, urea and formaldehyde. Formaldehyde generally marketed as 36 % or 37 % aqueous solution known as formalin. Thus, the next section will discuss about MUF resin.

2.3 Melamine Urea Formaldehyde (MUF) resin

Both the wood-based panels industry and the adhesive industry have shown a high commitment and great capability towards innovation. The best evidence for this is the considerable diversity of types of adhesives used for the production of wood-based panels (Dunky, 1994). MUF resins are used with plywood, particle board in construction, packaging, and furniture industries. The various forms of wood utilization represent an extremely large and diverse market for adhesives (Lambuth, 2003).

At present, MUF was used most commonly in production of wood composites. In 1998, the wood composites industry in North America consumed more than 1.78 million metric tons of adhesives. In 2001, the worldwide wood adhesive consumption was 13.3 million tons and total sale value reached $6.1 billion. Formaldehyde-based adhesives accounted for 92 % of the total consumption (Seller, 2001). However, formaldehyde-based adhesives are not environmentally friendly products. Most of them contain phenol and formaldehyde, a major cross-linking agent that causes environmental problems and even toxicity in both processing and product distribution. The formaldehyde issue will be discussed in section 2.5.

Adhesives are normally combined with five compositions, which include resin, extender, filler, pigment and hardener. The information about filler will be discussed in section 2.4. Pizzi (1994) reported that adding hardener in MUF and UF adhesive for production of plywood and particleboard was essential to accelerate the production time.

Commonly used hardener is a strong acid ammonium salt such as ammonium chloride or ammonium sulphate (Shields, 1975). This salt is suitable used as a hardening agent because their ability to discharge acid and reduce the resin pH also increases the resin hardening rate. Resin hardening rate was measured by reaction rate between ammonium salt and formaldehyde or between ammonia and formaldehyde. Besides that, the total heat supplied, and discharge acid rate need to consider. The reaction between ammonium chloride and free formaldehyde resin is shown below:

$$4NH_4Cl + 6HCHO \rightarrow 4HCl + (CH_2)_6N_4 + 6H_2O \tag{2.1}$$

The sum of ingredient use is around 1-5 % depending on the total of produced resin mass (Kosh et. al., 1987). Although hardener is added in 1 % only, hardening time was shorter and better hardening is resulted. The excess of hardener will cause over hardening where high acid residue percentage will create brittle crosslinked adhesive and this will weaken adhesive over water (Conner, 1996).

Ammonium chloride are normally added to amino resin adhesive and form a stable mixture because its enzyme effect merely will operate if mixed with water. Besides that, the blocked agents such as urea, melamine or hexamethylene tetramine mixed up into the enzyme to increase the duration of resin mixture storage. Furthermore, enzymes are usually connected with wood dust also resistant agent such as tricalcium phosphate (Savla and Skeist, 1977).

The sum and type of enzymes chosen to use in such adhesive depend on the hardening wood temperature of the resin. Time used for resin hardens maybe from few minutes at high temperature to few hours at ambient temperature. Melamine adhesive resin normally required high temperature to completely coagulation (Savla and Skeist, 1977). Chemistry and application of MUF resin will be discussed in section 2.3.1 and 2.3.2 respectively.

2.3.1 Chemistry Melamine Urea Formaldehyde (MUF) resin

Melamine urea formaldehyde (MUF) is a synthetic resin that belongs to the amino resin family. Other than MUF resin, MF and UF resin were the important amino resin used in wood industry (Pizzi, 1994).

The production of MUF resin consists of copolymerization and poly-condensates. There are several pathways to synthesize MUF resin that have been proposed. Normally, the MUF resin synthesis involves a two-step process which is the methylolation stage of amino groups and condensation of methylols to form polymeric chains (Angelatos et al., 2004). The mechanism of the formation of methylene or dimethylene ether linkages in the resin structure occurs during condensation. The presence of two monomers reactive with formaldehyde in the polymerization complicates the MUF resin structure (Philbrook et al., 2004).

Besides that, MUF resins obtained by copolymerization during the resin preparation stage were superior in performance to MUF resins prepared by mixing performed UF and MF resins because processing of such mixtures was difficult. The relations of melamine to urea used in these MUF resins generally in the range 50:50 to 40:60 (Clad and Schmidt-Hellerau, 1977).

There are many researchers who have studied the chemistry of condensation reaction between urea and formaldehyde in UF resin and condensation reaction between melamine and formaldehyde in MF resin for MUF resin synthesis (Pizzi, 1994). However, there are many conflicts in the opinion about the co-condensation reaction between melamine and urea during the MUF resin synthesis. According to Angelatos et al. (2004), during the MUF resin synthesis predominantly constitutes the self-condensation of melamine rather than co-condensation of melamine and urea during the condensation stage. Under certain laboratory conditions copolymerization between melamine and urea can occur in an uncured MUF resin. No and Kim (2004) reported that, it is difficult to make conclusions about the copolymerization between urea and melamine because the overlapping peaks in 13^{C} NMR during MUF synthesis.

Tohmura et al. (2004) reported that, cured MUF resin structure and formaldehyde emission will affect by the melamine content inside the MUF resin. The melamine contributes stronger in the crosslinking linkages structure for the resin cured with increasing the branch type of methylene bond. However, the formation of methylene and dimethylene ether linkages between melamine and urea during curing is unclear due to the unclear formation of melamine-urea linkage. Pizzi and Panamgama (1995) reported that, methylene or dimethylene ether linkages between melamine and melamine, melamine and urea, or urea and urea were formed during the resin curing process under acidic conditions for a co-condensation mechanism.

MUF resins can be made in different melamine levels, and synthesis procedures reveal different curing parameters and rigidity values (No and Kim, 2005; Gu et al., 2005; and Zanetti and Pizzi, 2004). The increasing melamine level increases the thermal stability and final rigidity of cured MUF resins as compared to cured UF resins (No and Kim, 2005). It has been shown that F/U+M ratio would allow to be lowered to reduce formaldehyde emission of particleboard and plywood as compared to UF resins and without lowering the strength properties (No and Kim, 2005). Higher temperature or longer pressing time are needed for MUF resin cure with increasing melamine content during the MUF resin synthesis as compared to UF resin (No and Kim, 2004, 2005). Kim et al. (2006) indicated that the MUF resin cured faster than UF resin at the early stage of the curing process due to the lower activation energy of the MUF resin.

2.3.2 Applications for Melamine Urea Formaldehyde resins

Amino resins are often used to modify the properties of other material (Williams, 1991). A major application of MUF resins is in the area of adhesives, primarily for plywood, chipboard and sawdust board markets. MUF resins are also used in processing (to impart wash and wear quality), automobile tires (to improve adhesion between rubber and tire cord) and paper processing (to improve the wet strength) (Greiner et. al., 2000). It is also used for molding products, such as electrical devices, jar caps, buttons and dinner ware and in the production of counter tops (Mukherjee and Subrata, 1996).

2.4 Modification of wood adhesive with various type of filler

Adhesives were compound with lingocellulosic; inorganic material; Proteinaceous and amylaceous material (filler) to increase viscosity, control rheology and reduce material cost. Fillers are used to fill up all small holes at the surface of wood to prevent or to reduce the formation of weaker bonding. Besides that, fillers are also used to reduce the penetration of resin into the wood and small hole of the wood (Pizzi, 1994). Other than that, amino filler will enhance the bonding formation between the adhesive and the wood surface.

The most famous industrial filler is wheat flour which is present in UF, MF and MUF based adhesive (Sellers, 1985; Robertson J.E. and Robertson R.R., 1977, and Perry, 1944). In addition, rye flour, cassava flour, oats, corn, rice, soybeans, douglas fir bark, wood hydrolysis residues, lignin, and dry soluble blood were evaluated, and satisfactory results obtain indicates that can be applied as alternative fillers in phenol-, and urea- resin based adhesive manufacturing (Iwakiri et al. 2000 and Perry, 1944).

The term filler and extender are interchangeable (Klein, 1980; Robertson J.E. and Robertson R.R., 1977, and Sellers, 1985). Adhesive properties to wood components were the difference between extenders and fillers. Filler without protein content does not have any ability to adhere to wood components while filler with protein content has little adhesive properties (Klein A. J., 1980; Robertson J. E. and Robertson R. R., 1977, and Sellers T. Jr., 1985). However, they have same functions such as tack consistency; better adhesion on dense woods; greater assembly time tolerance to dry out; better resistance to over penetration; faster and stronger pre-press bonds (Sellers, 1985):

The properties of various type filler/extender and application of renewable resources material as filler will be discussed in the following section. Section 2.4.1, 2.4.2, 2.4.3, 2.4.4 and 2.4.5 will discuss bark meal; soybean meal; sago flour; cassava flour and polyurethane powder respectively. Besides that, formaldehyde emission issue and physic-chemical interaction will be discussed in section 2.5 and 2.6 respectively.

2.4.1 Bark Meal

Muszynski and McNatt (1984) reported that bark can use as a substitute for phenolic resin. The studied on incorporation between the bark and wood in particleboard production were done but the result showed that particleboard strength decrease as usage of bark increases. Kreibich (1989) reported that utilization of bark has to reduce because both price and performance face difficulties during competing with entrenched phenolic adhesive system in wood panel production.

Sellers (1994) suggested that southern yellow pine (SYP) bark had the potential as filler for plywood adhesives. In preparing bark filler, specific techniques grinding and classification has been used by Eberhardt and Reed (2005, 2007) to obtain more fractions rich in periderm and obliterated phloem tissue compare to bark directly from bark received from mill. The dirt present in the bark can be removed by this process. Ottone and Baldwin (1981), and Ross and Krahmer (1971) concluded bark rich in different cell types and different level of extractives can be differentiated by using specific techniques of grinding and classification.

Seller et al. (2005) reported that Oat hull furfural residue laboratory panels had greatest shear strength performance among the fillers either in vacumm-pressure test or two-four hour boiling test. This due to greater protein content of the filler and high carbohydrate content, low fat content with low fiber content. Whereas, Oat hull furfural residue industrial panels comes as second higher shear strength among filler due to greater in protein and carbohydrate content and low fat content. Furthermore, 65 % E. walnut shell and 35 % oat hull furfural residue had the lowest shear strength performance due to high fiber and fat content. The high content in protein and carbohydrate will have a more probability for the cross-linkage formation occur between adhesive and wood surface. Therefore, high protein and carbohydrate content of filler has better shear strength performance.

Eberhardt and Reed (2005) reported that furfural residue control filler have better wood performance than whole bark meal because whole bark filler still contained high level of ash after simple screening process compared to furfural residue control filler. Eberhardt and Reed (2005) improved performance by further grind the bark meal to smaller particle size (200 meshes). After grind and blend process, bark meal is divided into two bark based filler which is periderm and obliterated phloem filler. The result shown that obliterated phloem filler have very low wood failure, which indicated that the sample was under cure.

Eberhardt and Reed (2005) reported that periderm filler wood failure was generally higher than obliterated phloem and whole bark filler after veneer moisture content was reduced. However, furfural residue filler, wood failure value was the highest compared to other fillers. Eberhardt and Reed (2007) further research in decrease the particle size of the bark meal using laboratory blender and ultra-centrifugal grinding mill. After applying multiple grinding and blending process, bark filler ash content decrease significantly (Eberhardt and Reed, 2007).

Eberhardt and Reed (2005) reported that higher ash content will influence the resin cure. Eberhardt and Reed (2007) indicated that, periderm filler has the good wood failure value among the filler and whole bark filler was intermediate among the bark filler. In contrast, the wood failure value for phloem filler was low and showed signs of under cure. By referring to Eberhardt and Reed (2005), under cure occurrence was done by oven dried the veneer. In addition, periderm filler had greater shear strength value compared to other filler. Eberhardt and Reed (2007) concluded that, grinding and classification operation could reduce the ash content and improve the plywood performance.

2.4.2 Soybean Meal

Late 1990s, soybeans have been extensively studied for their application as an exterior-grade adhesive resin. Recently the increasing prices in petroleum, formaldehyde emission concerns, and phenol safety issues. Huang and Sun (2000) modified the soy protein by denaturants or reducing agent for adhesive properties evaluation and found that water resistance and bond strength improved. Gross and Kalra (2002) indicated, that soybean meal can add into phenolic resins as filler to reduce the cost of petroleum based plastic.

Babcock and Smith (1947) studied that soybean meal filler has better performance compared to corn gluten filler by using PF resin. The shear strength performance of soybean meal was greater than corn gluten by using all three types of wood species. The wood types were birch, mahogany and poplar. Furthermore, shear strength performance of soybean was greater than corn gluten in all ratio resin to extender flour, 2:1, 3:2 and 1:1. However, corn gluten performance is better than soybean meal at ratio 1:1 with apply mahogany wood. The shear strength performance of soybean meal was greater than corn gluten mainly due to its protein and adhesive flow properties. The protein content of corn gluten was better than soybean meal but, the soybean meal shear strength performance was greater than corn gluten. This due to soybean meal had better adhesive flow properties than corn gluten. Both corn gluten and soybean meal protein are thermoplastic material, they had differed flow properties. As a conclusion, the better adhesive flow properties, the easier cross-linkage formation between adhesive and wood surface and the better shear strength performance.

Hojilla-Evangelista and Dunn (2001) screened foam extrusion glue by using soybean meal among other commercial soybean protein product. Hojilla-Evangelista and Dunn (2001) found that, soybean flour was not suitable as filler due to its poor solubility and foaming properties. However, the major protein sub-unit was still present in soybean meal. This finding suggested that, possibility of make soybean flour reactive by physical (eg. Grinding) or chemical means.

Hojilla-Evangelista (2002) investigated that soy protein foam based glue (Honeysoy 90, ISU-CCUR, Nutrisoy 7B, Soyafluff defatted, Arcon F and Procon 2000) were equally strong as control filler (Animal blood). The glue spread and assembly time found that no significantly effect on the shear strength value of plywood. Therefore, small amount of glue and shorter assembly time applied when the soy protein based foamed glue used to produce plywood. In addition, modified formulation of soy protein based glue was as strong as plywood bond by control glue. There are no significant different of the shear strength value between control glue and modified glue with different filler. As a conclusion, soy protein foam based glue and modified soy protein foam based glue had almost same shear strength value with control glue.

Hojilla-Evangelista (2010) indicated that, glue containing soybean meal as proteinfiller had mixing and viscosity properties that were comparable to wheat flour based plywood glue. The bonding strength of soybean based glue initially was weaker than wheat flour based glue. In order to improve plywood performance to an acceptable level, the amount of the soybean meal in the glue was increased. This can be proved by Wescott and Frihart (2004) with more protein can provide additional reactive group for participation in crosslinking and polymerization reaction between wood and resin. They concluded that soybean meal is viable filler in plywood adhesive industry.

2.4.3 Sago flour

Sumadiwangsa (1985) reported that it can be used as filler for UF adhesive. The sago flour consists of starch which suitable use as filler and applied in plywood production. The high viscosity sago flour applied in adhesive will increase the UF resin viscosity. Therefore, sago flour can act as a viscosity control agent. The commonly used viscosity control agent in industry was industrial wheat flour (IF) because it consists of high carbohydrate content. Usually, IF is added up to 50 % based on the resin weight (Sellers, 1985). Sumadiwangsa (1985) reported that, the bonding strength of wood sample lower when greater amount IF was added to the resin during adhesive production. Sago flour had poor performance as compared to IF because the chemical component especially protein compound consists in sago flour was lower than IF.

Sumadiwangsa (1986) discussed filler ratio and content factors of mixed sago flour with IF with several ratios. Ratio factors (IF/sago) consisted of 4 levels that were 10/0, 8/2, 6/4, and 4/6. Filler contents consisted of 4 levels that were 15, 20, 25, and 30 % based on resin weight. Filler ratio does not influence the bonding strength of plywood but the filler content influenced the bonding strength of plywood significantly.

Sumadiwangsa, et al. (1987) mixed sago flour with the tuber flour of iles-iles (Amorphophallus oncophyllus) by blending. The Amorphophallus flour contains mannan that which normally used an adhesive for wood or paper. Sumadiwangsa (1987) concluded that, mixed flour in ratio sago/iles-iles at 7/3 can be used as filler for UF based adhesive and had almost equal wood performance compared to wheat flour as filler.

Sumadiwangsa (1996) used natural sago (unmodified), acid-modified sago and phosphorylated sago starch flours as filler in UF based adhesive production. Automated Bonding Evaluation System (ABES) machine applied to obtain maximum curing rate and maximum bond strengths of the adhesive. The curing rates to an IF extended adhesive (0.027 MPa/s) for natural (0.035 MPa/s), acid modified (0.030 MPa/s), and phosphorylated (0.022 MPa/s) sago extended adhesives. All these adhesive mixtures had 30 %, resin solids and 1500 cPs viscosity.

Sumadiwangsa(1996)indicated that, phosphorylated sago extended adhesive has maximum shear strength among the fillers. The shear strength value of acid modified extended adhesive comes second high, and IF was the weakest among the fillers. As conclusion, sago starch can be used to formulate UF adhesive for wood. Phosphorylated sago flour is the best alternative sources to substitute IF because its properties are close to IF.

2.4.4 Cassava flour

Cassava (Manihot esculenta Crants) is one of the most important food producing crops in the tropics. The most widely used the term for cassava is “tapioca”. Cassava is able to adapt with a wide range of the environment such as tolerant to drought, acid soil and establish in high and low rainfall areas and relative resistance to pests and disease. Cassava basically consists of carbohydrate ($C6H12O6$) with 80 % of starch and 20 % of sugar (Kawano, 2000, and Liu and Zhuang, 2000) and its traditional role as human food.

The starch manufactured can be applied in paper, textile and plywood industrial (Sriroth et. al., 2000; Bacusmo, 2000, and Tan and Idris, 2000). Malaysia’s cassava is mainly applied in starch processing and then most of the starch is applied in food industries. Meanwhile, the interest in snack manufacturing using cassava was also slowly increasing in Malaysia as most of starch is applied to food industries (Tan and Idris, 2000).

Derkyi et al. (2008) reported that cassava flour can be used as filler for UF adhesive. They found that shear strength of cassava flour was comparable with IF in dry condition, but not comparable in wet shear strength where IF had better performance than cassava flour. The result exhibited IF extended adhesive had better moisture tolerance to plywood bonded compared to cassava flour. They concluded that, cassava can be used to replace the traditional IF as filler in plywood production. The extension level of cassava flour should reduce compared to IF in order to achieve appreciable moisture tolerance to plywood.

2.4.5 Polyurethane powder

Mansouri and Pizzi (2007) reported that recycled polyurethane powder (PUR) can be used as filler for UF and PF resin. Polyurethanes are one of the most versatile materials, with applications ranging from flexible foam in upholstered furniture to rigid foam as insulation in walls and roofs. The thermoplastic polyurethane also applied in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors (Chattopadhyay and Raju, 2007). In general, polyurethane polymers contain a significant number of urethane linkages (–NH-COO–), regardless of the other nature of the macromolecule (Zia et al., 2007).

Mansouri and Pizzi (2007) investigated that micronized Polyurethane powder (PUR) had better performance than wheat flour filler with applied UF resin. The dry and wet shear strength of PUR filler was greater than wheat flour filler. Moreover, PUR filler are water repellent which had better water resistance properties than wheat flour when joint with UF resin (Mansouri and Pizzi, 2007). In addition, 40 % PUR filler mix with 10 % wheat flour had the greater shear strength performance compared to other mixing ratio between PUR filler and wheat flour. This represented the waste material (PUR filler) can be used in substitute or partial substitute wheat flour (better used in the food sector) in wood adhesive production. However, the shear strength performance of PUR filler once again proved that greater than wheat flour with applied PF resin. Additionally, the portion used is 20 % for PUR filler in PF resin is low compare to UF resin which uses 40-50 %. This indicates that PUR filler is much less effective with the PF resin.

2.5 Formaldehyde emission

The wood based panels and flooring materials have gained great attention from the general public. Currently, inexpensive formaldehyde based thermosetting resin such as phenol formaldehyde, urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde adhesive was commercially used in wood industry. Since, formaldehyde became well known as a toxic air contaminant and carcinogenic agent. World Health Organization (WHO) intergovernmental agency, International Agency for Research on Cancer (IARC) reclassified formaldehyde from “probably carcinogenic to humans (Group 2A)” to “carcinogenic to humans (Group 1)” in June 2004 (IARC, 2004). Apart from this, with dwindling petroleum resources and unstable fossil fuel prices, a great deal of uncertainty regarding the future cost and availability of synthetic adhesives exists (Iman et al. 2001). Several efforts have been made to reduce or replace formaldehyde contents in the adhesive formulation or to develop new adhesive from natural materials. Reduced or formaldehyde contents replacement and new adhesive development will be discussed in section 2.5.1 and 2.5.2 respectively.

2.5.1 Reduce or replace formaldehyde contents

Currently, formaldehyde emission is a major health issue in the world. Therefore, many researches were done to reduce or replace the formaldehyde content. Polyethylene terephthalate (PET) bottles powder and borax pentahydrate was added in an equal amount into the formaldehyde based adhesive in the plywood was investigated (Ozalp, 2011). Bending, shear strength and formaldehyde emission test were evaluated according to BS EN320, BS EN314-2 and EN 717-2 respectively. Ozalp (2011) concluded that, PET bottles waste powder and borax pentahydrate in an equal amount to urea formaldehyde (UF) significantly increase the strength properties (bending strength and shear strength) of the plywood. In addition, formaldehyde emission from the plywood using PET bottles waste powder and borax pentahydrate shows a lower level emission.

Wang et al. (2011) modified the commercial resin such as glyoxal (GO), glutaraldehyde (GA), polymeric methylene biphenyl diisocyanate oligomer (p-MDI), phenol formaldehyde oligomer (PFO) and urea formaldehyde (UF) with whey protein, which is a by-product of cheese production. In this study, bonding test and formaldehyde emission test was conducted. They concluded that, UF resin, p-MDI, GA, GO are unsuitable to use for modifying the whey protein as a green adhesive. Whey protein solution adhesive was shown good results with passed standard value 1.18 MPa and 0.98 MPa for dry strength and wet strength respectively. The formaldehyde emission Results were shown relatively low with 0.042 mg/L which passed standard value (<0.5 mg/L). Therefore, a whey protein based adhesive was developed with good bond strength and low formaldehyde emission.

Moubarik et al. (2009) reduced the usage of phenol formaldehyde resin in the plywood production by using cornstarch and tannin. In this study, a part of the PF was substituted by cornstarch and quebracho bark tannin. The mechanical properties like modulus of rupture “MOR”, modulus of elasticity “MOE”, tensile strength and wood failure of the plywood was investigated. Other than that, formaldehyde emission test were also evaluated. They concluded that, cornstarch and quebracho tannin can substitute commercial PF up to 20 %. Plywood bonded with cornstarch-tannin-PF resin (15:5:80, w/w/w) exhibited better mechanical properties than plywood bonded with commercial PF only. The formaldehyde emission results show that plywood sample bonded with cornstarch-tannin-PF resin (15:5:80, w/w/w) has lower formaldehyde emission than commercial PF resin.

2.5.2 Develop new adhesive

Moubarik et al. (2010) developed new cornstarch-tannin adhesive without using formaldehyde as formaldehyde is a harmful agent as stated in section 2.5. In this study, mechanical properties like dry tensile strength, modulus of rupture (MOR) and modulus of elasticity (MOE) of plywood manufactured using formaldehyde free cornstarch-tannin adhesives were evaluated. Besides that, formaldehyde emission test are also evaluated. They concluded that cornstarch-tannin adhesive prepared without using formaldehyde which passed international standard specification with good mechanical properties. In addition, the formaldehyde emission results show lower than commercial formaldehyde based resin.

Kim (2010) developed, new cashew nut shell liquid (CNSL) and formaldehyde (CF) adhesives for engineered flooring veneer using natural cashew nut shell liquid without formaldehyde content. This new green adhesive was used to replace formaldehyde based adhesive in order to reduce it emission from the plywood. In this study, bonding test and formaldehyde emission test was evaluated. Kim (2010) concluded that, CF/PVAc hybrid adhesive had greater bonding strength than CF adhesive. Similar emission data was shown between the CF and CF/PVAc hybrid adhesive by using desiccator method. However, the formaldehyde emission was sufficiently reduced to satisfy the E_0 grade of the Korean standard. Therefore, the CF/PVAc resins were successfully applied as environmentally friendly adhesives of surface bonding for manufacturing engineered flooring.

Kim (2009) developed new environment-friendly adhesives for engineered flooring veneer using natural tannin without formaldehyde content. The environmental-friendly adhesive was used to replace formaldehyde based adhesive in order to reduce it emission from the plywood. In this study, bonding test and formaldehyde emission test was evaluated. Dessicator method and field and laboratory emission cell (FLEC) were chosen to evaluate the formaldehyde emission from the engineered flooring sample. Kim (2009) concluded that, tannin/PVAc hybrid adhesive had greater bonding strength than natural tannin adhesive. Similar emission data was shown between the natural tannin and tannin/PVAc hybrid adhesive by using desiccator method. However, the formaldehyde emission was sufficiently reduced to satisfy the E_0 grade of the Korean standard. The FLEC method showed a slight increase of formaldehyde emission in tannin/PVAc adhesive compared to natural tannin adhesive. Therefore, tannin/PVAc hybrid adhesives were successfully applied as environment-friendly adhesives of surface bonding for manufacturing engineered flooring.

Iman et al. (1999) developed an environmentally friendly wood adhesive using cornstarch and poly-vinyl alcohol) (PVOH) with hexamethoxymethylmelamine (Cymel 323/303). The adhesive was produced using starch, PVOH, hexamethoxymethylmelamine crosslinker, citric acid and latex. There is no formaldehyde added into adhesive. In this study, moisture resistant, veneer failure and tensile strength test were conducted. Iman et al. (1999) concluded that, at 63 ^{o}C and 27 % solution (w/v) adhesive viscosity was 7000 mPas, the adhesive could be easily spread on the veneer surface. Cymel 323 with high imino melamine formaldehyde cross-linking agent showed greater mechanical properties compared to cymel 303 with low imino melamine formaldehyde cross-linking agent. Curing time needed to cure adhesive using Cymel 323, and Cymel 303 are 15 min and 90 min respectively. Besides that addition, of latex (UCar 443) to the adhesive formulation enhanced moisture resistant and tensile strength of the plywood test sample. Other than that, Iman et al. (2001) continue the research by conducting moisture resistant test and scanning electron microscopy (SEM) analysis. They concluded that, starch and PVOH based cross-linked adhesive with added latex appeared to have the best performance in physical properties and moisture resistance. Therefore, starch and PVOH cross-linked based adhesive can be proposed as an environmental friendly adhesive because the adhesive does not contain formaldehyde or phenol that is considered potent environmental pollutants.

A new innovative formaldehyde free adhesive was developed by using soy protein isolate (SPI) and Kymene® 557H. (Li et al., 2004) In the study, shear strength and water resistant test were studied with wood composite sample bonded with alkaline SPI only; kymene only; phenol formaldehyde resin (PF) only; SPI-kymene adhesive (SPI-K) with ratio 1.33:1 (w/w); SPI-K with reaction time 60 mins. They reported that wood composite bonded with alkaline SPI had the lowest dry shear strength compared to other adhesives. PF have higher dry shear strength result than kymene while SPI-K had higher dry shear strength results than others. The water resistance of wood composite bonded with SPI-K adhesive system was further evaluated with boiling water test (BWT). The entire wood composite sample was completely delaminated in BWT except alkaline SPI alone. Wood composite bonded with kymene alone decrease dramatically in bonding strength after undergoing BWT, BWT/dry and BWT/wet strengths. The samples bonded with kymene only PF and SPI-K was shown BWT/wet strength lower than the dry strength, whereas the BWT/dry strength was higher than the dry strength. There is no delamination observed for wood composite bonded with SPI-K and PF adhesive whereas some delamination occurred for wood composite bonded with kymene alone. They concluded that, SPI-K system has these unique advantages; i) the key ingredient soy protein is abundant and renewable; ii) it is formaldehyde free; iii) product are attractive because glue line for SPI-K is light, whereas PF give dark glue line. SPI-K adhesive had the potential to meet the strength and water resistant requirement for industrial standard (Li et al., 2004).

At the same year, Li et al. (2004) also developed the other new type wood adhesive using condensed tannins and polyethylenimine (PEI). In this study, wood samples were evaluated using shear strength and water resistant test. They study the effect of the mixing time on shear strength; total solids content of tannin-PEI adhesive on shear strength; tannin/PEI weight ratios on shear strength and water resistance; storage time of tannin-PEI on shear strength. They concluded that condensed tannin from Douglas's fir inner bark used with EPI to form tannin-PEI adhesive were easy to prepare and applied. Tannin-PEI adhesives without the extender with solid content 12-24 % were shown that the adhesive can easily be applied to wood veneer. The tannin-PEI weight ratio (2:1) showed highest shear strength and water resistant. The optimum pressing temperature and time used to produce wood composite are 100 ^{o}C and 2 mins. Due to the ease mixing, formaldehyde free, good shear strength and water resistant result. Tannin-PEI wood adhesive has the potential applied in wood industry to solve the formaldehyde emission issue, which was stated in section 2.5.

Liu and Li (2006) developed new formaldehyde free wood adhesive using demethylated kraft lignin (DKL) and polyethylenimine (PEI). In this study, the wood composite samples will be evaluated using shear strength and water resistant test. They study the effect of mixing time on shear strength; total solid content on shear strength; water resistance of samples bonded with DKL-PEI and DKL/PEI weight ratio on shear strength. They concluded that DKL-PEI adhesives were easily prepared and applied on wood veneer. The optimum pressing temperature and time for prepared lap-shear specimens are 120 ^{o}C and 5mins respectively. Besides that ration, 1:1 was the optimum ratio to enhancing the strength and water resistance properties of wood samples.

Therefore, in this research DKL/PEI wood adhesive had these unique advantages; i) DKL is a by-product in the production of dimethyl sulfoxide from kraft lignin. ii) Formaldehyde free adhesive. Therefore, DKL-PEI has the potential to be applied in wood industry.

In the year 2007, they developed the other type of formaldehyde free adhesive (MA-modified SPI (MSPI)) which used soy protein isolate (SPI), maleic anhydride (MA) and polyethylenimine (PEI). In this study, the wood composite samples will be evaluated using shear strength and water resistant test. They study the cross-linking interaction of MSPI-PEI adhesive and curing chemistry of MSPI-PEI adhesive. They concluded that MA was successfully grafted onto SPI to form MSPI via amide linkage and ester linkage. They found that, maleyl groups of MA will react with amino groups of SPI and faster than MA with hydroxyl groups of SPI. Increasing amount of MA during modification of SPI will significantly increase the amount of the ester linked maleyl groups of MA. However, MSPI was not good enough to bond wood. Therefore, PEI was added into MSPI, and it enhanced the performance of adhesive. Wood composite bonded with MSPI-PEI had a higher dry shear strength than wood composite bonded with commercial PF resin. However, BWT/wet shear strength of MSPI-PEI showed lower performance than commercial PF resin. Temperature range from 120-160 ^{o}C was studied, and it had a little impact on strength and water resistant to the wood composite. Furthermore, pressing time longer than 2 mins also had a little effect on the dry shear strength. In this research, the MSPI-PEI adhesive can be commercialized for the industry used.

Huang and Li (2008) invented a new soy flour based adhesive which is formaldehyde free adhesive. This new soy flour based adhesive using soy flour (SF), polyethylenimine (PEI) and maleic anhydride (MA). In this study, the optimum formulation and hot press condition were studied. Shear strength and water resistance was used to evaluate the performance of the plywood samples. They concluded that, the weight ratio of SF/PEI/MA is 7/1.0/0.32 was the optimum formulation which gives highest water resistance result. Moreover, temperature 140-170 ^{o}C, the result of water resistance and shear strength of plywood bonded with SF-PEI-MA was statically same except temperature 170 ^{o}C sample was lower as compared to 160 ^{o}C. Besides that, hot press time at 5min was shown highest BWT/wet shear strength and dry shear strength.

Schwarzkopf et al. (2010) was using SF-PEI-MA for oriented strand board (OSB) application. In their research, they studied the internal bond strength (IB), modulus of rupture (MOR) and modulus of elasticity (MOE). They concluded that hot press temperature at 170 ^{o}C and hot press time at 4-5 min were given highest IB, MOR and MOE. Besides that, the adhesive usage rate at 7 % was given highest performance. Moreover, the OSB panels bonded with formaldehyde free adhesive were given comparable performance compared to the commercial OSB panels which purchased from the market.

Gu and Li (2011) also using SF-PEI-MA as adhesive for particleboard application. In their study, modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond strength (IB) was used to optimize the hot press temperature, time, particleboard density and adhesive usage. They concluded that optimum operating conditions are hot press temperature of 170 ^{o}C, hot press time of 270 sec, the adhesive usage of surface particles at 10 wt%, the adhesive usage of the core particles at 8 wt%, and the targeted particleboard density is 0.80 g/cm3. The MOR, MOE and IB met the minimum industrial standard with the particleboard manufacture according to the optimum operating condition. Therefore, SF-PEI-MA adhesive these unique i) SF are an inexpensive material, abundant, renewable and readily available. ii) Formaldehyde free adhesive. iii) Environmental friendly. So, SF-PEI-MA adhesive has the potential to be applied in wood industry for multi-product application.

Jang et al. (2011) established a formaldehyde free adhesive which consists of soy flour (SF) and a new curing agent (CA) for plywood application. Water resistant test was used to evaluate the plywood sample bonded with SF-CA adhesive. Effects of the reaction time, reaction temperature, NaOH usage, heat treatment of CA, addition order of reactants in the preparation of the CA, and storage time of the CA on the water resistance of plywood panels bonded with SF–CA adhesives were studied. They concluded that CA can be easily prepared when the reaction temperature is in the range 45-60 ^{o}C. During CA preparation, epichlorohydrin (ECH) and ammonium hydroxide added will effectively cure with SF. Further heat treatment of CA will not be beneficial to the performance of samples except for five-ply panelsat 50 °C. Storage life for CA is around two months without affecting the water resistance of the resulting plywood panels. SF-CA adhesive water resistance and dry shear strength can be enhanced by adding the NaOH.

Prasittisopin and Li (2010) were using the SF-CA adhesive to produce particleboard. They found that SF-CA adhesive with high viscosity cannot be easily sprayed onto wood particles. Therefore, they developed a new method to produce particleboard. Effects of particleboard density, adhesive usages for both core and face particles, the solids content of the soy slurry, hot-press time, hot-press temperature, the storage time of the wet soy-coated wood particles, and the SF/CA weight ratio on the internal bond strength (IB), the modulus of rupture (MOR), and the modulus of elasticity (MOE) of particleboard were studied. They concluded that strength of particleboard increased and then flattened when density of particleboard reached 760 kg/m3. The optimum operating conditions were: ≥10 wt.% of the adhesive usage for the core particles, ≥12 wt. % of the adhesive usage for the face particles, 10–20 % of the total solids content of the soy slurry, 224–245 sec of the hot press time, 180–190 °C of the hot-press temperature, 1/10–1/4 of the CA/SF weight ratio, and 0.5–36 hour of the storage time of the wet soy-coated wood particles. Therefore, SF-CA adhesive had the potential to be applied in wood industry for multi-product application.

Li et al. (2010) modified soy flour (SF) using urea, citric acid and boric acid. Shear strength and water resistant test was used to evaluate the wood samples. They concluded that optimum hot press conditions are 30 °C and 0.5 hours for pressing temperature and time respectively. They found the optimum adhesive formulation exhibited shear strength of 0.82 MPa when wood sample bonded with modified SF adhesive and underwent water treatment. This phenomenon indicated that present of boric acid enhanced the water resistance of wood samples. However, they found that modified SF adhesive exhibited lower water resistance compared to commercial resin such as UF. In order to solve the limitation, further research will be continued with modified the adhesive.

2.6 Physico-chemical interaction

Adhesion was an important physico-chemical phenomenon that has attracted considerable attention from many researchers in many field or science. There are mainly five types of adhesion theory such as mechanical interlocking; diffusion; electronic; adsorption (hydrogen bond, van der waals, electrostatic and others) and covalent chemical bonding. The most widely accepted and applicable theory of adhesion was adsorption theory because intermolecular and interatomic forces between atoms and molecules formed when adhesive adhere to a substrate. In the case, of wood adhesion, wan der waals, hydrogen bonds and electrostatic interaction appeared in the bonding interaction especially hydrogen bond (Pizzi, 1994). Therefore, many researches were done to determine the bonding interaction of adhesive by using 13^{C} Nuclear magnetic resonance (13^{C} NMR), Fourier Transform Infrared Red (FTIR) spectroscopy and other techniques.

Khan et al. (2004) used FTIR to characterize the adhesive prepared. Lignin phenol formaldehyde adhesive (LPF) and control phenol formaldehyde adhesive (CPF) were characterized by using FTIR and comparison was made. The lignin used in producing LPF was extracted from bagasse. They reported that IR spectra for CPF and LPF show similar dispositions of the peak which indicates that the structures of two adhesive systems were similar. Furthermore, characterization of lignin extracted from bagasse was done. However, the comparison between bagasse lignin extracts and commercial lignin was not done. Therefore, the interaction study was not clear but, the similar IR spectra of CPF and LPF indirectly shows that lignin extracts have interaction with PF.

Soto et al. (2005) used tannin isolate, diglycidyl and polyglycidyl ether type epoxide resins to produce adhesive. In characterization part, they used FTIR to analysis. Tannin-epoxide adhesive was prepared in different pH and checked using FTIR. The results were shown that, sample prepared with pH 10 had the similar spectrum shape with tannin-paraformaldehyde system. They proposed that pH 10 sample had the similar reaction pathway with tannin-paraformaldehyde system. However, the interaction study was unclear.

Liu and Li (2006) produced Demethylated lignin-polyethylenimine (DKL-PEI) adhesive using de demethylated kraft lignin (DKL) and polyethylenimine (PEI). In adhesive characterization part, FTIR was used for analysis. DKL and DKL-PEI samples were characterized. They found that C=O functional group at 1702 cm^{-1} was weak in temperature 20 ^oC implied that C=O content was low. At temperature 120 ^oC, C=O content increased as peak 1702 cm^{-1} intensity increase. They proposed that C=O groups increased mainly due to the oxidation of phenolic hydroxyl groups. DKL-PEI blended at temperature 20 ^oC, FTIR spectra was shown shoulder of C=O groups still appeared while at a temperature 120 ^oC the shoulder disappeared. This phenomena indicated that the C=O groups in DKL disappeared. They proposed that, the reaction between DKL and PEI to be very similar to those between condensed tannins and PEI. However, the interaction between wood and DKL-PEI adhesive was not ruled out in this research.

Mansouri and Pizzi (2007) were using FTIR to investigate the reaction between polyurethane (PUR) waste powder and PF resin on alkaline condition. PR resin, PUR powder, and PR+PUR mix was checked with FTIR. The results show that, PUR C=O peak at 1700-1730 cm^{-1} and 1650 cm^{-1} almost disappeared and become smaller. The peak overlaps with C=O peak of PF resin and the intensity decreased. This indicated that a marked decrease of free formaldehyde present in the system. They concluded that there are no reaction possible happened for the system with FTIR analysis only.

Mishra and Sinha (2010) produced polyurethane adhesive using polyols obtained from cellulosic waste. Three types of polyols were prepared which is a) castor oil based polyols; b) blend of castor and soy oil based polyols and c) blend of castor and rice bran oil based polyol. FTIR was used to evaluate these three types of adhesive. The results show that, spectra a have board absorption band at 3420 cm^{-1} attributed to urethane N-H linkage. Besides that, high intensity and broad band indicated that pure castor oil based polyols adhesive have high reactivity. At 1720 cm^{-1} indicated the H-bonded and non H-bonded carbonyl overlaps and gives an asymmetrical absorption band. Moreover, spectra c as compared to a and b shows less interaction of the carbonyl group with hydrogen bond. They concluded that the adhesive shows some physic-chemical interaction. However, interaction between adhesive and wood was not investigated.

Li et al. (2010) used soy flour (SF), urea solution, citric acid and boric acid to produce environmentally friendly soy flour based adhesive for plywood application. For chemistry investigation part, they used FTIR to analysis the samples. Aqueous SF adhesive, cured adhesive, and pure SF was checked using FTIR technique. They concluded that, cross-linkage between $-NH_2$, -COOH and –OH had happened, while absorption peaks for N-H, O-H and –COO were less intense and narrower for cured adhesive spectrum as compared to aqueous SF and pure SF. In addition, peaks for COO- and $–C-NH_2$ of cured adhesive shown were less intense and narrower than the corresponding peaks for aqueous SF and pure SF. This indicated that, further acylation reaction and chemical bonding occurred during hot pressing to enhance bonding strength of samples.

Kong et al. (2011) produced a novel bio based poly (ether ester) polyol using canola oil. The novelty of the work was polyol derived from canola and react with diphenylmethane diisocyanate (pMDI) to produce polyurethane (PU) adhesive. The canola oil polyol and PU adhesive was investigated by FTIR technique. They concluded that a strong absorption peak of N-H group and an urethane band exhibit formation of urethane linkage in PU upon cross-linking with pMDI. Therefore, there are physico-chemical interaction happened in PU adhesive.

However, limited researches have been done to investigate the interaction between adhesive and veneer. So in this research, this topic was analysed further.

CHAPTER 3

METHODOLOGY

This chapter is divided into six sections. They are materials and apparatus, production of Melamine Urea Formaldehyde (MUF) resin, production MUF resin based adhesive with various types of filler, production Type II Plywood and testing of boards based on Japanese Agriculture Standard (JAS) (JAS for Plywood, 2003), Optimization of the process parameters using Response Surface Methodology (RSM) and physico-chemical studies are given in section 3.1, 3.2, 3.3, 3.4, 3.5 and 3.6 respectively.

3.1 Materials and Apparatus

3.1.1 Materials

The materials used in this research were melamine, urea, formalin (37%), NaOH, industrial flour, palm kernel, palm shell, ammonium chloride, veneer, 2-propanol, acetyl-acetone ammonium acetate solution and potassium bromide. All the chemical was use as receive without further purification.

3.1.2 Apparatus and instruments

The apparatus and instrument used for this research were three-necked flask, motor (VELP Scientifica stirrer), heating mantle, stirrer, thermometer, pH meter, Brookfield DVII Pro Viscometer with a small adaptor, moisture meter, mixer, solid liquid extraction equipment, oven, sieving machine, glue spreader, cold press machine, hot press machine, water bath, universal testing machine, UV/Vis spectrophotometer, Fourier Transform Infrared Red (FTIR), scanning electron microscope (SEM), field emission scanning microscope (FESEM) and light microscope (LM).

3.2 Production of Melamine Urea Formaldehyde (MUF) resin

The methodology of Melamine Urea Formaldehyde (MUF) resin preparation was adopted from Bono et. al (2003).

The experimental set up is shown in Figure 3.1. The composition for prepared MUF resin is shown in Table 3.1. Firstly, required amount of formalin (37 %) was poured into the three-necked flask. After that, melamine and urea were added into the system. The mixture was blended homogenously using a stirrer connected to a motor (VELP Scientifica stirrer), which was set the speed at 50 rpm. The final mixture turned into a white color solution. The pH of the solution was adjusted to a range of 8.8 to 9.0 by adding few drops of 1M NaOH. The temperature and pH was recorded for every 5 minutes till the end of the production process.

The mixture was heated and maintained at 80 ℃ until end point was reached. The end point can be determined by dropping the mixture solution into a beaker of water at 30 ℃ temperature for every 5 to 10 minutes. If the droplet is diluted in the water, without any trace (no whitish streak), meaning the end point has not achieved yet. The condition of the solution was observed during this period. (The initial white solution would turn clear at the temperature between 70 to 80 ℃). When the end point was reached, the heating process was stopped while continued stirring. 1M NaOH solution was added slowly to increase the pH value to a range of 8.8 to 9.5 (To stop the polymerization of resin). The solution was allowed to cool down to ambient temperature by immersing the three-necked flask into cool water. Required amount of urea was added when the temperature dropped to 60 ℃. The cooled resin was transferred to a plastic container for further testing and plywood production.

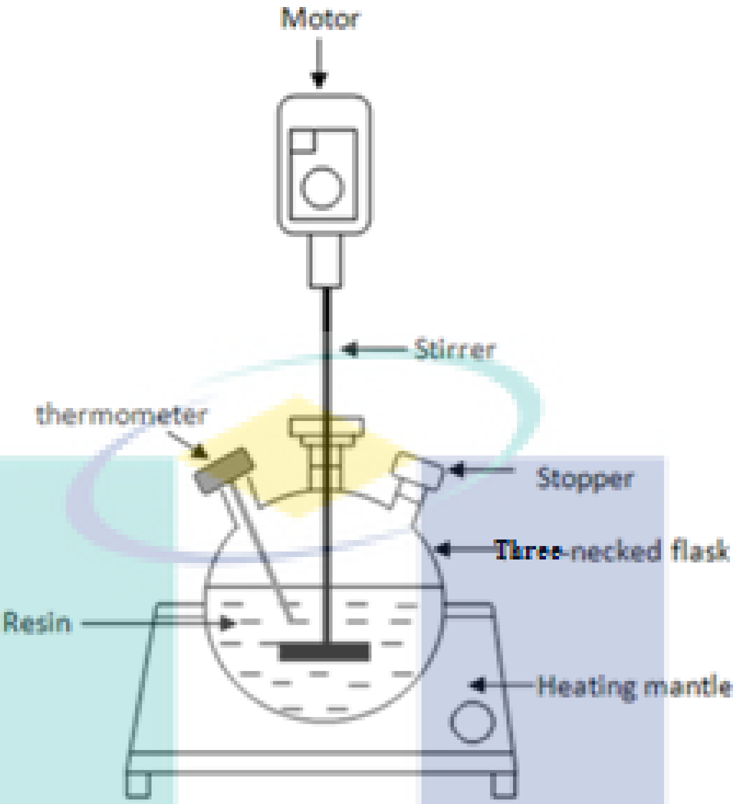

Figure 3.1: Setup of MUF resin

Table 3.1: Molecular weight and quantity of Formalin (37 %), Urea and Melamine

Chemicals (g)	**Molecular weight, MW (g/mol)**	**Quantity (g)**
Formalin (37 %)	30.03	289.00
Urea$_1$, U$_1$	60.06	26.75
Urea$_2$, U$_2$	60.06	36.75
Melamine (M)	126.12	147.50
Total		500.00

(Source: Bono et al., 2003)

3.3 Modification of production Melamine Urea Formaldehyde (MUF) resin based adhesive with various types of filler

Wheat flour (IF) was substituted with Palm Kernel Meal (PKM) and Palm Shell (PS) in this research. In order to get a different type of filler, the preparation of Palm

Kernel Meal powder was carried out. Besides that wheat flour and Palm Shell powder was provided by Shin Yang Chemical Sdn Bhd, Sabah, Malaysia.

Wood adhesive was produced in two stages: i) preparation of veneer ii) preparation of glue (wood adhesive).

In veneer preparation stage, 2 set of 3-ply of veneer were prepared where the dimension for face/back veneer was 300 mm x 300 mm x 1.3 mm while for core veneer was 300 mm x 300 mm x 3.3 mm. The moisture content of the veneer was determined by using Moisture Meter (mini LIGNO E).

In glue preparation stage, MUF resin (300g) was weighted into beaker. Urea (12 g) was added into the MUF resin mixed well with a mixer for 5 minutes by using a mixer. This was followed by fillers (wheat flour, Palm Kernel Meal, Palm Shell) (50 g) and mixed well for 5 minutes. After that, hardener (ammonium chloride) (13 g) was added into the mixture and mixed for 5 minutes.

3.3.1 Preparation of Palm Kernel Meal powder

PKM obtained from palm oil mill contained trace of oil. The trace oil was removed to avoid interference during the production of wood adhesives. For the removal of the trace oil removal from PKM soxhlet solid-liquid extraction technique was used. Prior to the oil removal the palm kernel cake was grinded to form fine particle for higher extraction efficiency. 2-propanol was selected as an extraction solvent. The extraction was conducted at solvent boiling temperature, 82.5 ℃ for 10 hours. This extraction process was repeated for three times to complete remove the oil. The oil free palm kernel was then dried in the oven for removal of trace solvent at 60 ± 3 ℃ for 24 hours. The dried PKM was sieve pass through a 50 µm sieve to obtain uniform fine powder. The range of the particle size was 65 – 40 µm.

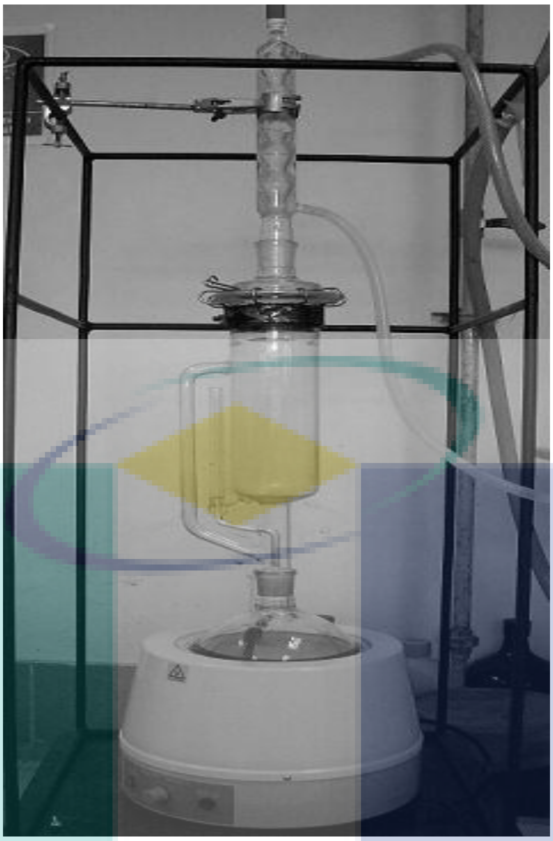

Figure 3.2: Soxhlet solid-liquid extraction equipment

3.4 Production of Type II Plywood

The production of type II plywood was carried out to produce plywood by using MUF resin based adhesive. Type II plywood was used in the sections where occasionally exposed to wet conditions (environment) (JAS, 2003).

Production of type II plywood was conducted using Red-Meranti 300 mm x 300 mm x 3.3 mm veneer. In order to get consistence result, equal amount of wood adhesive was used at every plywood produced. The adhesive was applied onto two sides of a core veneer using a glue spreader. The spread rate of the adhesive was 23 mg/cm^2. The adhesive-coated core veneer was stacked between two uncoated face veneers. The grain directions of the two adjacent veneers are perpendicular to each other as shown in Figure 3.3. The unfinished plywood was left at room temperature for 5 minutes, before it was cold pressed 9 kg/ cm^2 for 20 minutes.

The unfinished plywood was removed after 20 minutes from the cold press device and left free 5 minutes before it was transferred to hot press device. During hot pressed, pressure at 9 kg/cm^2 and temperatures of 100 to 150 ℃ were applied. The process was conducted for 50 sec to 250 sec. After the hot press completed, the plywood product was released from the device and stored at room environment for further testing.

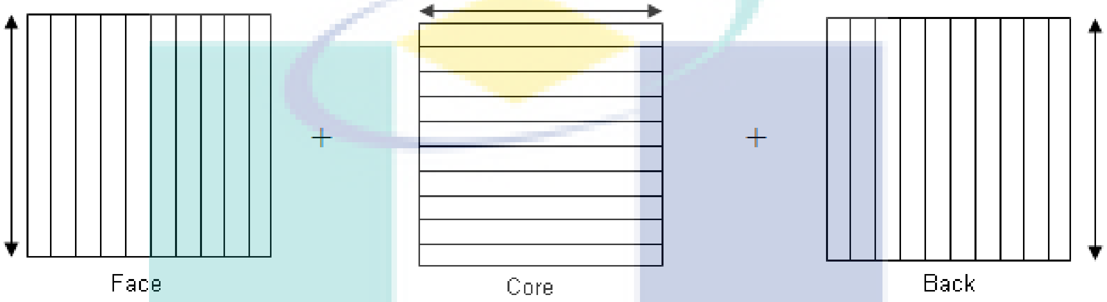

Figure 3.3: Grain direction of core and veneer that need to be considered

Figure 3.4: Cold press instrument

Figure 3.5: Hot press instrument

3.4.1 Shear Strength test of plywood

The shear strength test of type II plywood produced was determined by using bonding test according to the Japanese Agriculture Standard (JAS) (JAS for plywood, 2003). Total of nine plywood test pieces (25 mm x 80 mm) were tested for every plywood panel produced. The dimension of plywood test pieces is shown in Figure 3.6. Prior the test, the test pieces were soaked in a hot water bath at 100 ℃ for 4 hours. After that, test pieces will dry at 60 ± 3 ℃ for 20 hours. Futhermore, the test pieces soaked in hot water bath at 100 ℃ for 4 hours. After that, test pieces was soaking in cold water bath at room temperature. The test pieces reached cold state, then it was used for shear strength testing. Test was conducted using universal bonding testing instrument while the plywood test pieces were wet.

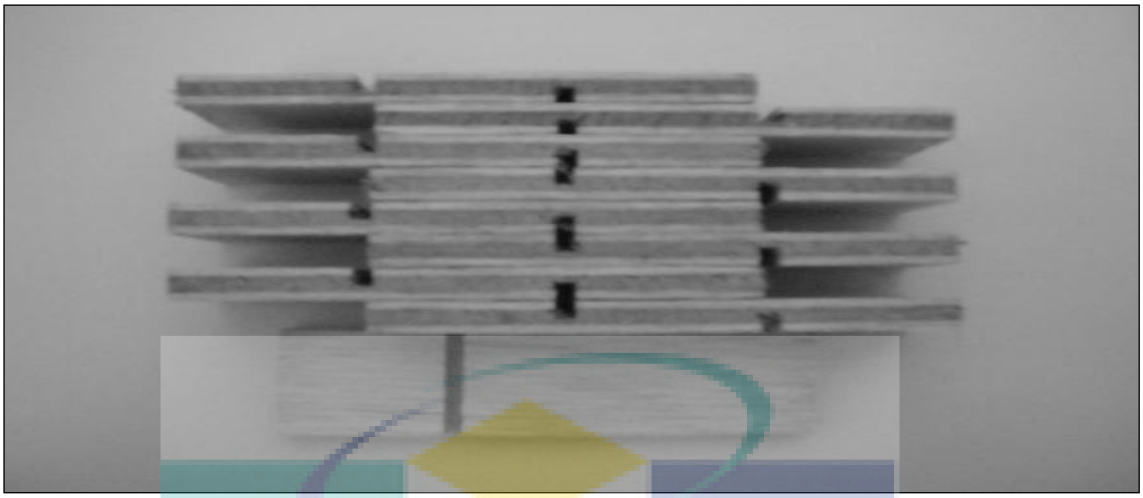

Figure 3.6: Plywood Test Piece for Bonding Test

The test pieces shear strength value can obtain by using equation 3.1. The thickness ratio of core veneer and Co-efficient was stated at Table 3.3 According to the standard, the shear strength of plywood panel less than 0.7 MPa is considered fail.

$$Shear\ Strength\ (MPa) = (P_s \times \mathrm{g} \times Co)/(B \times H) \qquad (3.1)$$

where P_s = maximum load (reading from bonding machine),

g= 9.81 m/s^2,

Co = co-efficient,

B = width of the piece (mm), and

H = distance between saw cuts (mm).

Table 3.2: Coefficients according to the classes of thickness ratios

Thickness Ratio	**Co-efficient**
1.50 or more, and less than 2.00	1.1
2.00 or more, and less than 2.50	1.2
2.50 or more, and less than 3.00	1.3
3.00 or more, and less than 3.50	1.4
3.50 or more, and less than 4.00	1.5
4.00 or more, and less than 4.50	1.7
4.50 or more	2.0

Figure 3.7: Bonding Test instrument

3.4.2 Formaldehyde emission test of plywood

The formaldehyde emission test of type II plywood produced was determined according to the Japanese Agriculture Standard (JAS) (JAS for plywood, 2003). Total of ten rectangular test pieces with a length of 150 mm and width of 50 mm were prepared from each plywood panel sample. The dimension of plywood test pieces was shown in Figure 3.8.

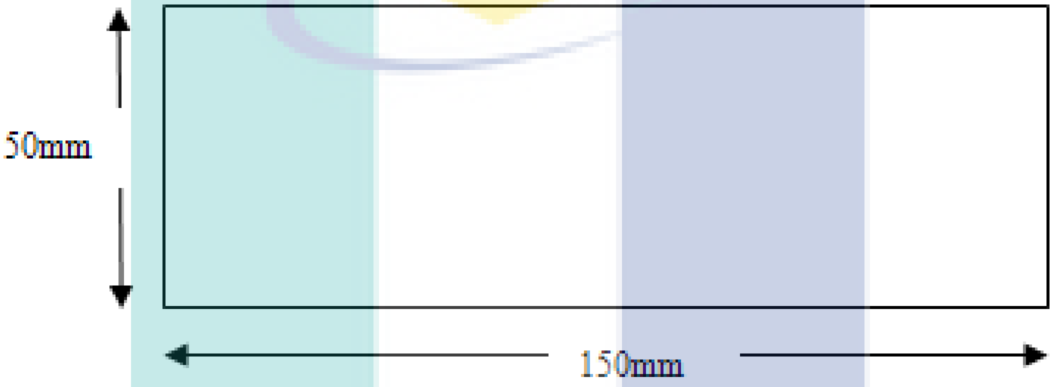

Figure 3.8: Dimension of Plywood Test Piece for free formaldehyde Test

A crystallizing dish with a diameter of 120 mm and a height of 60 mm was placed at the center of (inner volume 9-11 liters) desiccator. 300 ml of distill water was filled the crystallizing dish. The test pieces were fixed apart from each other and hold ed by a metallic holder. After that, metalic holder was placed on the crystallizing dish and keep for 24 hours at 20 ℃. After 24 hours, distilled water used as sample solution for measure the formaldehyde concentration because it absorbed formaldehyde evaporated release from test pieces.

The measurement of formaldehyde concentration was conducted by using method of ethyl-acetone luminous intensity absorbance. 25 ml of sample solution was put into a conical flask with a co-ground stopper. After that, 25 ml of acetyl-acetone ammonium acetate solution is added into conical flask. The conical flask with a co-ground stopper was warm at 65 ℃ for 10 minutes. The solution was transferred into an absorbance cell and measured at a wavelength of 412 nm using an UV/V spectrophotometer.

The formaldehyde concentration of sample solution can calculated by using equation 3.2.

$$C = F \times (A_d - A_b) \tag{3.2}$$

Where C : Formaldehyde concentration of test pieces (mg/L)
Ad : Absorbance of a sample solution
Ab : Absorbance of blank test (freshly distilled water)
F : Inclination of calibration curve (mg/L)

3.5 Experimental Design

The experimental settings were performed by using Respond Surface Methodology 3 level factorial. The experimental design was conducted using Design Expert software (version 6.10, Stat Easy Inc., Minneapolis, USA). The investigated variables were hot press temperature, time and different types of fillers. The constraint of component proportion was shown in Table 3.4.

Table 3.3: Temperature and Pressing time range for Hot Press of Plywood production

No.	Variables	Low limit	High limit
1	Hot press temperature, ℃	100	150
2	Hot press time, sec	50	250
3	Different types natural fillers	PKM, IF, PS	

3.6 Physico-chemical interaction study between adhesive and veneer

Fourier Transform Infrared Red (FTIR) spectroscopy machine (PerkinElmer) was used to study the physico chemical properties of adhesive and plywood. In order to observe the heat effect on the individual components of adhesive, PKM, plywood powder and resin was hot pressed at pressure 9 kg/cm^2 under 150 ℃ and 250 seconds. The raw and treated samples were mixed with potassium bromide and FTIR spectrum was recorded and the transmittance range was 400 – 4000 cm^{-1}. Samples with wood-PKM, wood-resin, resin-PKM and resin-PKM-wood were also prepared accordingly. In addition, the plywood slice (cracked and un-cracked) was checked by using scanning electron microscope (SEM) technique (JOEL) to visual the morphology of plywood sample and PKM. The samples was coating by platinum before investigate by SEM. Besides that, the 13% PKM sample was checked by using field emission microscope (FESEM) and coated with gold before investigated. In addition, light microscope (LM) also used. The samples with different concentration of PKM were stained with aqueous toluidine blue stai on a glass slide prior to examination with LM.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter is divided into four sections; they are synthesis of melamine urea formaldehyde resin (MUF), effect of different fillers on shear strength of the plywood, effect of hot press conditions on shear strength of the plywood, effects of filler content on shear strength and formaldehyde emission of the plywood.

4.1 Melamine Urea Formaldehyde resin (MUF) synthesis

MUF resin has been synthesized by the method proposed by Bono et al. (2003). In order to disperse adhesive onto the veneer, the MUF resin should have specific viscosity and the viscosity was monitored at different time intervals. The results are presented in Figure 4.1. The viscosity of MUF was increased slowly from reaction time 0 to 95 min and thereafter a sharp increase in viscosity is observed. The MUF resin is too difficult to disperse onto the surface when it is too viscous. The viscosity range of 35 – 85 cp was used for adhesive formulation. The resin prepared by this method at different reaction time was used as adhesive. Total 21 g of adhesive was applied on 1 ft^2 of wood and hot pressed at 125 ℃ and 150 sec. The press time and temperature were maintained as recommended by Bono et al. (2011). The shear strength value of plywood made by MUF resin in this viscosity range is shown in Figure 4.2. As the viscosity increases, shear strength value increases sharphly until 55 cp and thereafter it shows a plateu. Figure 4.2 indicates that, the low viscosity resin have low shear strength value. This is expected, as at initial 20 min the resin conversion is too low and as a result when the adhesive is formulated with this resin, very low amount of resin fraction could stay on the wood surface leading to a very poor shear streagth velue (Qiao et al., 1999). For the high viscosity resin (55 cp and 75 cp), the resin conversion was high. The amount of resin penetrated into the wood matrix was less compared to low vixcosity resin (Qiao et al., 1999). Therefore, the shear strength value was high as sufficient of the resin was remain on the wood surface which involved in chemical interaction with wood. Moreover when the resin with a viscosity of 75 cp was mixed with certain amount of filler, it formed non-dispersible adhesive. The adhesive was too difficult to disperse onto the surface when it is too viscous. Hence the reaction was stopped at 70 min, when the viscosity was reached at 55 cp and used for further studies.

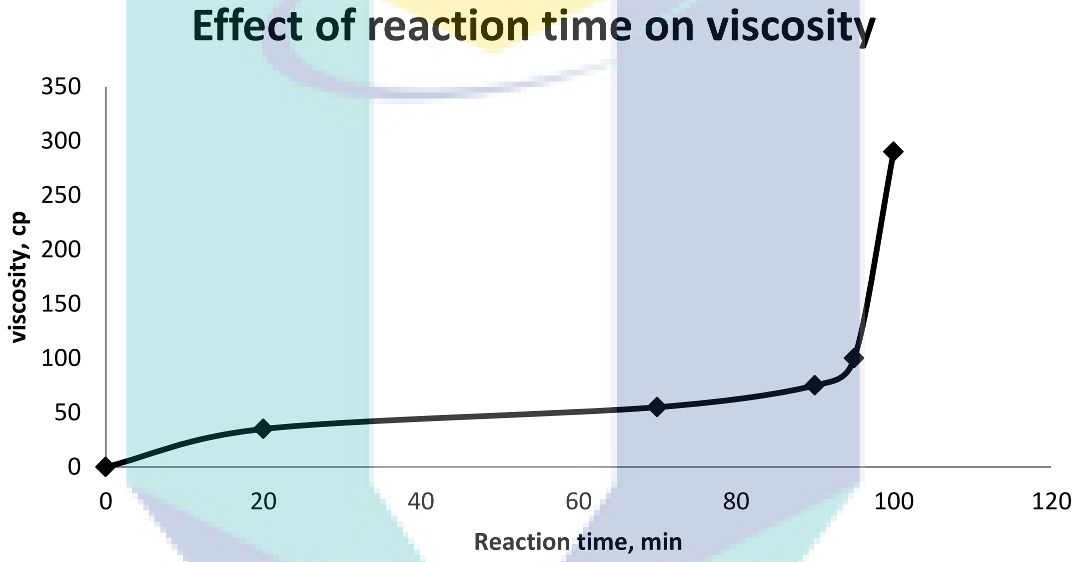

Figure 4.1: Effects of reaction time on viscosity of MUF resin (Total volume: 500g; Ratio, M:U:F; 2.32:1:4.55)

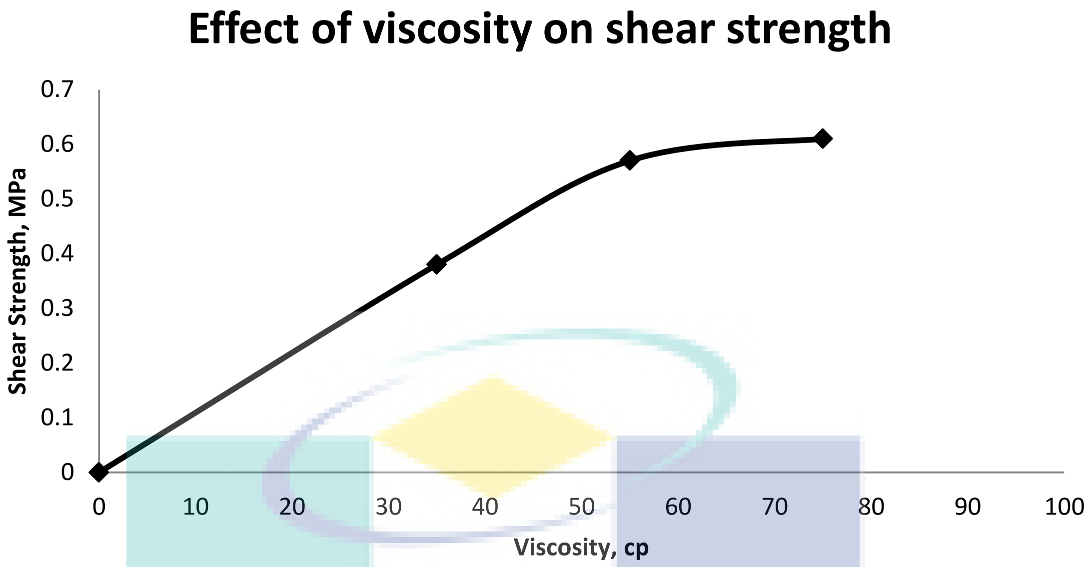

Figure 4.2: Effect of viscosity on shear strength of MUF resin (Temperature, 125 ℃; Time, 150 sec)

4.2 Effect of filler on shear strength of plywood

The effects of filler on shear strength properties of the plywood are shown in Figures 4.3. It was showed that the shear strength value of the plywood bonded with MUF resin with filler such as PKM, IF and PS was greater when compared to MUF resin alone.

The result shown in Figures 4.3 confirmed that, addition of filler to MUF resin can improve the shear strength of plywood. The role of the filler is to fill the pores of the wood surface and reduce the penetration of MUF resin into wood (Pizzi, 1994). Moreover, the filler also participates in crosslinking and polymerization reaction with resin and wood (Frihart and Wescott, 2004), which will strengthen the adhesion. Besides that, the plywood bonded with PKM-MUF resin with higher protein content had greater shear strength performance as compared to others. It is due to the protein content which enhances the bonding formation between adhesive and wood thus PKM had greater shear strength performance than IF and PS. The mechanism of the chemical interaction between adhesive and wood will discuss in chapter 6. The results obtained were in agreement with the work of Hojilla-Evangelista and Bean (2011) and Hojilla-Evangelista (2010). They reported that filler with high protein content had greater shear strength performance than low protein content. Bono et al. (2011) also found that considerable amount of PKM can enhance the hydrogen bonding between wood adhesive and wood surface. Moubarik et al. (2009) and Mansouri and pizza (2007) reported that shear strength value of plywood bonded with resin and filler was greater than plywood bonded with resin alone.

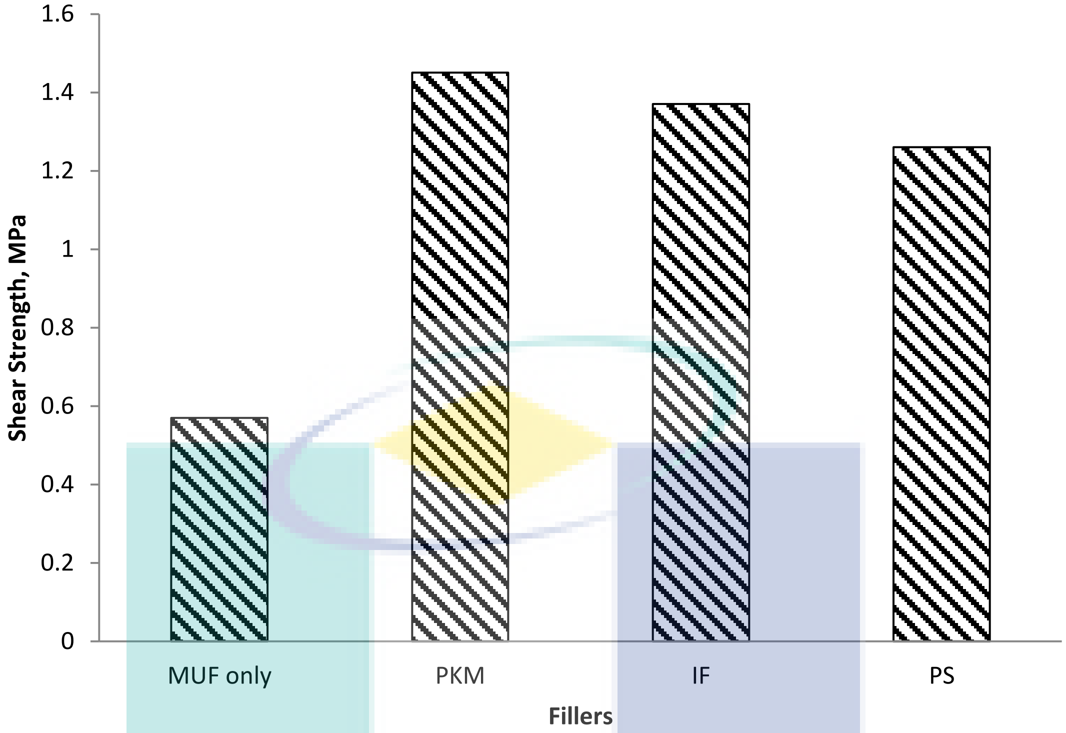

Figure 4.3: Effects of filler on shear strength of the plywood (Temperature, 125 ℃; Time, 150 sec)

4.3 Effect of hot press conditions on shear strength of the plywood

Effect of filler was studied in section 4.2, and concluded that the shear strength value of PKM and PS were comparable with IF. Therefore, the effect of hot press condition (hot press temperature and time) on shear strength was studied in this section. The temperature was varied from 75 ℃ to 175 ℃ whereas the time was varied from 50 sec to 650 sec.

4.3.1 Effect of hot press temperature

Effect of hot press temperature on the shear strength of plywood samples are shown in Figure 4.4. As per the study, at all hot press temperatures the shear strength results exceeded the minimum industrial requirement of 0.7 MPa (horizontal dashed line) for type II plywood panels. The average shear strength value significantly increased by 52.63 %, 75.64 % and 80.00 %, when hot press temperature was raised from 75 to

125 ℃ for PKM, IF and PS respectively. Whereas, in the range of 125 to 175 ℃ the average shear strength value significantly decreased by 27.58 %, 31.39 % and 29.37 % for PKM, IF and PS respectively. At the same hot press temperature, the shear strength value of PKM was significantly higher than IF and PS. Based on the shear strength value obtained, temperature at 125 ℃ showed maximum shear strength value. At 150 sec the press temperature below than 75 ℃ could not be investigated. This is due to the fact that the veneers failed to stick with core face at this given conditions. These phenomena occurred because, it has failed to do bond formation to hold the veneers and core face together. In addition, the experiment at press temperature above 175 ℃ was also impossible to evaluate the results. This is due to the fact that the plywood failed to cut into pieces for bonding test. Therefore, the bonding test couldn't be conducted in that range. This phenomenon occurs due to the large air bubbles formed between the veneers and core face. Furthermore, cracks and burnt wood surfaces were found during the hot press.

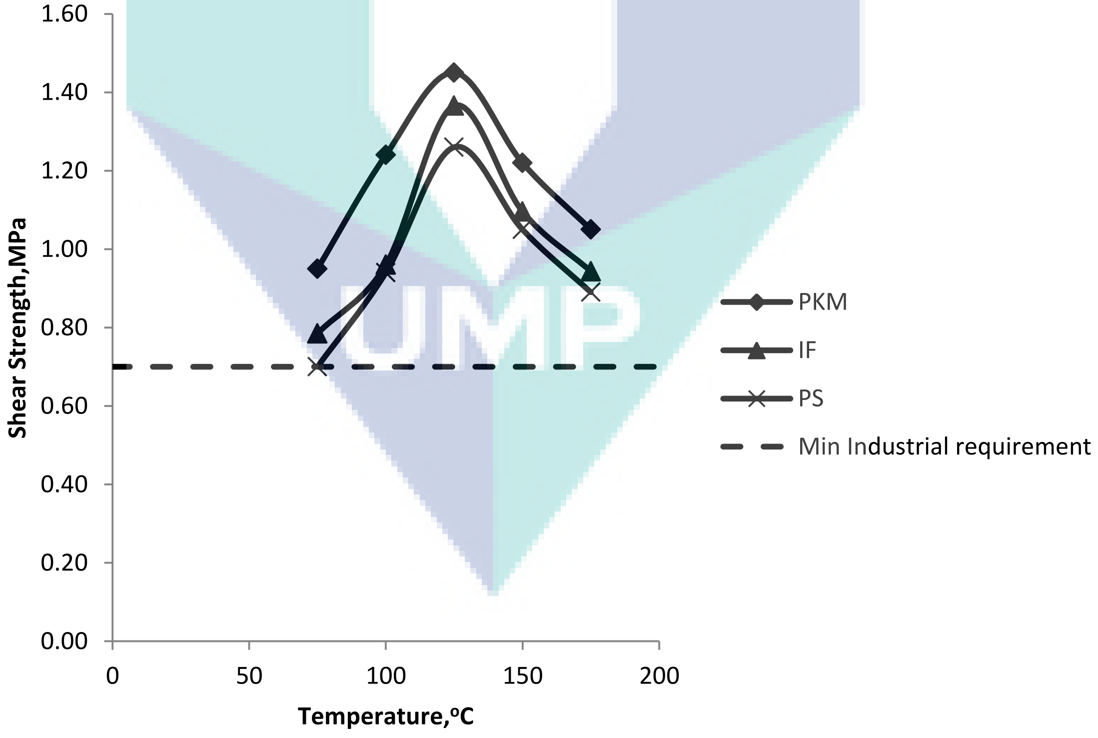

Figure 4.4: Effects of hot press temperature on shear strength of natural filler (Time, 150 sec)

The function of the hot pressing in plywood production is to provide the necessary heat and pressure for curing the adhesive and dispersing the filler particle into a solid board. During hot pressing, the heat is transferred from surface to core, so the core temperature is generally lower than the surface temperature. Complete curing of an adhesive can be achieved by increasing hot press temperature at a fixed press time or increasing hot press time at a fixed press temperature. The shear strength would either remain the same or decrease because of partial degradation of adhesives and wood (Gu and Li, 2011). Therefore, hot press temperature and time should be optimized, and it will be discussed in the chapter 5. At fixed hot press time of 150 sec, it appeared that the adhesive was fully cured at 125 ℃ and further increase in temperature, the shear strength was significantly decreased (Figure 4.4). The results obtained were in agreement with the work of Claub et al. (2010; 2011) which reported that wood tensile shear strength bonded was initially increase until maximum and drop down as the pressing temperature was vary from 20 ℃ to 200 ℃.

4.3.2 Effect of hot press time

Effect of hot press time on the shear strength of plywood was shown in Figure 4.5. The average Shear Strength value significantly increased by 28.32 %, 30.48 % and 35.48 % when the hot press time was raised from 50 sec to 150 sec for PKM, IF and PS respectively. Further increase in press time from 150 sec to 650 sec the average shear strength value significantly decreased by 52.42 %, 51.82 % and 53.17 % for PKM, IF and PS respectively. The shear strength value of all samples were met the minimum industrial requirement (horizontal dashed line) except hot press time at 650 sec and 550 sec for PS. At the same hot press temperature, sample shear strength value using PKM was significantly higher than IF and PS. At hot press time of 150 sec, the shear strength value was shown maximum value. At 125 ℃ the press time below than 50 sec could not be investigated. This is due to the fact that the veneers failed to stick with core face at this given conditions. These phenomena occurred because, it has failed to do bond formation to hold the veneers and core face together. In addition, the experiment at press time above 650 sec was also impossible to evaluate the results. This is due to the fact that the plywood failed to cut into pieces for bonding test. Therefore, the bonding test couldn’t be conducted in that range. This phenomenon occurs due to the large air bubbles formed between the veneers and core face. Furthermore, cracks and burnt wood surfaces were found during the hot press.

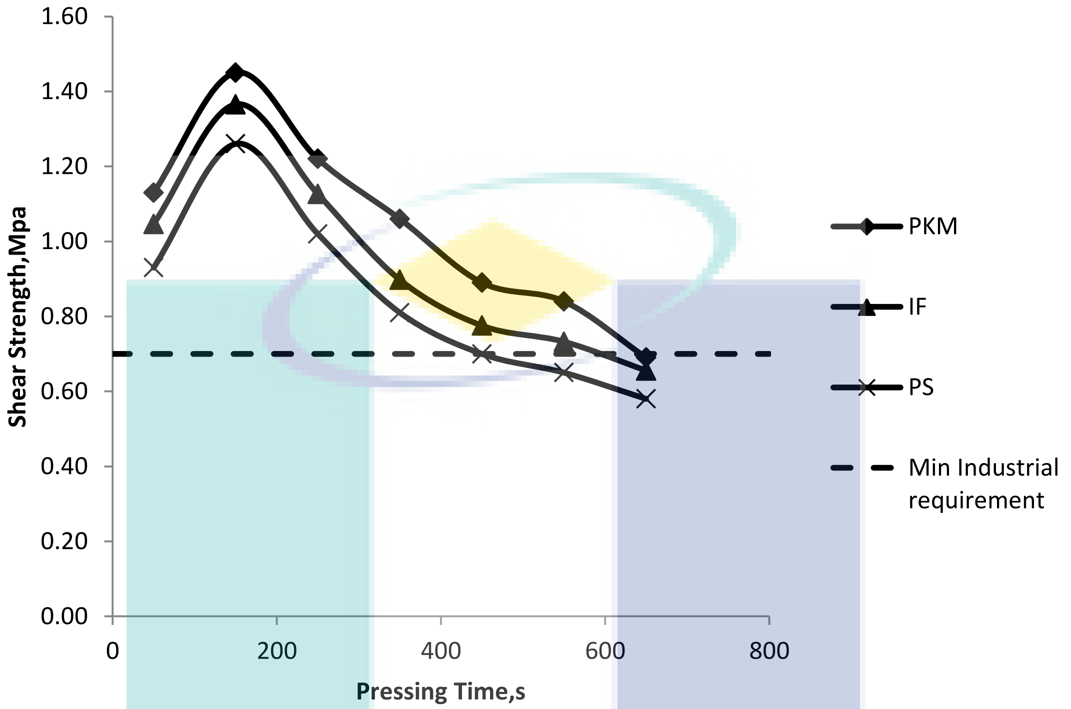

Figure 4.5: Effects of hot press time on shear strength of natural filler (Temperature, 125 ℃)

At fixed hot press temperature of 125 ℃, it appeared that the adhesive was completely cured at 150 sec. The decreased shear strength value at the hot press time 250 to 650 sec implied that the hot press time of 650 sec was too long (Figure 4.5). The results obtained were in agreement with the work of Bono et al. (2011) which reported that plywood shear strength bonded with MUF resin initially increases until maximum and drop down as the pressing temperature was vary from 50 sec to 250 sec. Derkyi et al. (2008) found that, the shear strength of the plywood bonded with formaldehyde resin was increase as the hot pressing time increased from 4 min to 6 min which indicate that better polymer curing at higher temperature. Babcock and Smith (1947) reported that the shear strength performance of plywood bonded with PF resin initially increases until maximum and drop down as the pressing temperature increases from 2 min to 5 min.

4.4 Effect of filler content on shear strength and formaldehyde emission of the plywood

Effects of filler content on the mechanical performance are shown in Figure 4.6 and 4.7. The adhesive was prepared with six different amounts of filler (0 %, 3 %, 8 %, 13 %, 18 % and 23 %) and at a fixed amount of MUF resin, urea and ammonium chloride. After that, total 21 g of adhesive was applied on 1 ft^2 of wood and hot pressed at 125 ℃ and 150 sec. In the range of 0 % to 13% of filler, the average shear strength value was significantly increased. Further increase in the amount of filler until 23 %, the shear strength value was markedly decreased. At the same amount of filler, sample shear strength value using PKM was significant higher than IF and PS. The shear strength value IF was higher than PS. Moreover, the formaldehyde emission was significantly decreased from 0 % to 18 % of filler content. Further increase in filler amounts to 23 %, the formaldehyde emission was increased (Figure 4.7). All the result of formaldehyde emission was in the range of industrial requirement (JAS, 2003). At the same amount of filler, formaldehyde emission value of plywood bonded with IF was significant lower than PKM and PS. The formaldehyde emission value of sample bonded with PKM was lower than PS.

The results, shown in Figure 4.6, confirmed that the concentration of filler in the adhesive formulation played an important role for MUF adhesion properties. The results obtained were in agreement with the work of Qiao et al. (1999) which reported that shear strength of wood bonded with poly(vinyl acetate) was initially increases until maximum and dropped down as the filler was added from 5 % to 25 %. This is due to the viscosity of adhesive increased as the filler content increased. The adhesive with low viscosity will penetrate too deep into the wood pores while a very little amount of adhesive was left on the surface to adhere the wood. On the other hand, the high viscous adhesive leaves maximum amount of resin on the surface with little penetration into the wood pores which leads to the reduced interlocking effect and as a result the efficiency of contact area between wood and adhesive decreases. The thick glue layer leads to weak adhesive strength (Qiao et al., 1999). Derkyi et al. (2008) also found that plywood shear strength value was decreased as the viscosity of the adhesive increases. Claub et al. (2010) and Ozalp (2011) found that the shear strength value of wood increases as the filler content increases when the filler content increase from 0 % to 30 %. Mansouri and Pizzi (2007) and Babcock and Smith (1947) reported that, shear strength of plywood bonded with PF was initially increased until maximum and drop down as the filler was increased.

When the filler content was increased from 0 % to 18 % the formaldehyde emission dropped and reached to a minimum value, but at further increase in filler amount the formaldehyde emission increased (Figure 4.7). The formaldehyde emission was increased at filler content above 18 %. This might be due to excess of filler usage and also the system become highly heterogeneous. The morphology analysis will be discuss in chapter 6. The results obtained were in agreement with the work of Ozalp (2011). The author reported that the formaldehyde emission of plywood bonded with UF decreased as the filler content increased.

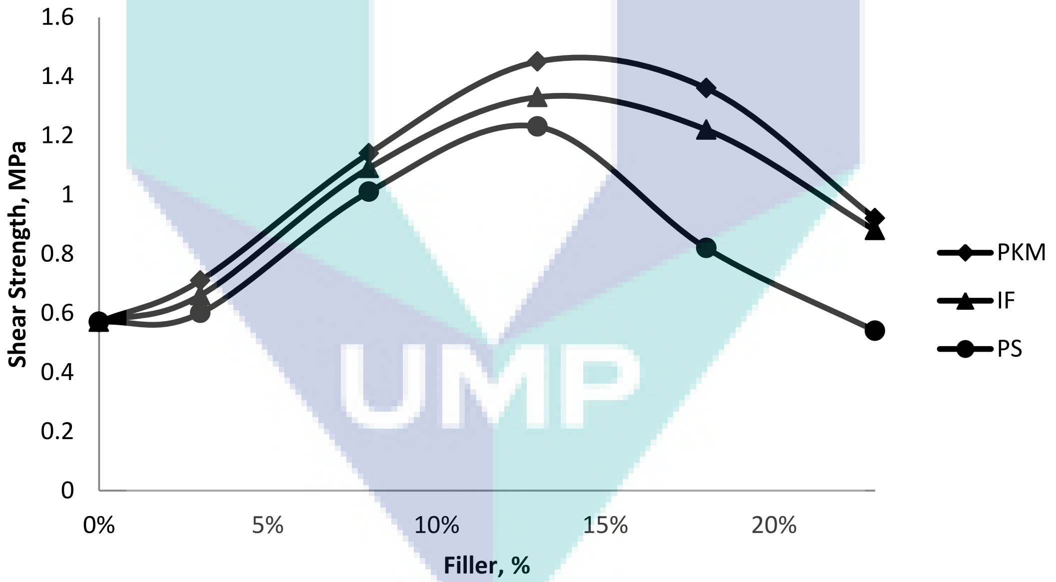

Figure 4.6: Effects of filler content on shear strength of the plywood (Temperature, 125 ℃; Time, 150 sec)

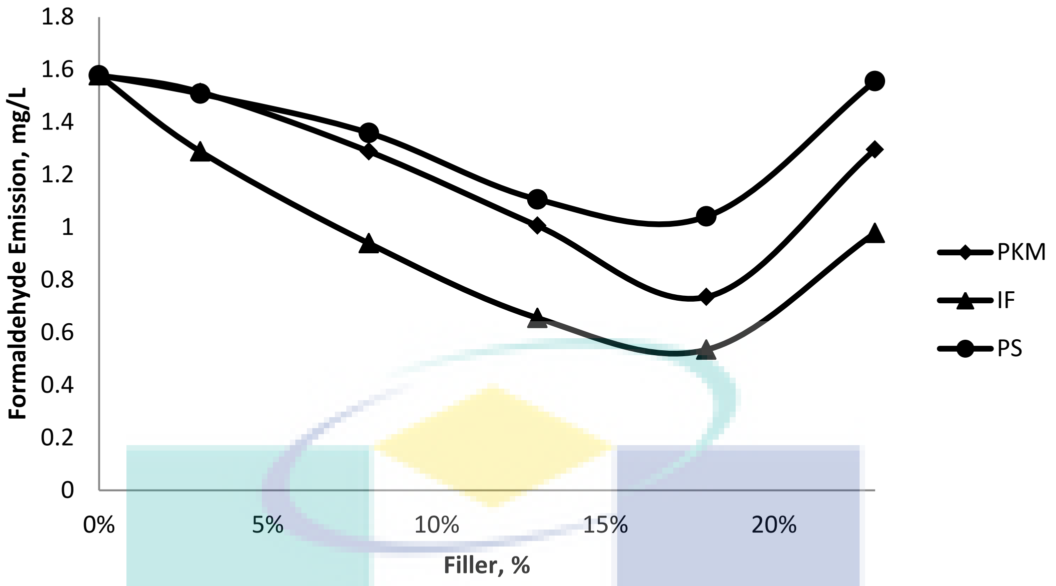

Figure 4.7: Effects of filler content formaldehyde emission of the plywood (Temperature, 125 ℃; Time, 150 sec)

Effects of filler type on formaldehyde emission of the plywood are showed in Figures 4.8. It can be seen that the plywood samples bonded with MUF resin with filler showed less formaldehyde emission than plywood bonded with MUF resin alone. Formaldehyde emission value of IF was lower than PKM and PS (IF<PKM<PS).

The result shown in Figures 4.8 confirmed that, addition of filler to MUF resin can reduce the formaldehyde emission of plywood. Tang et al. (2012) reported that, formaldehyde emission from plywood caused due to small amount of free formaldehyde was remained inside the resin matrix. In the formaldehyde based resin synthesis, amount of free formaldehyde is residual because it is not participating in the reaction. During the hot pressing and solidification of plywood process, the cleavage of methylene ether bond in formaldehyde resin occurs and hydroxyl methyl group polycondenses and crosslinks into methylene, which releases free formaldehyde. In the hot press process of plywood, due to slow heat transfer, the methylene and hydroxymethyl ether in the centre layer of formaldehyde resin may not be completely crosslinked. Therefore, Tang et al. (2012) suggested that, adding filler into glue solution can absorb free formaldehyde and inhibit degradation of formaldehyde resin to reduce the formaldehyde emission. Besides that, Moubarik et al. (2009), Wang et al. (2011) and Ozalp (2011) also suggested that renewable resources can substitute formaldehyde resin and reduce the emission of plywood panel. The formaldehyde emission of IF and PKM was lower than PS, because the free formaldehyde reacted with hydroxyl and amino groups of protein molecule during hot press process (Gao et al., 2012). The formaldehyde emission for PKM was higher than IF, theoretically, PKM supposed to have a lower formadlehdye emission than IF because the protein content of PKM is higher than IF. However, the resin layer formed with more void after curing process because the big molecular weight of PKM, so that the free formaldehyde was much easier to release compared to IF. The results obtained were in agreement with the work of Gao et al. (2012) which reported that, protein molecule causes form void in resin layer after the resin cured, therefore, the free formaldehyde was easy to release. Besides that, the solubility of IF inside MUF was high, so the interaction of the IF protein with free formaldehyde was greater compared to PKM. Therefore, the formaldehyde emission of high protein filler have high formadlehdye emission value compared to low protein filler.

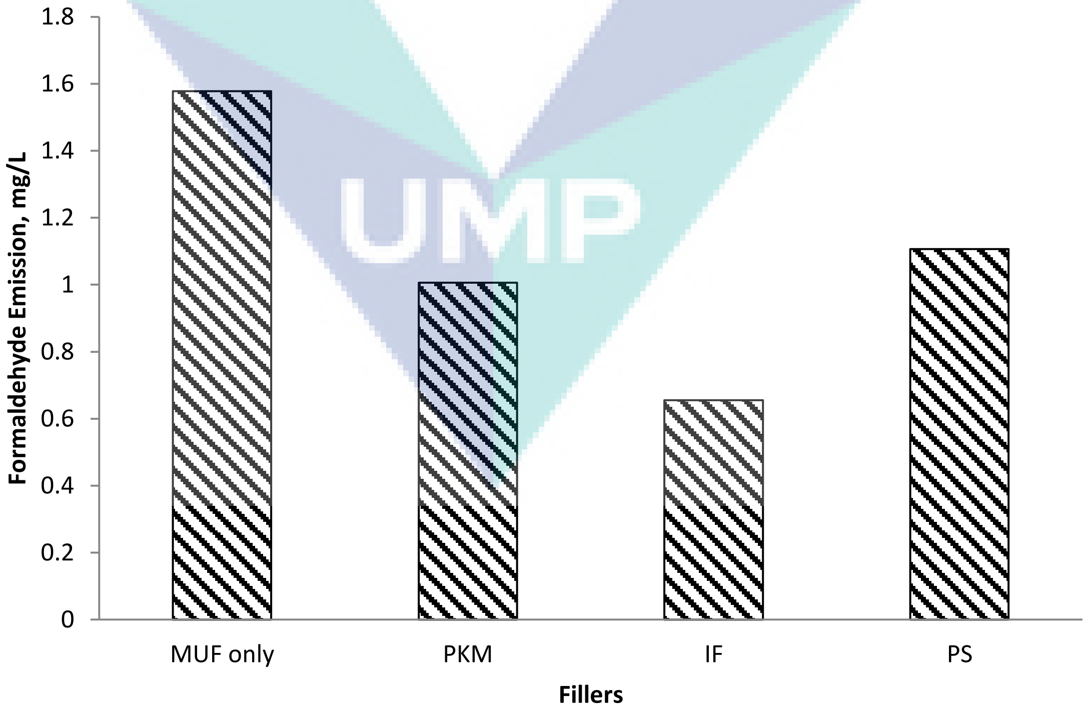

Figure 4.8: Effects of filler on formaldehyde emission of the plywood (Temperature, 125 ℃; Time, 150 sec, filler content 13%)

CHAPTER 5

RESULT AND DISCUSSION (OPTIMIZATION)

This chapter discussed about the optimization on processing parameter during the hot pressing process. Response surface methodology was used to investigate the individual parameter such as hot press temperature, time and various types of natural fillers.

5.1 Optimization on processing parameter

The optimized values obtained for hot press temperature and time of PKM, IF and PS as filler were used in this study. The proposed experimental design is given in Table 5.1. The experiments were carried out to figure out the optimum and maximum shear strength and minimum formaldehyde emission of MUF resin in the particular range of hot press temperature and time.

Table 5.1: Average shear strength and formaldehyde emission of various types of natural fillers.

No.run	Temperature,x_1 (℃)	Pressing Time, x_2 (sec)	Average Shear Strength of 10 Specimens of Plywood, Y_1 (MPa)			Formaldehyde Emission of Specimens of Plywood, Y_2 (mg/L)		
			PKM, x_3	**IF, x_3**	**PS, x_3**	**PKM, x_3**	**IF, x_3**	**PS, x_3**
1	100.00	50.00	1.08	0.90	0.91	1.5773	1.0215	2.1502
2	125.00	250.00	1.22	1.11	1.02	0.8524	0.4555	0.7431
3	150.00	50.00	1.12	1.08	0.97	0.9973	0.3785	1.4422
4	100.00	150.00	1.24	0.96	0.94	1.3997	0.9516	1.5774
5	125.00	150.00	1.45	1.36	1.21	1.0283	0.6151	1.2798
6	125.00	50.00	1.13	1.03	0.93	1.1891	0.7374	1.4985
7	100.00	250.00	1.13	0.93	0.87	1.1066	0.6759	1.0002
8	125.00	150.00	1.37	1.37	1.26	0.9809	0.5750	1.1673
9	150.00	250.00	1.11	1.06	0.92	0.5367	0.3383	0.9212
10	150.00	150.00	1.22	1.10	1.05	0.7735	0.3563	1.1513
11	125.00	150.00	1.49	1.33	1.23	1.0080	0.6224	1.4989
12	125.00	150.00	1.49	1.30	1.26	0.8956	0.5275	1.2392
13	125.00	150.00	1.35	1.28	1.19	1.0984	0.6479	1.4489

5.1.1: Development of regression model equation

A polynomial regression equation was developed by using three level factorial design to analyze the factor interactions by identifying the significant factors contributing to the regression model. The complete design matrix together with the response values obtained from the experimental works are given in Table 5.1. The shear strength and formaldehdye emission of filler was found from 0.90 MPa to 1.45 MPa and 0.3383 mg/L to 3.1502 mg/L.

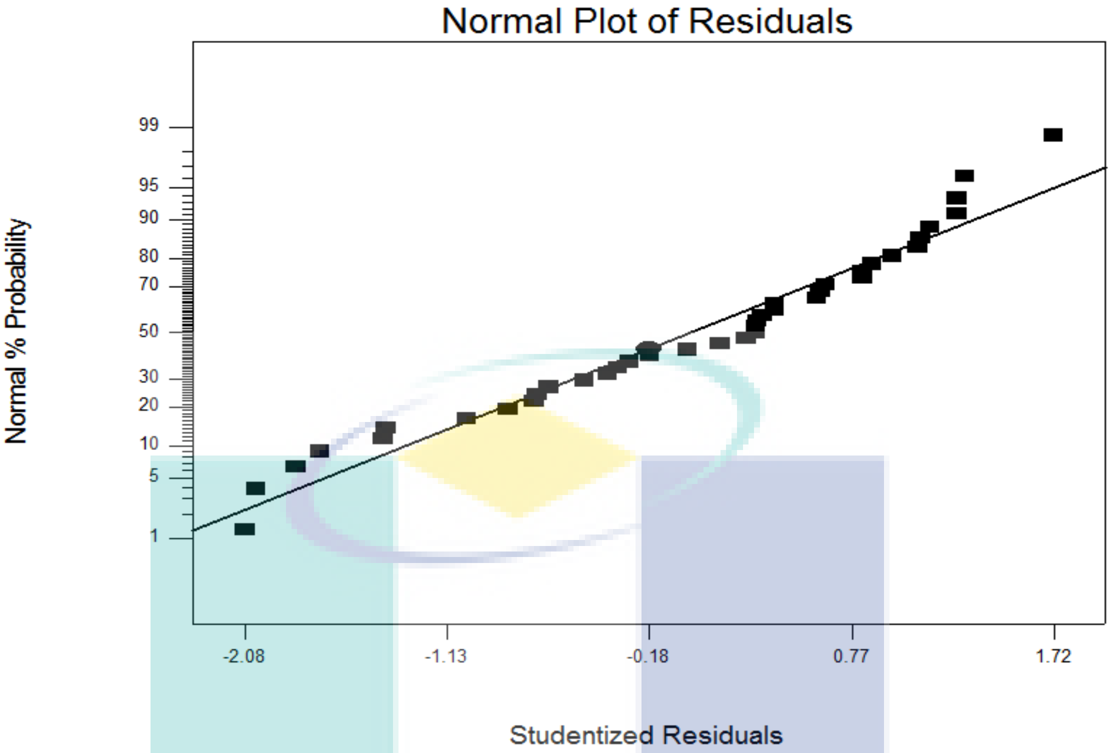

Figure 5.1: Normal % probability of studentized on shear strength performance

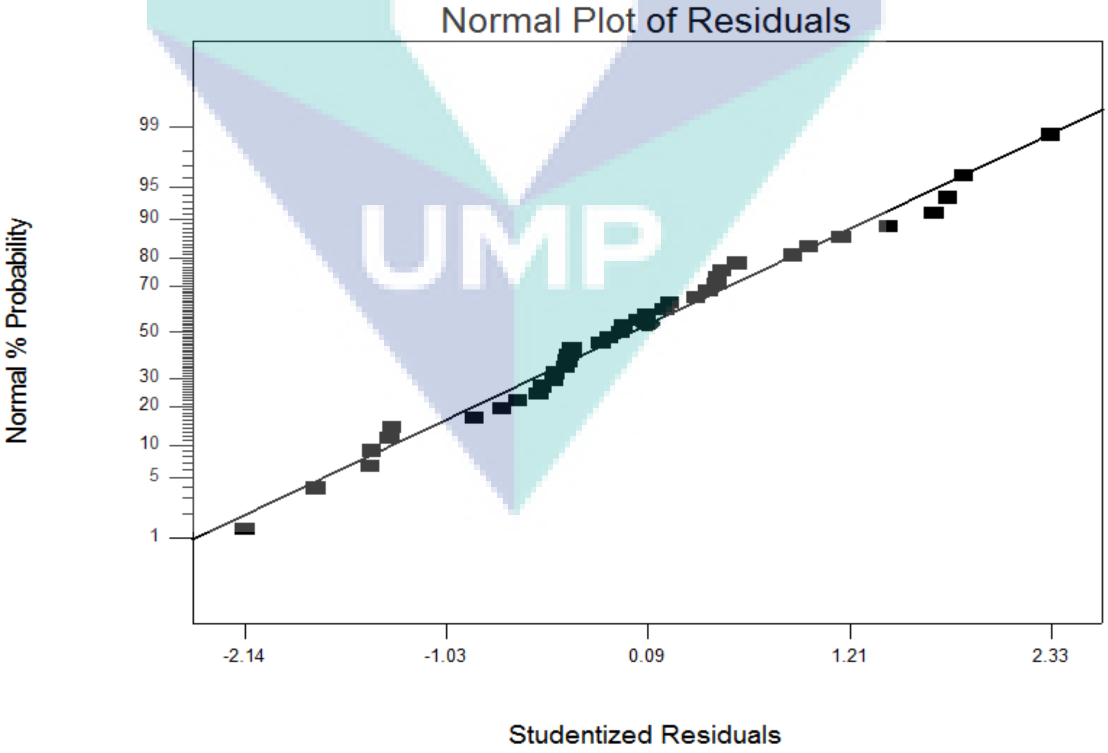

Figure 5.2: Normal % probability of studentized on formaldehyde emission performance

According to the sequential model sum of squares, the models were selected based on the highest order polynomials, where the additional terms were significant, and the models were not aliased. For shear strength and formaldehdye emission of plywood, the quadratic models were selected due to higher order polynomial. Besides that, normal probability of studentized from the quadratic model for shear strength and formaldehyde emission performance were shown at Figures 5.1 and 5.2. The plots were satisfactory. So it was concluded that, the quadratic model was adequate to describe the shear strength and formaldehyde emission response surface of the processing parameter optimization (Bono et al., 2008). The final empirical models in terms of actual factors for shear strength performance (Y_1) and formaldehyde emission performance (Y_2) shown in Eqs 5.1 to 5.6 respectively.

$$Y_1[\mathrm{PKM}] = -3.0413 + 0.0640x_1 + 5.8235 \times 10^{-3}x_2 - 2.5370 \times 10^{-4}{x_1}^2 - 1.7023 \times 10^{-5}\,{x_2}^2 - 4.0000 \times 10^{-6}\,x_1x_2 \tag{5.1}$$

$$Y_1[\mathrm{IF}] = -3.5286 + 0.0670x_1 + 5.7569 \times 10^{-3}x_2 - 2.5370 \times 10^{-4}{x_1}^2 - 1.7023 \times 10^{-5}\,{x_2}^2 - 4.0000 \times 10^{-6}\,x_1x_2 \tag{5.2}$$

$$Y_1[\mathrm{PS}] = -3.3952 + 0.0655x_1 + 5.6069 \times 10^{-3}x_2 - 2.5370 \times 10^{-4}{x_1}^2 - 1.7023 \times 10^{-5}\,{x_2}^2 - 4.0000 \times 10^{-6}\,x_1x_2 \tag{5.3}$$

$$Y_2[\mathrm{PKM}] = 5.5659 - 0.0516x_1 - 5.7410 \times 10^{-3}x_2 + 1.3627 \times 10^{-4}{x_1}^2 - 3.7133 \times 10^{-6}\,{x_2}^2 + 3.7933 \times 10^{-5}\,x_1x_2 \tag{5.4}$$

$$Y_2[\mathrm{IF}] = 5.0504 - 0.0515x_1 - 5.0630 \times 10^{-3}x_2 + 1.3627 \times 10^{-4}{x_1}^2 - 3.7133 \times 10^{-6}\,{x_2}^2 + 3.7933 \times 10^{-5}\,x_1x_2 \tag{5.5}$$

$$Y_2[\mathrm{PS}] = 5.6690 - 0.0478x_1 - 7.6717 \times 10^{-3}x_2 + 1.3627 \times 10^{-4}{x_1}^2 - 3.7133 \times 10^{-6}\,{x_2}^2 + 3.7933 \times 10^{-5}\,x_1x_2 \tag{5.6}$$

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value, R^2 and R^2_{adj}. The R^2 value for the Eqs. 5.1 to

5.3 was 0.9032 and Eqs. 5.4 to 5.6 was 0.9625. This indicated that 90.32 % and 96.25 % of the total variation in the shear strength and formaldehyde emission performance of the plywood respectively. The closer the R^2 value to 1.0, the model is able to provide predicted values which are closer to the actual values. The R^2 value of Eqs 5.1 to 5.6 were considered relatively high, indicating that there was good agreement with the experimental, predicted shear strength and formaldehyde emission performance of plywood from this model. R^2_{adj} (adjusted determination coefficient) is the correlation measure for testing the goodness of fit of the regression equation. If the R^2_{adj} value is high, degree of correlation between the observed and predicted values will be higher (Ravikumar et al., 2006). The the R^2_{adj} was 0.8638 and 0.9472 for Eqs 5.1 to 5.3 and Eqs. 5.4 to 5.6 respectively, which were reasonably close to one, and it was confirmed that the model was highly significant and indicated a high degree of correlation between the observed and predicted data. Furthermore, coefficient of variation (CV) indicates the degree of precision with which the experiments are compared. A relatively low value of CV obtained for shear strength and formaldehyde emission performance of the plywood as 5.58 and 9.36 respectively, which showed better precision and reliability of the experiments carried out.

5.1.2 Statistical analysis

The result of the surface quadratic model in the form of analysis of variance (ANOVA) is given in Table 5.2 for shear strength of plywood. ANOVA is required to justify the significance and adequacy of the models. The mean squares were obtained by dividing the sum of the squares of each of the variation sources, the model and the error variance, by the respective degrees of freedom. If the value of Prob > *F* less than 0.05, the model term are considered as significant (Cai et al., 2008; Qiao et al., 2009). From the Table 5.2, the model *F* - value is 22.90 and Prob > *F* is < 0.0001 it implied that this model was significant. The significant of each coefficient can determined using Prob > *F* value in Tables 5.2 and 5.3. The Prob > *F* value can be used as a tool to check the significance of each coefficient and the interaction strength between each independent variable. The corresponding variables would be more significant at greater F value and smaller Prob > *F* value (Guo et al., 2010). In this case, x_1, x_3, x_1^2 and x_2^2 factors were significant model term whereas x_2, x_1x_2, x_1x_3 and x_2x_3 were insignificant to the response.

The lack of fit measures the failure of the model to represent the data in the experimental domain at a point which are not included in the regression (Zhong and Wang, 2010). As showed in Table 5.2, *F* - value and Prob > *F* of the lack of fit were 2.48 and 0.0600 respectively. It also implied that it was not significant relative to the pure error and indicated that the model equation was adequate for predicting the shear strength value of the plywood under any combination of values of the variable.

The ANOVA for the quadratic model for formaldehyde emission performance is listed in Table 5.3. From the ANOVA for response surface and quadratic model for formaldehyde emission, the Model *F* – value is 243.26 and Prob > *F* is < 0.1000. It showed that the model was significant. In this case, x_1, x_2, x_3, x_1^2, x_1x_2 and x_2x_3 were significant model terms whereas x_2^2 and x_1x_3 were insignificant to the response. As showed in Table 5.3, *F* - value and Prob > *F* of the lack of fit were 0.85 and 0.6264 respectively, which implied that it was not significant relative to the pure error and indicated that the model equation was adequate for predicting the formaldehyde emission value of the plywood under any combination of values of the variable.

Table 5.2: Analysis of variance (ANOVA) for response surface quadratic model for Shear Strength of plywood

Source	**Sum of Squares**	**DF**	**Mean Square**	***F* Value**	**Prob > *F***	**Comment**
Model	1.04	11	0.095	22.90	< 0.0001	significant
x_1	0.025	1	0.025	6.02	0.0208	
x_2	2.689E-03	1	2.689E-03	0.65	0.4273	
x_3	0.27	2	0.014	32.83	< 0.0001	
x_1^2	0.21	1	0.21	50.32	< 0.0001	
x_2^2	0.24	1	0.24	58.00	< 0.0001	
x_1x_2	1.200E-03	1	1.200E-03	0.29	0.5947	
x_1x_3	0.017	2	8.439E-03	2.04	0.1498	
x_2x_3	1.478E-03	2	7.389E-04	0.18	0.8375	
Residual	0.11	27	4.140E-03			
Lack of Fit	0.084	15	5.633E-03	2.48	0.0600	not significant
Pure Error	0.027	12	2.273E-03			
C.V.	5.58					
R^2	0.9032					
R^2_{adj}	0.8638					

Table 5.3: Analysis of variance (ANOVA) for response surface quadratic model for formaldehyde emission of plywood

Source	**Sum of Squares**	**DF**	**Mean Square**	***F* Value**	**Prob > *F***	**Comment**
Model	5.97	11	0.54	62.95	< 0.0001	significant
x_1	1.26	1	1.26	145.89	< 0.0001	
x_2	1.15	1	1.15	133.71	< 0.0001	
x_3	3.14	2	1.57	181.89	< 0.0001	
x_1^2	0.060	1	0.060	6.97	0.0136	
x_2^2	0.011	1	0.011	1.32	0.2598	
x_1x_2	0.11	1	0.11	12.52	0.0015	
x_1x_3	0.035	2	0.017	2.02	0.1525	
x_2x_3	0.22	2	0.11	12.75	0.0001	
Residual	0.23	27	8.623E-03			
Lack of Fit	0.12	15	7.975E-03	0.85	0.6264	not significant
Pure Error	0.11	12	9.434E-03			
C.V.	9.36					
R^2	0.9625					
R^2_{adj}	0.9472					

From the statistical results obtained, it was shown that the above models were adequate to predict the shear strength and formaldehyde emission performance within the range of variables studied. Figures 5.3 and 5.4 were shown the predicted values versus the experimental values for shear strength and formaldehyde emission performance respectively. The predicted values obtained are close to the experimental values, indicating that the models developed were satisfactory in capturing the correlation between operating parameter to the response.

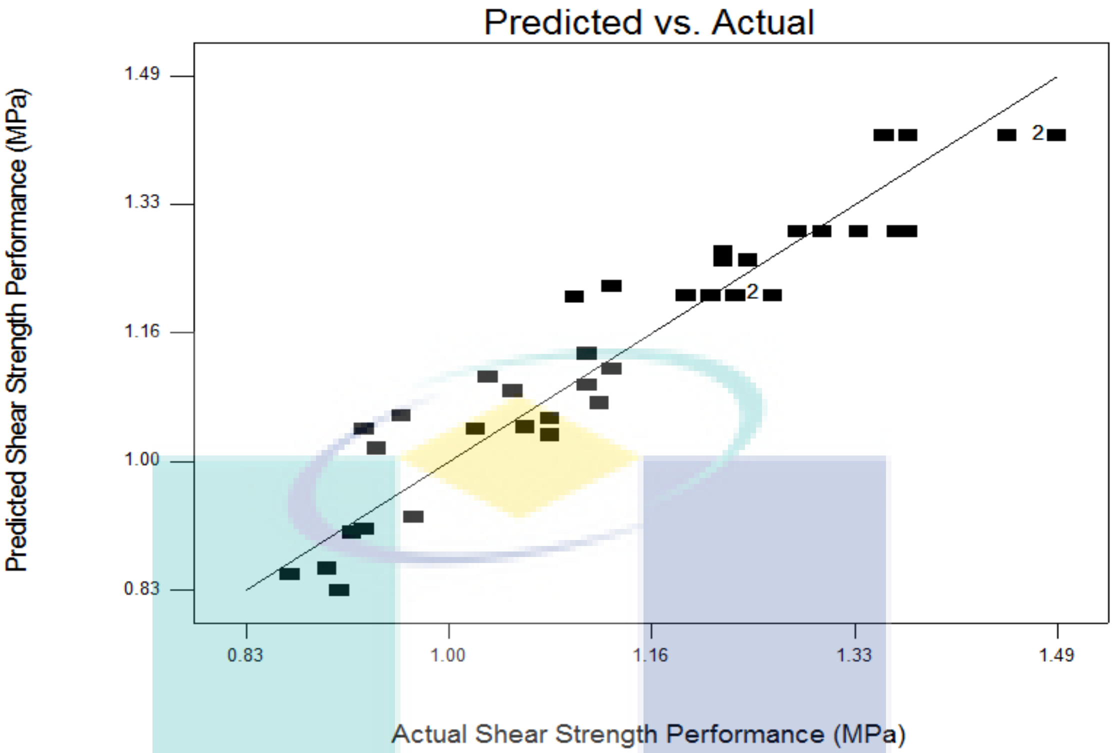

Figure 5.3: Predicted vs experimental Shear Strength Performance (MPa)

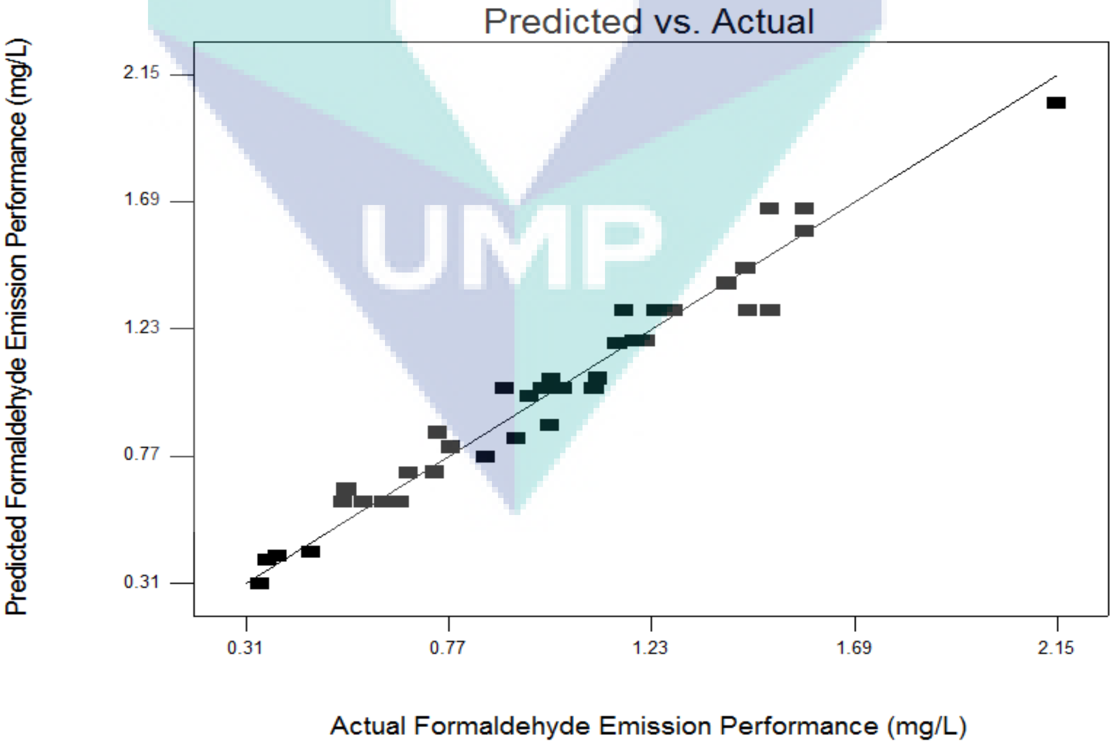

Figure 5.4: Predicted vs experimental Formaldehyde Emission Performance (mg/L)

5.1.3 Shear strength performance

Referring to Table 5.2, different types of fillers showed the largest *F* - value 32.83 among the factors, indicating that this variable imposed the significant effect on the shear strength performance of plywood. The effect of hot press temperature was significant. However, the effect of hot press time on the response was relatively insignificant. The interaction effects between the variables were insignificant. Figures 5.5 to 5.7 shows the three dimensional response surface shows the effects of the hot press temperature, time and different types of fillers on the plywood shear strength performance. The effects of hot press temperature and different types of fillers were studied and they have significant effects on the response. It is shown in figures 5.5 to 5.7, shear strength performance increases with an increase in hot press time and temperature. However, shear strength performance decrease with further increase in hot press time and temperature after the response met the highest value. The response surface in Figures 5.5 to 5.7 shows elliptical contours. These are obtained when there is a perfect interaction between the independent variables (Muralidhar et al., 2001). In this research, all variables studied were found to have synergistic on the shear strength performance in plywood application. The highest shear strength performance value was obtained when both the variables (pressing time and temperature) were at the middle within the range studied.. As shown by the analysis, PKM was shown greater result than IF due to protein content of PKM was higher than IF. The shear stregth value of IF was higher than PS. It indicated that filler with high protein content can enhance shear strength of the wood adhesive. This is due to the amino group $-NH_2$ inside the fillers enhanced the bonding formation between the wood adhesive and surface of veneer (Ong, 2010; Bono et al., 2011). This result obtained were in agreement with the work done by Ong (2010) which reported that amino group $-NH_2$ inside the filler can enhanced the bonding formation between the wood adhesive and wood surface. Therefore, plywood bonded with high protein content had greater shear strength value than plywood bonded with low protein content. Bono et al. (2011) also found that the considerable amount of protein inside PKM can enhance the hydrogen bonding between wood adhesive and wood surface. The protein content of PKM and IF is 20 % and 8 % respectively (Boateng et al., 2008 and Perry, 1944).

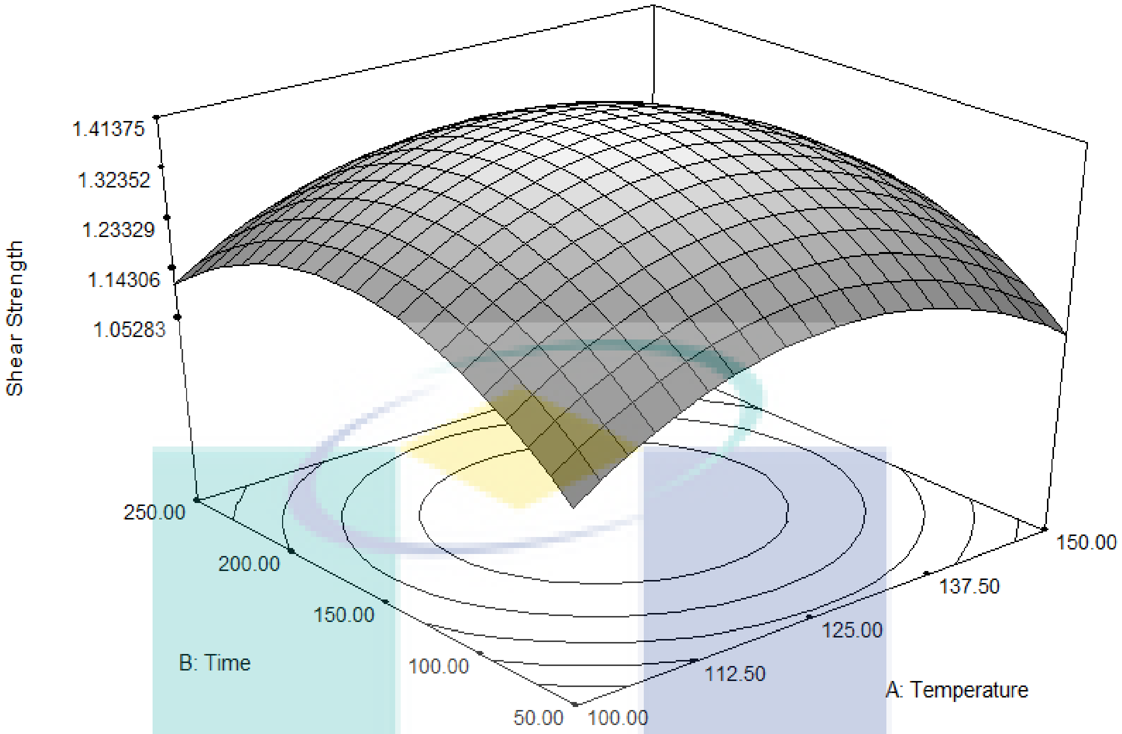

Figure 5.5: Three-dimensional response surface plot of shear strength for PKM as filler

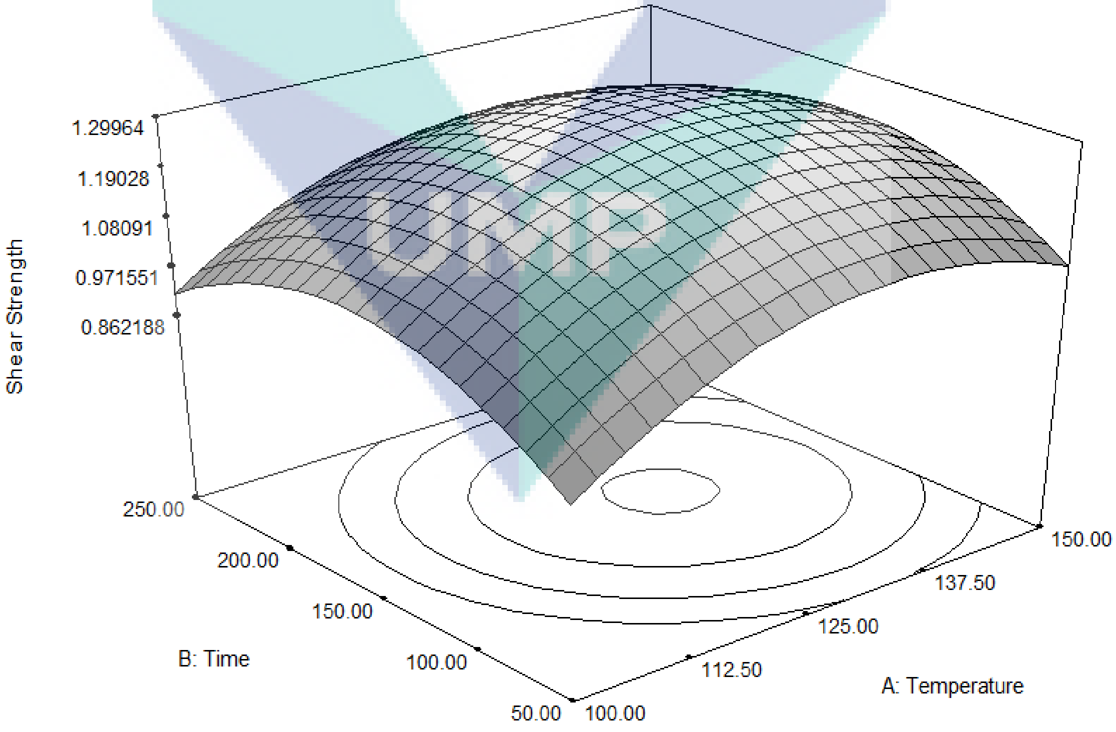

Figure 5.6: Three-dimensional response surface plot of shear strength for IF as filler

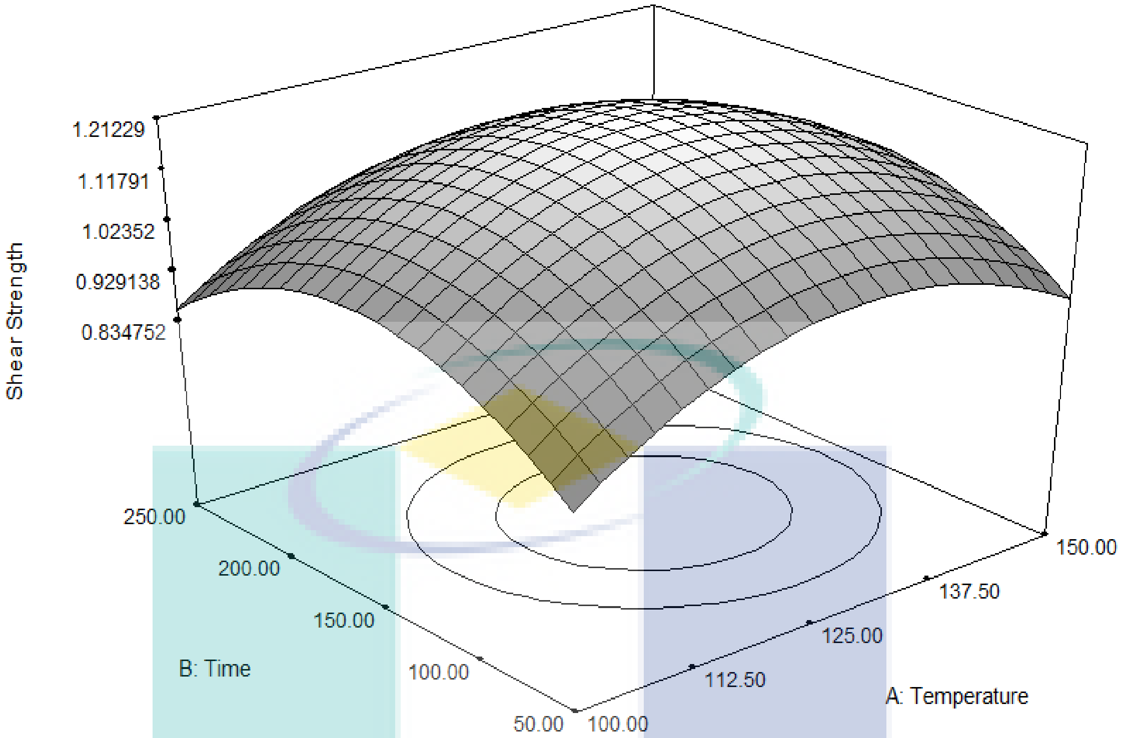

Figure 5.7: Three-dimensional response surface plot of shear strength for PS as filler

5.1.4 Formaldehyde emission performance

In the formaldehyde emission performance (Y_2), different types of filler were found to have the greatest effect on it. The effects of different types of fillers, hot press temperature and time were studied since they found to have significant effects on the response. Figures 5.8 to 5.10 shows the three-dimensional response surface constructed to show the effects of the hot press temperature, time and different types of fillers on the formaldehyde emission performance (Y_2). It was found that to decrease with increasing hot press temperature and time. The lowest response was obtained when hot press temperature and time were at the maximum point within the range of study. Besides that, IF has given lowest formaldehyde emission performance value among the fillers. The results obtained were in agreement with works by Martins et al. (2007). Martins et al. (2007) found that hot press temperature and time played an important role in the formaldehyde emission performance. The increase in hot press temperature at fixed hot press time vice versa will significantly decrease the formaldehyde emission of the wood based panels (Martins et al. 2007). Besides that, effect of different types of fillers was given different result. The filler with higher protein content did not show lower formaldehyde emission than others filler, while IF with less protein content compared to PKM has shown lower formaldehyde emission. This may be due to the nature of PKM because the functional group did not effectively react with free formaldehyde in MUF resin.

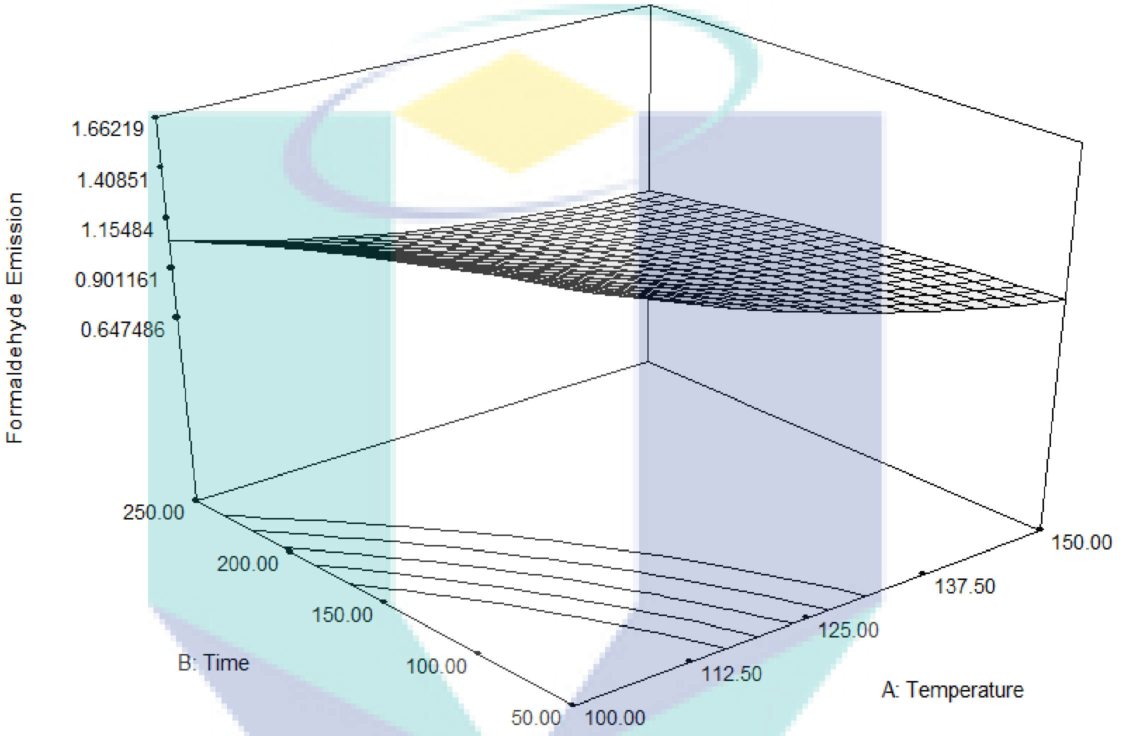

Figure 5.8: Three-dimensional response surface plot of formaldehyde emission for PKM as filler

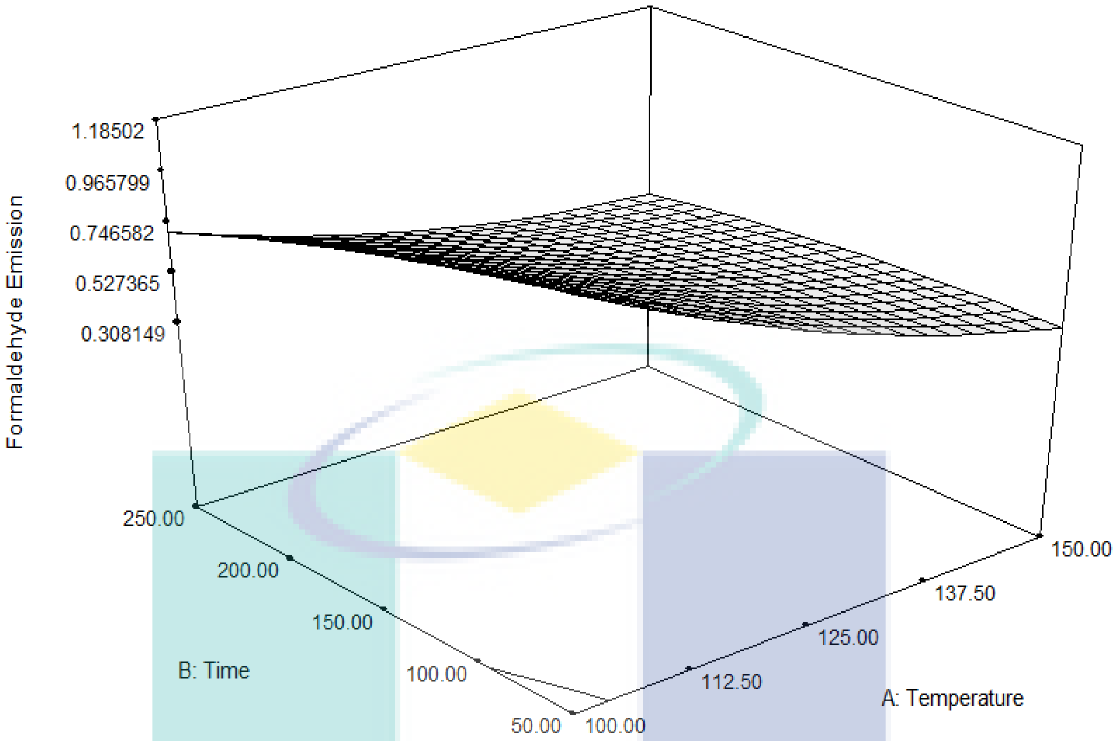

Figure 5.9: Three-dimensional response surface plot of formaldehyde emission for IF as filler

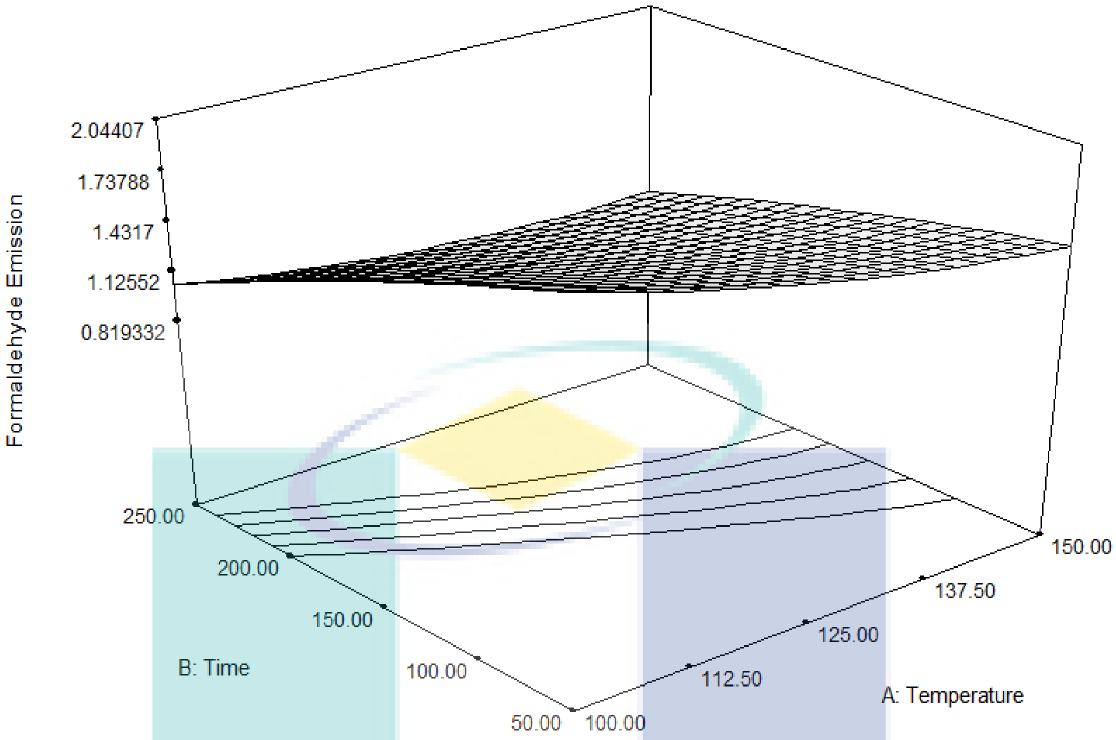

Figure 5.10: Three-dimensional response surface plot of formaldehyde emission for PS as filler

5.1.5 Process optimization

The three level factorial designs has been used to optimize the parameters affecting the shear strength and formaldehyde emission test response. In this optimization analysis, the target criteria were set as maximum and minimum values for shear strength and formaldehyde emission respectively. The optimum processing parameter provided by the model was shown in Table 5.4. The predicted and experimental results of shear strength, and formaldehyde emission obtained at optimum conditions were shown in Table 5.5. The optimum shear strength and formaldehyde emission performance of PKM, IF and PS were 1.41 MPa; 1.30 MPa; 1.21 MPa and 0.9988 mg/L; 0.5345 mg/L; 1.2735 mg/L respectively. In addition, the optimum hot press temperature and time of PKM, IF and PS were 124.9 ℃; 130.9 ℃; 127.9 ℃ and 156 sec; 130 sec; 121 sec respectively. It was observed that the experimental values obtained were in good agreement with the value calculated from the models, with relatively small errors.

Table 5.4: Optimum processing parameter on responses

Temperature, ℃	**Time, sec**	**Fillers**	**Shear Strength, MPa**	**Formaldehyde Emission, mg/L**	**Desirability**
124.9	156	PKM	1.41	0.9988	0.877
130.9	153	IF	1.30	0.5345	0.694
127.9	149	PS	1.21	1.2735	0.552

Table 5.5: Model Validation

Fillers	**Shear Strength Performance (MPa)**			**Formaldehdye emission Performance (mg/L)**		
	Predicted	**Experimental**	**Error (%)**	**Predicted**	**Experimental**	**Error (%)**
PKM	1.41	1.36	3.55	0.9988	0.9613	3.75
IF	1.30	1.26	3.08	0.5345	0.5176	3.15
PS	1.21	1.17	3.30	1.2735	1.2345	3.06

CHAPTER 6

RESULT AND DISCUSSION

This chapter will discuss the physico-chemical interaction between the adhesive and wood surface. Scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), light microscopy (LM) and Fourier transform infrared spectroscopy (FTIR) techniques were used. The results are discussed in section 6.1.1, 6.1.2, 6.1.3 and 6.1.4 respectively.

6.1 Physico-chemical Interaction

6.1.1 Scanning electron microscopy (SEM)

The morphological analysis of PKM and plywood were carried out by using scanning electron microscopy (SEM). The SEM of PKM particle is shown in Figure 6.1. It can be seen that, the distribution of the particle is highly heterogeneous with different particle size and irregular shape. The diameter of PKM particle was presented in the range of 10 to 55 µm. One of the mechanisms is mechanical interlocking of the binding between resin, PKM and wood. In order to demonstrate the mechanism, sample with wood powder and PKM was prepared. From Figure 6.2, PKM particle (red circle) was attached on the wood particle which means binding between PKM and wood particle is possible. However, there is no confirmation of PKM able to penetrate into wood. Therefore, plywood pieces compound with resin was prepared for further investigation.

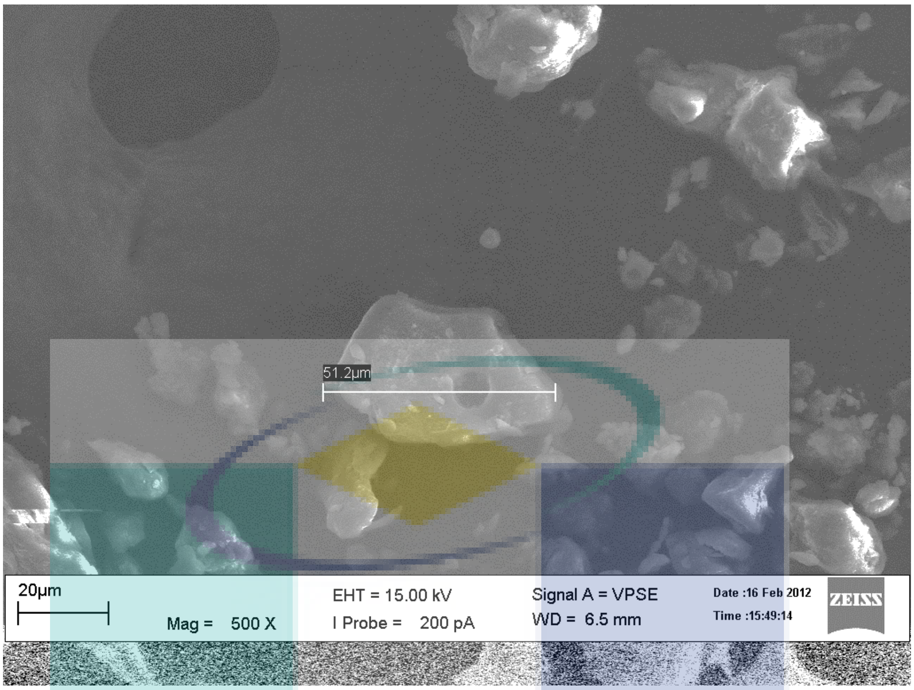

Figure 6.1: Scanning electron micrograph (500x) of PKM.

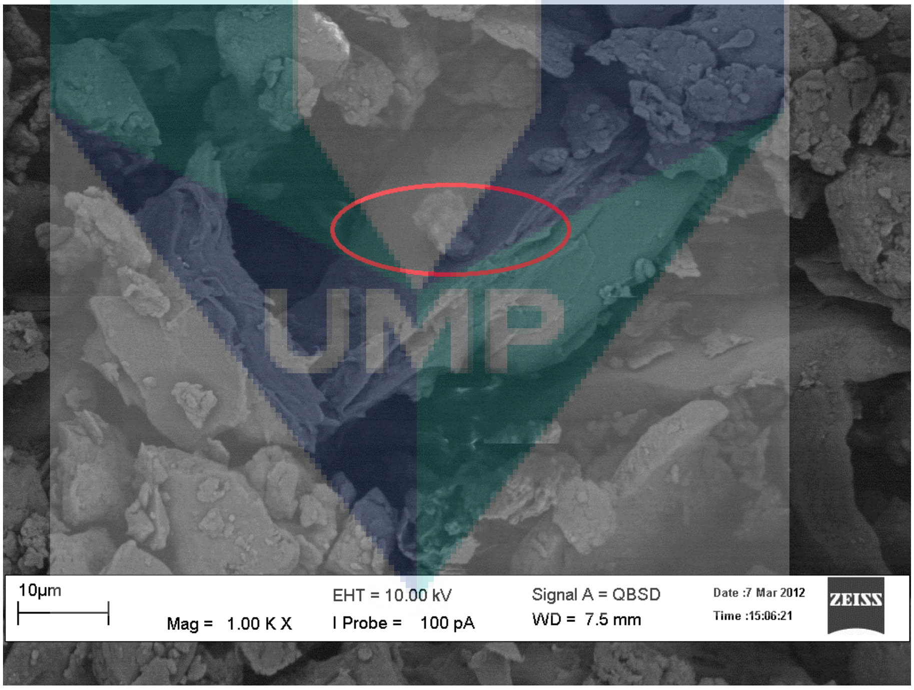

Figure 6.2: Scanning electron micrograph (1000x) of PKM and wood blend.

As mention in chapter 4, the samples of plywood were prepared with different PKM concentration (0% to 23%), the shear strength and formaldehyde emission results were presented in Figure 4.6 and 4.7. Therefore in this section, the SEM samples was also prepared with different concentration of PKM (0% to 18%) and presented in Figure 6.3 to 6.7. Figure 6.3 shows the sample without PKM with having only MUF resin was prepared after hot press under 125 ℃ and 150 sec. The resin and wood layer was observed (red circle) from the SEM micrograph. Figure 6.4 and 6.5 shows the sample compound with 3% and 8% PKM respectively, the PKM particle (white arrow) was observed in the micrographs. However, the adhesive and wood layer was difficult to distinguish in the micrographs. Adhesive layer (red circle) and particle (white arrow) were observed from the SEM micrograph which shown in Figure 6.6. In Figure 6.7, adhesive and wood layer (red circle) was observed. From SEM micrograph, the interface between wood and adhesive is more visible, therefore the mechanical interlocking is possible. Furthermore from the micrograph, micro-fracture of wood (white circle) was observed. This is due to excess usage of PKM cause the system become highly heterogeneous, therefore different thickness of adhesive layer was observed. Moreover, some vacant space (white arrow) was detected in the micrograph. From Figure 6.3 to 6.7, the SEM micrographs were shown the interface between wood and resin layer. Besides that, the PKM particle also observed. However, the information of mechanical interlocking between resin, PKM and wood was no shown in the SEM micrographs. In order to further understanding the penetration of adhesive into wood cells and mechanical interlocking between PKM particle, resin and wood, the sample with 13% PKM was selected and analyses using field emission scanning electron microscopy (FESEM) in the next section.

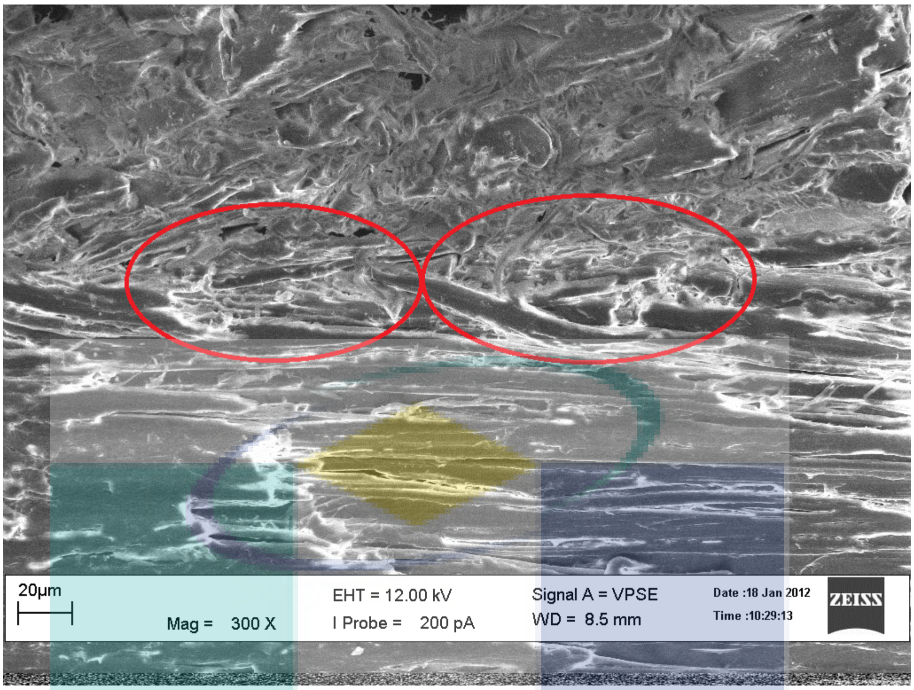

Figure 6.3: Scanning electron micrograph (300x) of plywood compound with 0% of PKM.

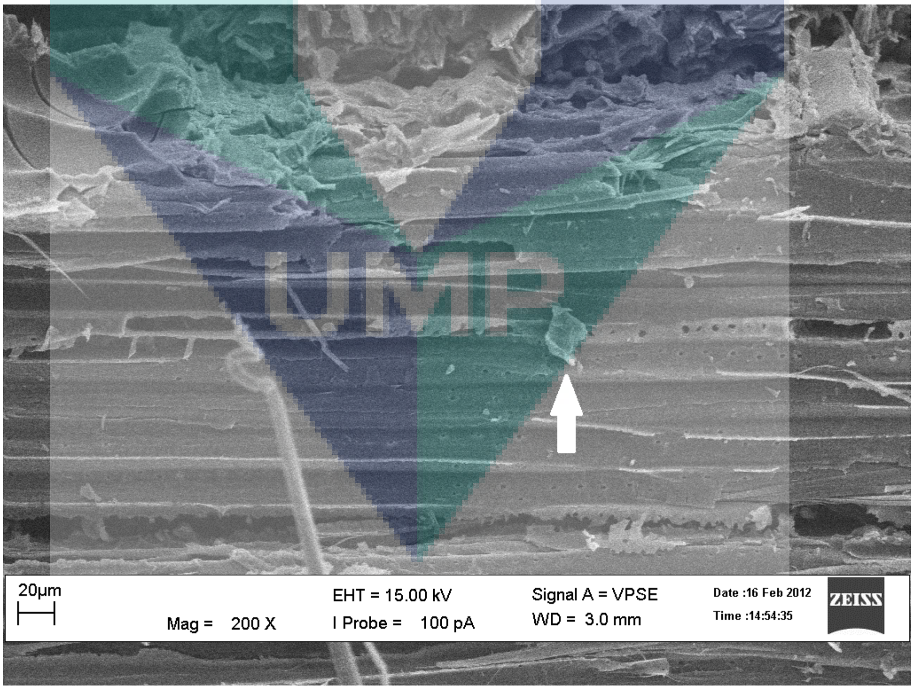

Figure 6.4: Scanning electron micrograph (200x) of plywood compound with 3% of PKM.

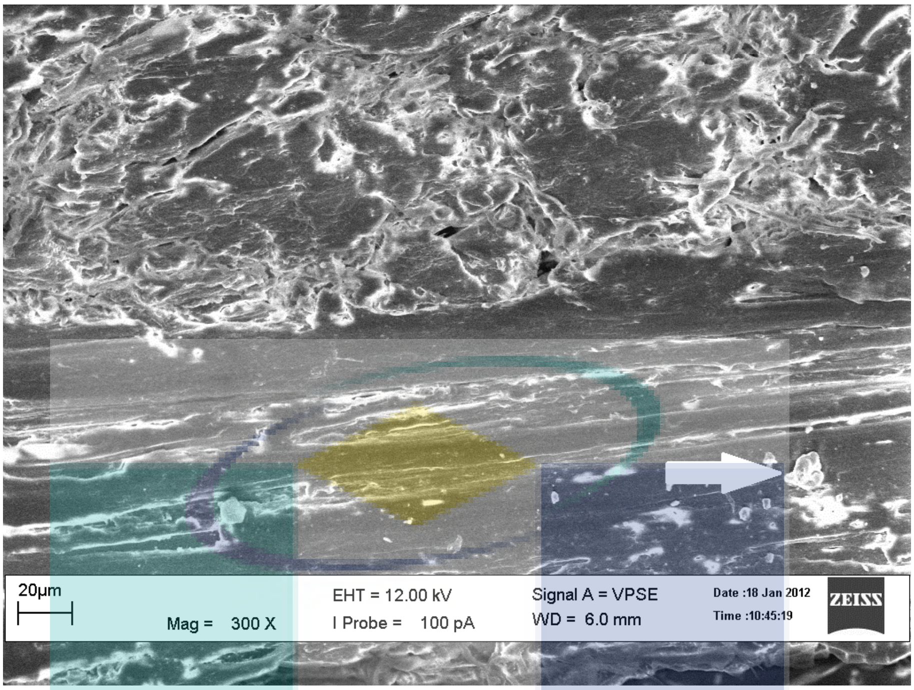

Figure 6.5: Scanning electron micrograph (300x) of plywood compound with 8% of PKM.

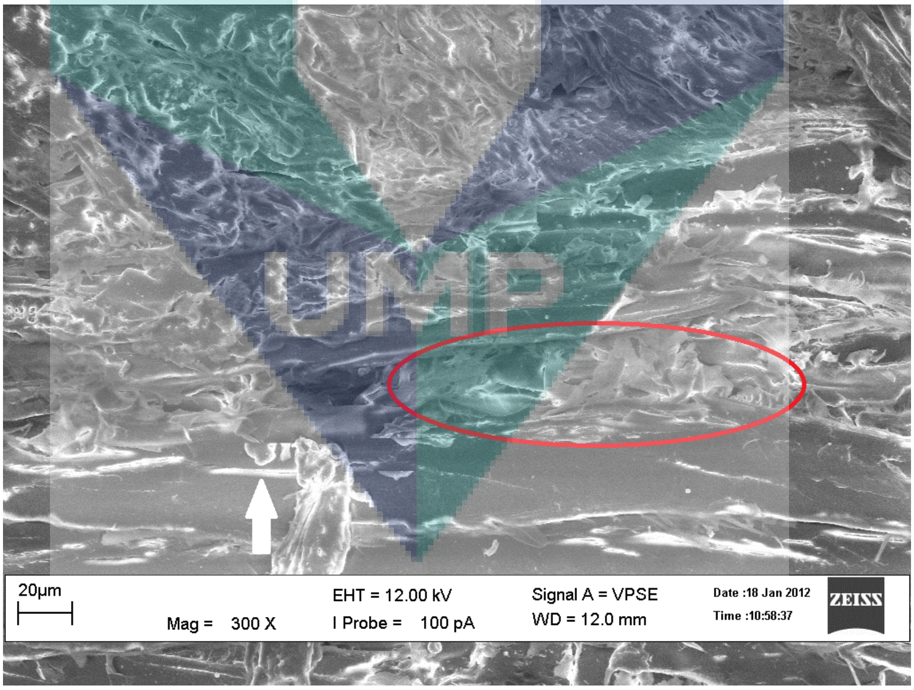

Figure 6.6: Scanning electron micrograph (300x) of plywood compound with 13% of PKM.

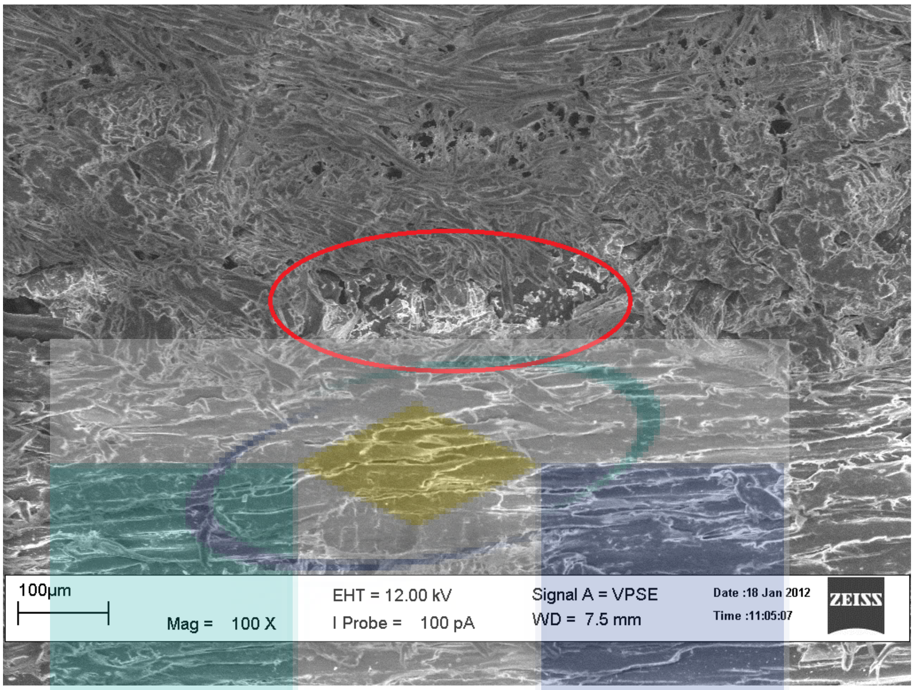

Figure 6.7: Scanning electron micrograph (300x) of plywood compound with 18% of PKM.

Furthermore, fracture of the wood has study and shows at Figure 6.8 and 6.9. It shows that, the breakthrough was at the wood surface. The adhesive and wood interface was not disturbed by the shear strength break up. From the Figure, it shows that part of the wood was attached to the resin surface, which indicates that wood and resin is in good interaction. FTIR analysis was conducted to further understanding the blend samples (MUF, PKM and wood powder) in section 6.1.4.

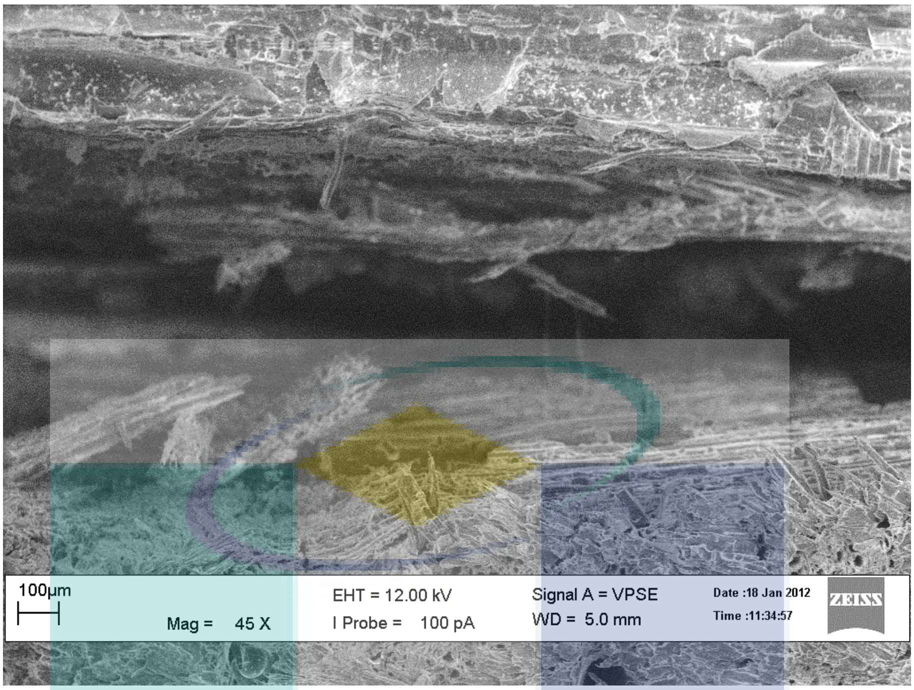

Figure 6.8: Scanning electron micrograph (45x) of plywood fracture surface with 13% of PKM content.

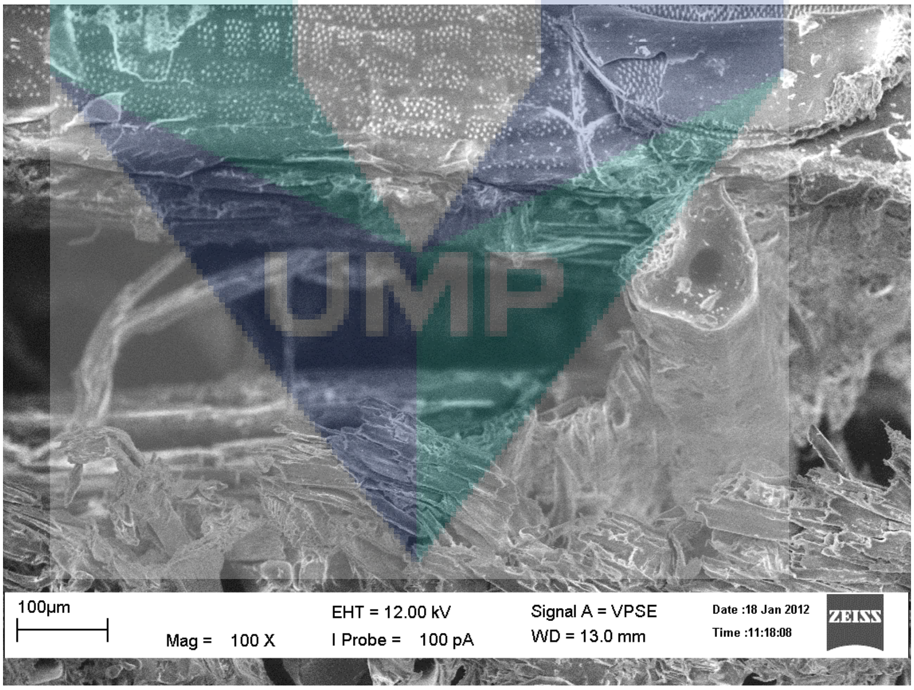

Figure 6.9: Scanning electron micrograph (100x) of plywood fracture surface with 13% of PKM content.

6.1.2 Field Emission Scanning electron microscopy (FESEM)

In order to further investigate the mechanical interlocking, FESEM technique has been occupied. FESEM provided high definition of wood-adhesive interface, made possible by the high resolution capability of this instrument and enhancement of differentiation between the adhesive and wood cell walls. Figure 6.10 and 6.11 shows the sample prepared with 13% PKM after hot press under 125 ℃ and 150 sec. In comparison to the poor differentiation between wood and adhesive layer when imaged with SEM, excellent differentiation between wood and adhesive layer was achieved. The adhesive distribution within wood tissues was clearly visualized, as shown in Figures 6.10 and 6.11. In Figure 6.10, a low magnification FESEM image, the pathway of adhesive penetration (white arrow) into the wood tissues of plywood is clearly visible. The adhesive is present within the lumens of tracheids and also in the tissue regions containing cracks. The adhesive distribution within wood tissues is observable in the high resolution image shown in Figure 6.11, which is a high magnification view of a region of the wood-adhesive interface (white arrow) in Figure 6.10. The presence of adhesive is detectable even in small dimension wood tissue. The results obtained were in agreement with Singh et al. (2008) which reported that, FESEM able to visualize the adhesive distribution within wood tissues. Besides that, adhesive penetration into damaged surface tissues of wood was clearly visualized. Other than that, De Meijer et al. (1998) found that high solid alkyd (HSA) binder and solvent borne alkyd (SBA) were able penetrate into the pine and meranti wood cells (lumens of rays and tracheid).The conclusion of this section is FESEM can successfully differentiating the wood and adhesive layer. It was observed that the adhesive distribution within the wood tissues therefore, the penetration of the adhesive into the wood is possible. However, the presence of PKM particle inside the wood cells was not detected in Figure 6.10 and 6.11. In order to further understanding the mechanical interlocking and presence of PKM particle inside the wood tissue, light microscopy (LM) was chosen to analyses the sample blend with PKM from concentration 0% to 23%.

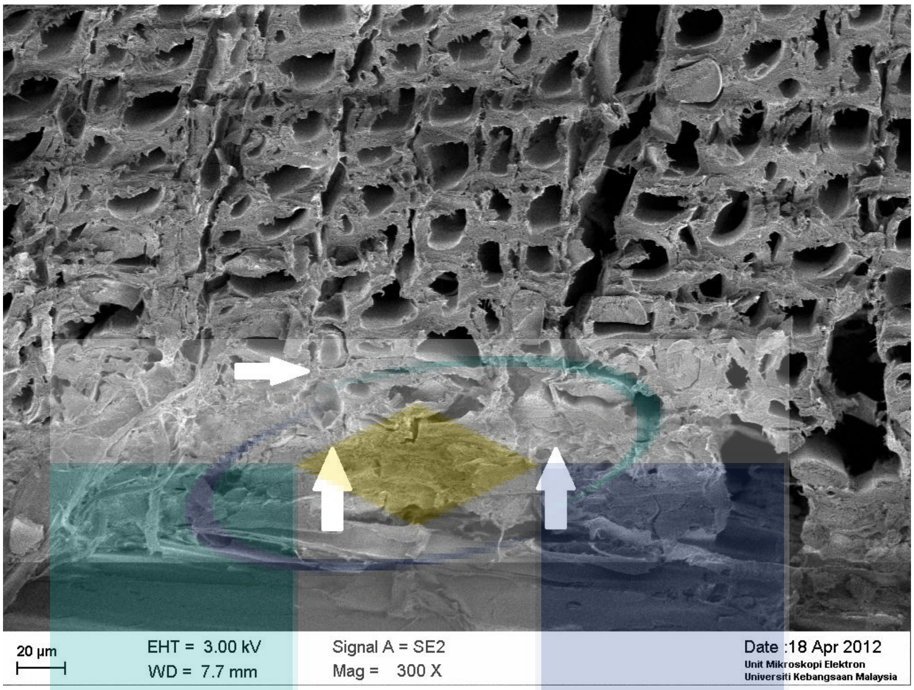

Figure 6.10: Field emission scanning electron micrograph (300x) of plywood compound with 13% of PKM.

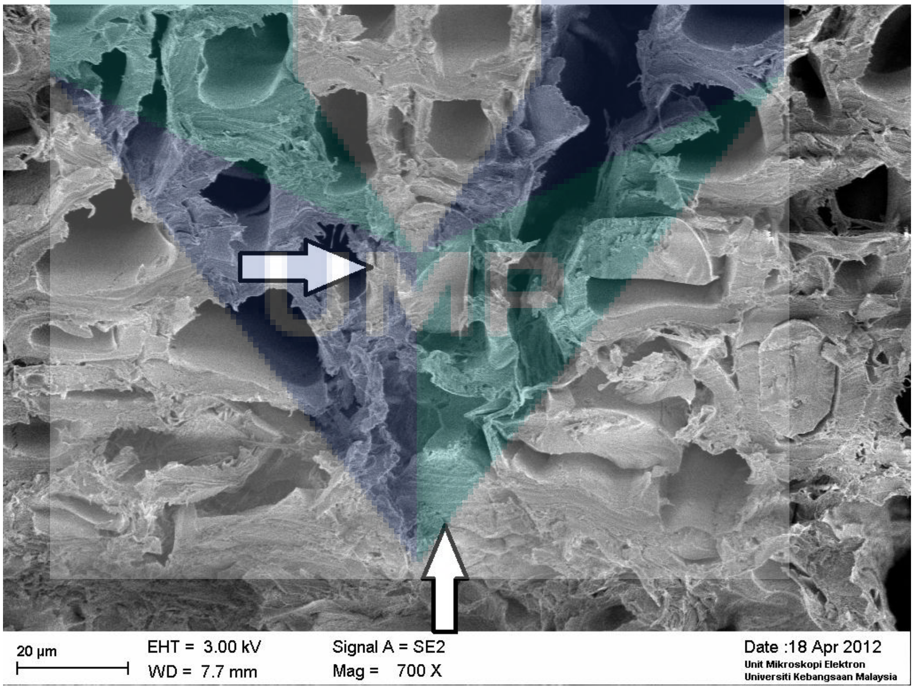

Figure 6.11: Field emission scanning electron micrograph (700x) of plywood compound with 13% of PKM.

6.1.3 Light microscopy (LM)

The use of LM is very rare in investigate the wood and resin layer. Singh et al. (2008) was used LM to identify the wood and resin interface. In our case, PKM particle was clearly seen in the micrograph. In LM the toluidine blue stain, which imparts a bluish red colour to the wood cell walls can differentiate the wood cells from MUF adhesive. The LM samples were prepared with PKM concentration from 0% to 23% after hot press under 125 ℃ and 150 sec, the micrograph were presented in Figure 6.12 to 6.17. In comparison with FESEM, excellent differentiation between wood and adhesive layer was achieved with LM images provided different colour for wood and adhesive layer. The adhesive distribution within the wood tissues was clearly visualized, as shown from Figures 6.12 to 6.17. In Figure 6.12, penetration of MUF resin into lumens of rays was observed (white arrow) and penetrated over deeply into the wood cells (white arrow). This might due to low viscosity of the sample which prepared without PKM. Qiao et al. (1999) also found that, the adhesive with low viscosity will penetrate too deep into the wood pores while a very little amount of adhesive was left on the surface to adhere the wood. Xie et al. (2006) also found that, solvent-borne alkyd (Novayech 006) able to penetrate into wood cells of earlywood and latewood. Besides that, De Meijer et al. (1998) found that HSA binder and SBA were able penetrate into the pine and meranti wood cells (lumens of rays and tracheid). Buckley et al (2002) reported that, pMDI was able to penetrate into the wood cell lumens and pits. However, pMDI resins were not to able penetrating into the smaller parenchyma and tracheid cells. Gruver and Brown (2006) were indicated that, penetration of pMDI resin was observed and detected in the vessel and lumens area. Kim et al. (2007) reported that, glue line was observed between the veneers. They also found that, the voids in wood near the glue line were filled with adhesive.

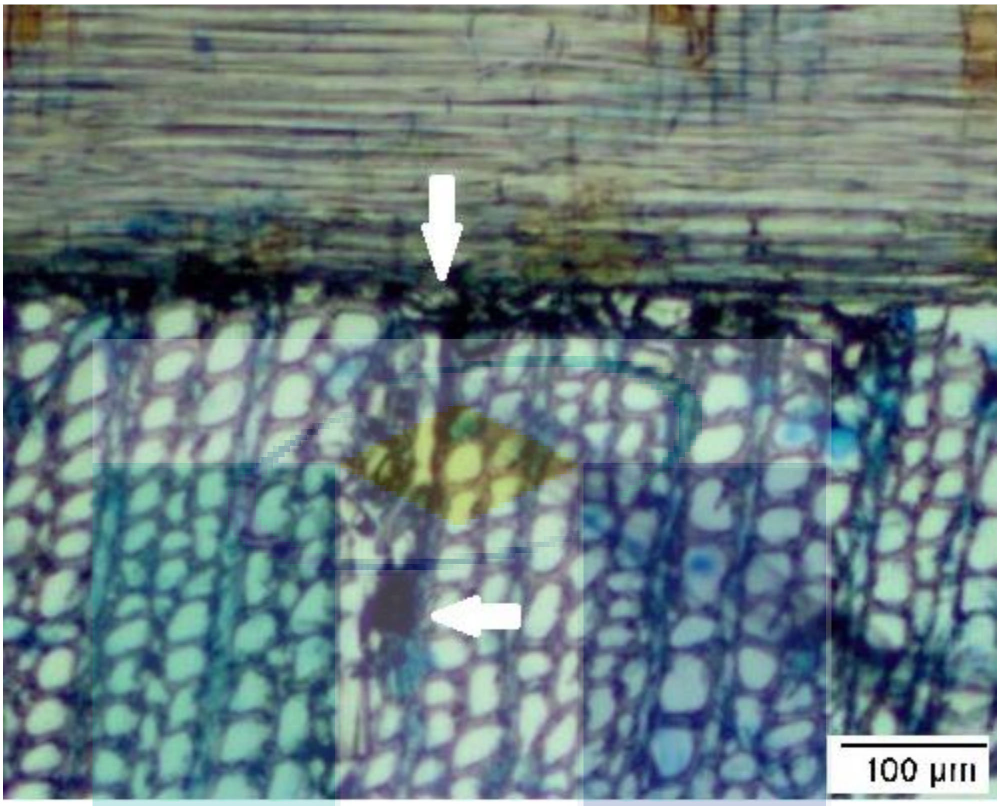

Figure 6.12: Light micrograph (100 µm) of plywood compound with 0% of PKM.

From Figure 6.13 to 6.17, penetration of MUF adhesive into the wood tissues was observed (white arrow). Besides that, the presence of PKM particle insides the axial tracheid was detected (black arrow) in LM micrograph shown in Figure 6.13 to 6.17. Moreover, the PKM particle increased as the concentration of PKM increased. In comparison to the over penetration of MUF resin into the wood cells which shown in Figure 6.12, excellent mechanical interlocking was achieved when presence of PKM particle inside the wood cells. The resin remain on the wood surface was more compared to Figure 6.12. Therefore, the interlocking effect and efficiency of resin contact with wood were increases.

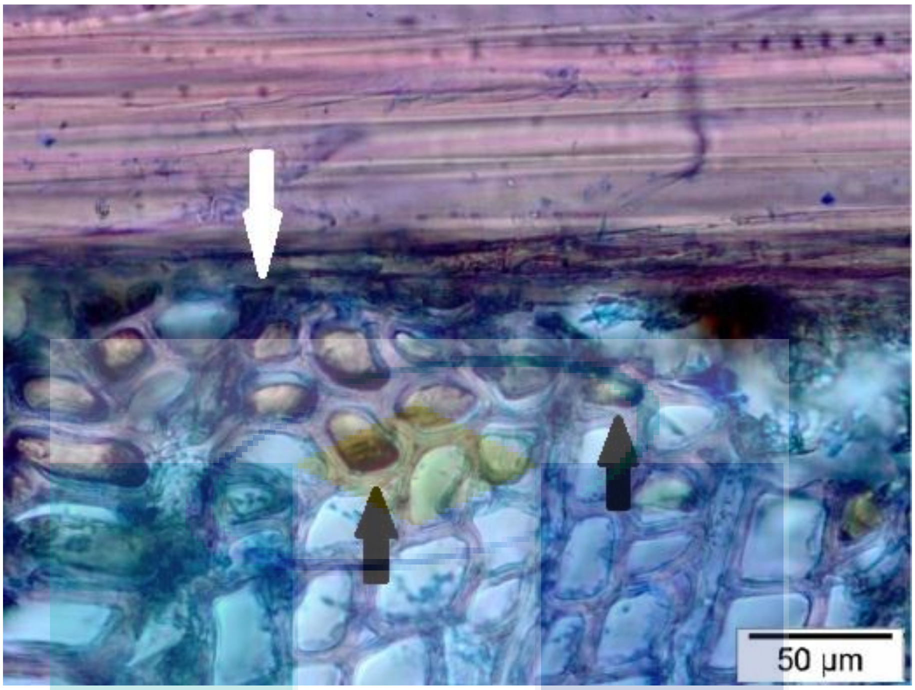

Figure 6.13: Light micrograph (50 μm) of plywood compound with 3% of PKM.

In Figure 6.14 and 6.15, similar evidence was shown as Figure 6.13, but the thickness of the resin leave on the wood surface was thicker than Figure 6.13. Therefore, the efficiency contact between wood and resin is greater than Figure 6.13. As can be seen that, PKM concentration increase, the effect of interlocking was better, therefore, more bonding formation was the presence between adhesive and wood. The bonding formation will further discuss in section 6.1.4.

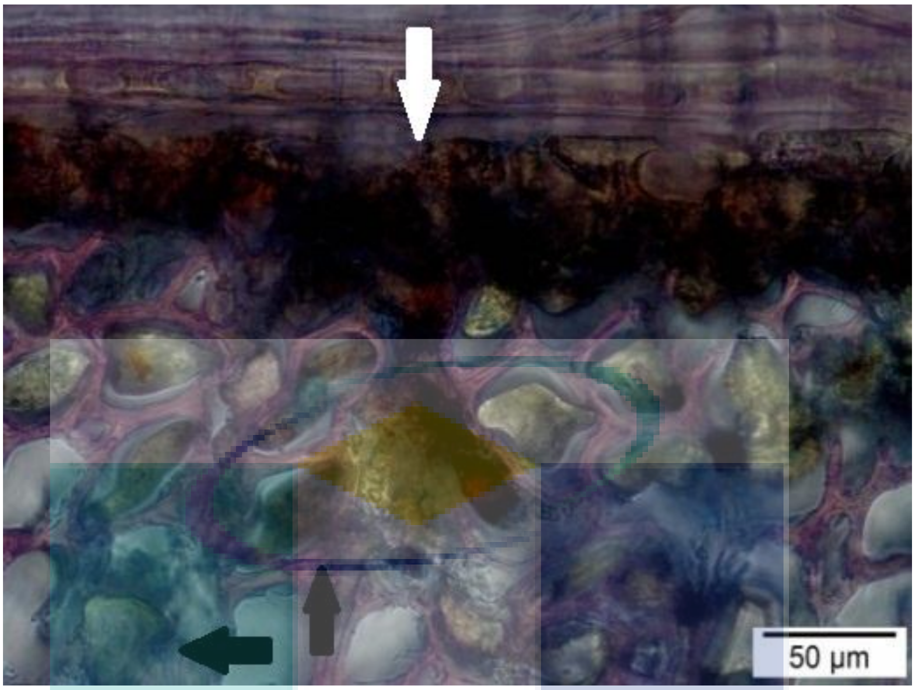

Figure 6.14: Light micrograph (50 µm) of plywood compound with 8% of PKM.

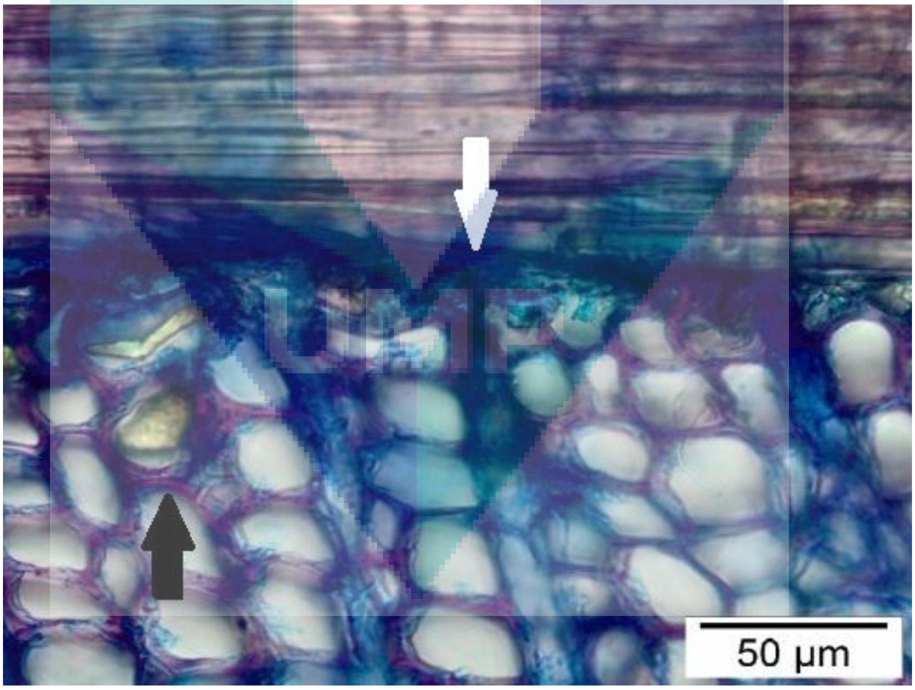

Figure 6.15: Light micrograph (50 µm) of plywood compound with 13% of PKM.

In Figure 6.16, wood surface crack was observed (red circle mark) because the excess of PKM usage causes the system become highly heterogeneous. The high viscous adhesive leaves maximum amount of resin on the surface with little penetration into the wood pores which leads to weak mechanical interlocking and as a result the efficiency of contact area between wood and adhesive decreases. The thick glue layer leads to weak adhesive strength. Qiao et al. (1999) found that, weak adhesive strength occurred when the adhesive viscosity is high. These leaves maximum amount of resin on the wood surface, the effect of interlocking and efficiency contact area between wood adhesive also reduced. In Figure 6.17, the non-uniform adhesive distribution on the wood surface was observed (red circle mark). This due to the highly density of the adhesive cause the uniformly adhesive dispersion on the wood surface cannot be done. Besides that, Singh et al. (2008) also found that, adhesive able to penetrate into the lumens rays and axial tracheids by using LM. It's indicated that, adhesive able penetrated into tracheid up to four cells deep from the glue line.

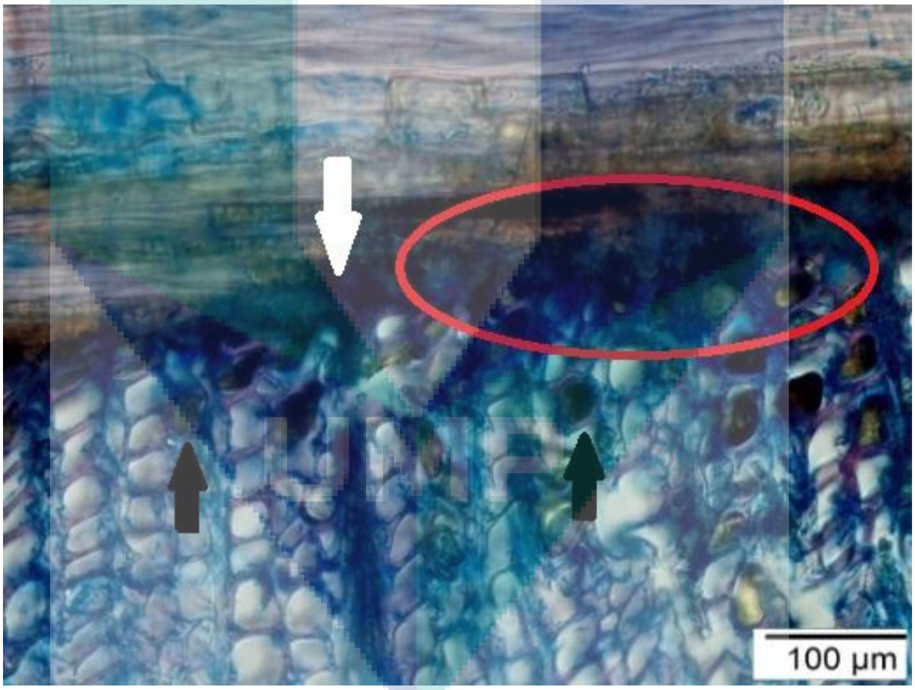

Figure 6.16: Light micrograph (100 µm) of plywood compound with 18% of PKM.

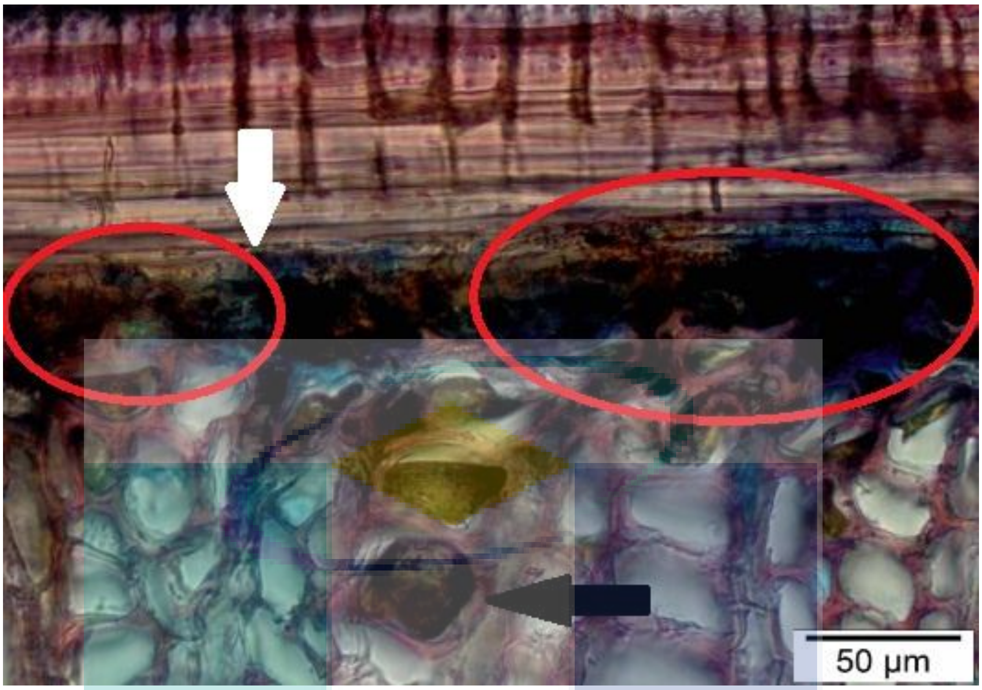

Figure 6.17: Light micrograph (50 µm) of plywood compound with 23% of PKM.

Referring to section 4.4, the plywood samples were prepared with PKM concentration from 0 % to 23 % and subjected to shear strength and formaldehyde test. The shear strength result was significantly increased from 0 % to 13 % and further increase PKM concentration, the shear strength value was markedly decreased (Figure 4.6). From the micrograph shows in Figure 6.12 to 6.15, the thickness of the resin remain on the wood surface was increased; therefore the contact efficiency between wood and resin was improved. Moreover, the PKM detected inside the tracheid also increased as the concentration increase from 0 % to 13 %. The PKM particle was locked the tracheid to prevent resin penetrated deeply into the wood system and sufficient resin was remains on the wood surface to participate in bonding formation with wood. Therefore, the shear strength value was increase from 0 % to 13 %. The micrograph shows in Figure 6.16, the excess usage of PKM causes the system become highly heterogeneous. Wood crack was observed in micrograph, which weaken the bonding formation between wood and resin. Therefore, the shear strength value was decrease after 13 %. In Figure 4.7, the formaldehyde emission value was decrease from 0 % to 18 % as the PKM concentration increased and further increase PKM concentration, the formaldehyde emission was increased. In Figure 6.12 to 6.16 shows that, the efficiency of mechanical interlocking was improved, as the PKM concentration increases. As mention before, the PKM concentration increase, more PKM particles was detected inside the tracheid. Therefore, the free formaldehyde in adhesive could react with hydroxyl and amino groups of protein molecule during the hot press process (Gao et al., 2012). Therefore, the formaldehyde emission value was decrease from 0 % to 18 % (Figure 4.7). The results obtained in Figure 4.7 were in agreement with the work of Ozalp (2011), which reported that the formaldehyde emission of plywood bonded with UF decreased as the filler concentration increased. However, the non-uniform adhesive distribution on the wood surface was observed in Figure 6.17, which lead to some area was weak in binding. Therefore, the free formaldehyde was free to release from the plywood. Therefore, the formaldehyde emission was increase after 18 % (Figure 4.7).

6.1.4 Fourier transform infrared spectroscopy (FTIR)

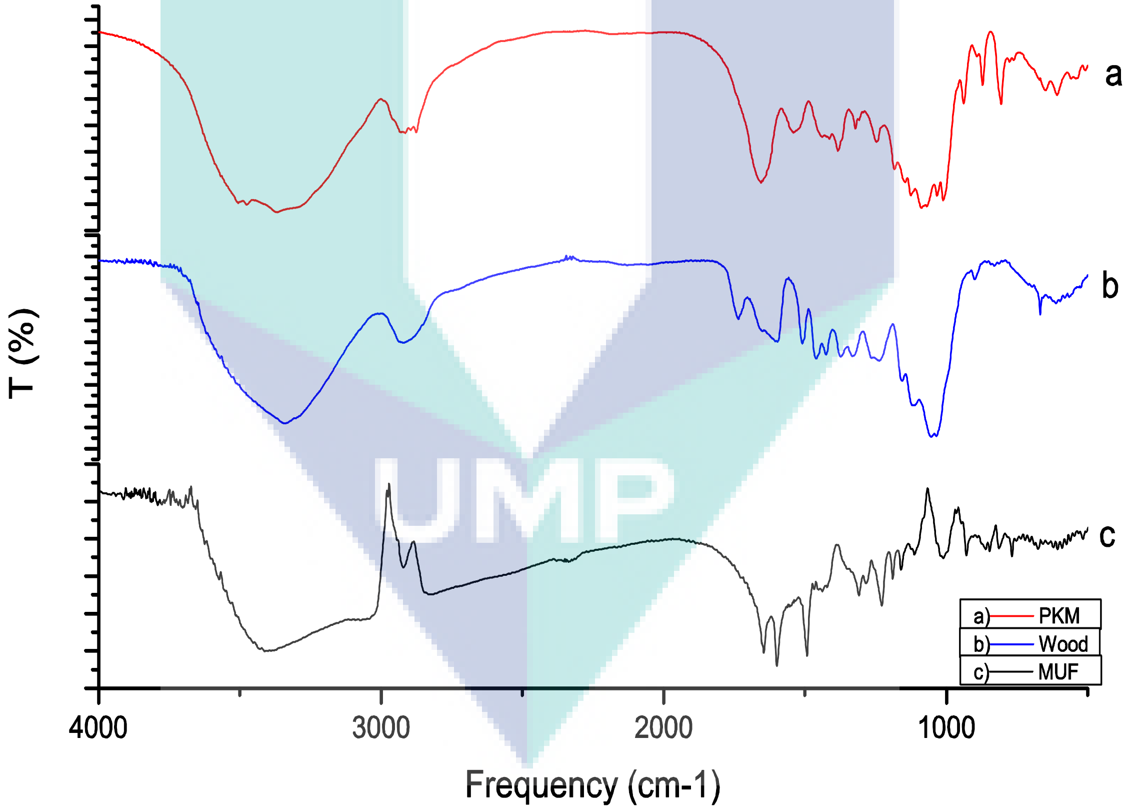

Figure 6.18: FTIR spectra of PKM, Wood and MUF after heat treatment at 150 ^{o}C and 250 sec

The FTIR spectra of PKM, Wood and MUF are shown in Figure 6.18. As shown in Figure 6.18, the spectra demonstrate a number of absorption peaks, representing the multipart nature of the substance examined. The FTIR spectrum analysis provided that broad bands at 3500-3300 cm^{-1}, correspond to the hydrogen bonded O-H and N-H groups (Kim and Kim, 2006 and Uddin et al., 2009). However, in PKM the individual peaks for O-H and N-H are visible but in other components such individuality is absent and this may be due to the different degree of hydrogen bonding or it show as an overlapped shape peaks. This phenomenon reveals that a new pattern of hydrogen bonding formation results from the competition between amine–amine, hydroxyl-hydroxyl, hydroxyl-carbonyl and amine–carbonyl interactions (Kim and Kim, 2006). The bands observed at 2930–2915 cm^{-1} is assigned for stretching frequency of C-H stretching (Minamisawa et al., 2004) of cellulose, hemicellulose, mannose and lignin moieties of the components. The band observed at 1740-1640 cm^{-1} is assigned for stretching frequency of different types of carbonyl (C=O) groups (Minamisawa et al., 2004), as revealed by the peaks at 1655 cm^{-1}, 1740 cm^{-1} and 1647 cm^{-1} are for carboxylic acid, aldehyde and amide respectively in the particular components. In particular, it is seen that in MUF, the characteristic peak observed at the frequency of 1600 cm^{-1} (calculative value according to Hook's Law for C=N stretching frequency) (Pavia et al., 2001). Whereas, such peak is absent in both PKM and Wood sample. The peak observed at 1543-1498 cm^{-1} corresponds to the NH_2 scissoring vibrations (Soto et al., 2005 and Uddin et al., 2009) and which may come from the amino acid moiety of PKM, protein part of wood and amide faction of MUF. However, the N-H wagging peak in the 700–750 cm^{-1} range could not be recognized and the N-H stretch peak in the 3200–3300 cm-1 range overlapped with the O-H peak in the range 3200–3500 cm^{-1} (Soto et al., 2005). The peaks at 1088-1015 cm^{-1} are attributed due to the C-O stretching vibrations (Malkoc and Nuhoglu, 2006).

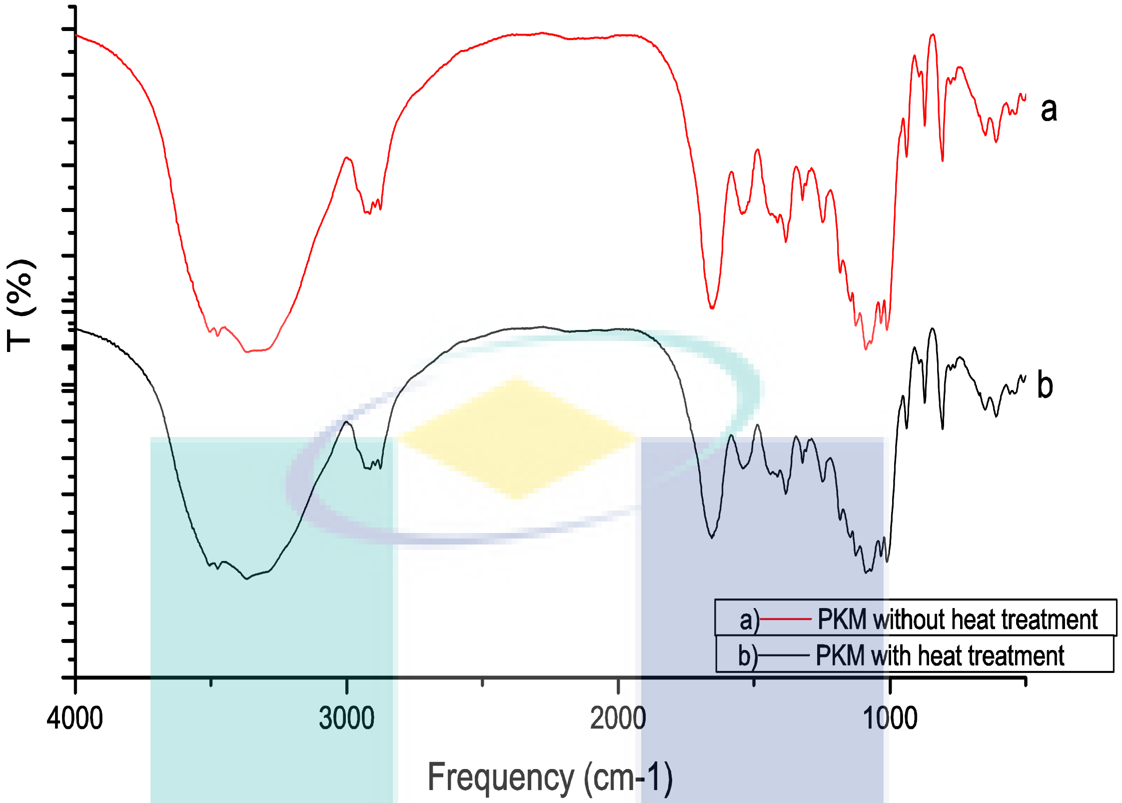

Figure 6.19: FTIR spectra of PKM without and with heat treatment

The effect of heat treatment on the PKM is studied, and the FTIR spectra of PKM with heat treatment and untreated are shown in Figure 6.19. As shown in Figure 6.19, the spectra exhibits a number of absorption peaks, indicating the complex nature of the materials examined. The FTIR spectrum analysis clarifies the broad bands at 3476-3365 cm^{-1}, representing the hydrogen bonded O-H and N-H groups. Figure 6.19, two spectra's are alike without some exceptions. These are observed after the heat treatment, where the peaks for stretching vibration of C=O and N-H groups are shifted from 1650 cm^{-1} and 3365 cm^{-1} to 1655 cm^{-1} and 3369 cm^{-1} respectively. As a result, certain amount of blue shift or increasing of frequency observed. It is possible due to the heat treatment. The weak hydrogen bonding interactions between the N-H and C=O groups may be diminished. Therefore, both groups in the treated sample experienced freer environment than that of the untreated sample.

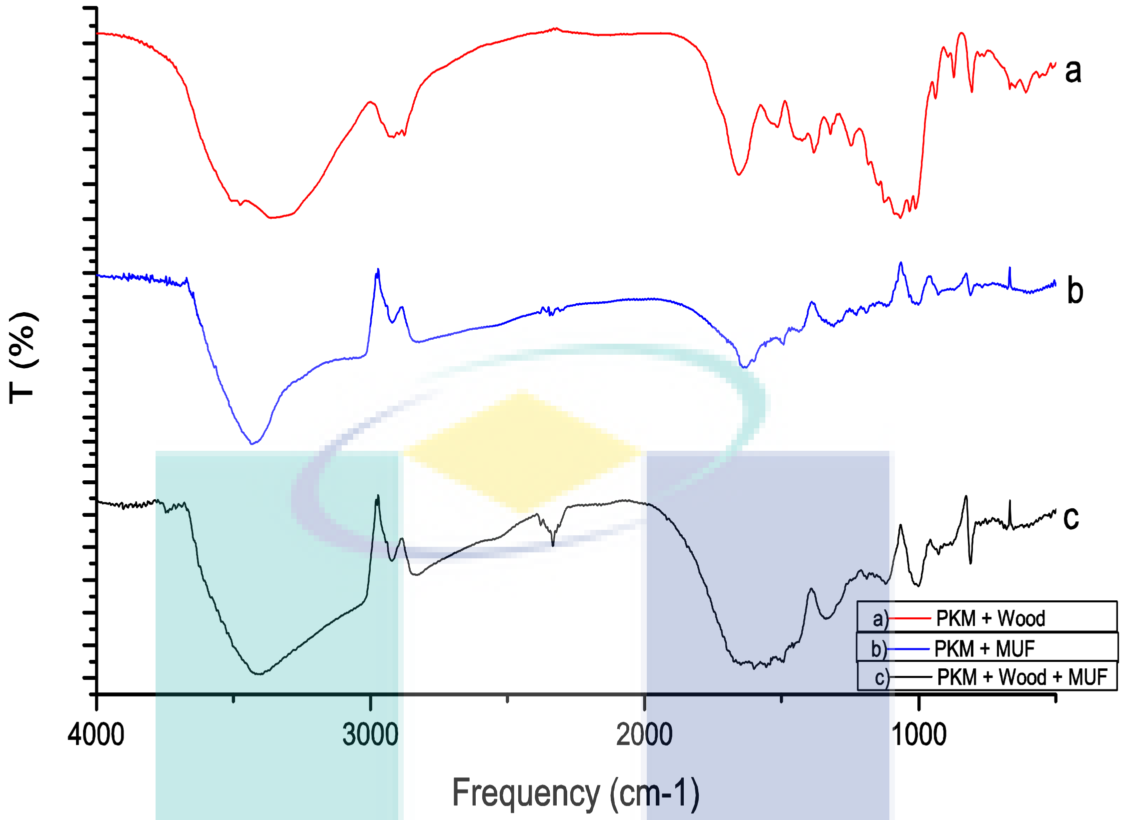

Figure 6.20: FTIR spectra of PKM+Wood, PKM+MUF and PKM+Wood+MUF

The FTIR spectra of three blends consisting of PKM, wood and MUF is shown in Figure 6.20. As shown in Figure 6.20 the spectra exhibits a number of absorption peaks, indicating the complex nature of materials with the existence of some interactions. Notably, it was mentioned that the O-H and N-H groups of wood are experiencing higher degree of hydrogen bonding; however, the N-H group of PKM is relatively free. On the other hand, the aldehydic C=O group of wood is more reactive compare to the other C=O containing functional groups. Moreover, from spectra of 6.18b and 6.20a, it is observed that after blend formation, the stretching vibration of C=O(for wood) and N-H (for PKM) groups are shifted from 1740 cm^{-1} and 3369 cm^{-1} to 1653 cm^{-1} and 3363 cm^{-1}, respectively. Therefore, a significant amount of red shift observed for both groups. In addition, this explanation also coincides with the characteristic absorption frequency of NH_2 scissoring vibrations. For example, from PKM to blend the scissoring vibration of NH_2 shifted from 1543 cm^{-1} to 1518 cm^{-1}, that is another red shift takes place but this trend not observed for wood to blend. Furthermore, in Figure 6.18a the absorption frequency of C=O group showed a broad band compare to its components, which is also indicating the existence of interactions. Therefore, considering the Figures 6.18a, 6.18b and 6.20a, it is possible to summarized that in this PKM-Wood blend, the existing interactions are involved between the N-H group of PKM and C=O group of wood. In this case, no characteristic peak is observed at the frequency of 1600 cm^{-1} for C=N stretching, which suggests that the condensation reaction between NH_2 and C=O, is not confirmed through FTIR analysis. Whilst, from the shown spectrum 6.20b it is clear that after blend formation, the stretching vibration of C=O (for PKM) group is shifted from 1655 cm^{-1} to 1651 cm^{-1}. Therefore, a remarkable amount of red shift observed for C=O groups. For instance, in MUF, the C=O group experienced some extent of resonance effect because it is flanked by two NH groups like this way –HN-CO-NH-. However, we belief that the C=O group in PKM comes from the xylene moiety, where the –COOH group residing in axial position with lesser stability. As a result, more reactive C=O group of PKM may involve in an interaction with the N-H of MUF with a greater degree. Summarizing the Figures 6.18a, 6.18c and 6.20b, it is possible to say that in this PKM-MUF blend existing interactions are involved between the C=O group of PKM and N-H group of MUF. Recall that in MUF, a characteristic peak of 1600 cm^{-1} for C=N stretching was present and blend also contains such peak with no significant change of intensities, which indicates that the condensation reaction between NH_2 and C=O, is not confirmed through FTIR analysis. Considering the Figures 6.18a, 6.18b, 6.18c and 6.20c, it is possible to state that in this PKM-Wood-MUF blend the existing interactions of blend of PKM-MUF. Additionally, the C=O groups of wood are involved in the interaction since, in most of the cases red shift observed.

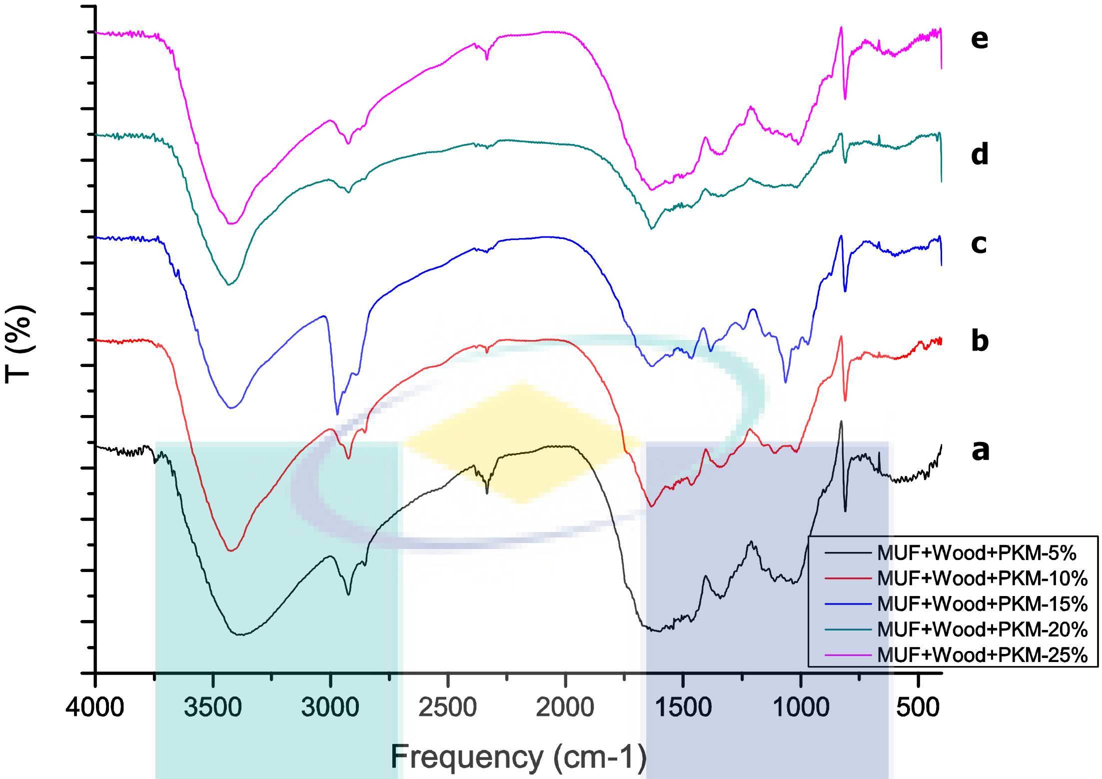

Figure 6.21: FTIR spectra of PKM+Wood+MUF with 5 different level of PKM amount

The FTIR spectra of blend MUF, wood and PKM with five different level of PKM amount is shown in Figure 6.21. The FTIR spectrum analysis provided that broad bands at 3500-3300 cm^{-1}, correspond to the hydrogen bonded O-H and N-H groups (Kim and Kim, 2006 and Uddin et al., 2009). The band observed at 1740-1640 cm^{-1} is assigned for stretching frequency of carbonyl (C=O) groups (Minamisawa et al., 2004). The peak observed at 1543-1498 cm^{-1} corresponds to the NH2 scissoring vibrations (Soto et al., 2005 and Uddin et al., 2009). It is known that intra-molecular hydrogen bonding interactions are independent on concentration, but inter-molecular hydrogen bonding interactions are depended on the concentration. Therefore, we can consider that the above five types of intra molecular interactions were present but not changed due to the variation of PKM percentage rather, from FTIR spectra only the effect of inter molecular interactions were observed. Therefore, the possible intra or inter molecular hydrogen bonding interactions are as follows:

I. C=O……H-O
II. C=O……H-N
III. O-H ……H-O
IV. N-H ……H-N
V. N-H ……H-O

From the spectra, 6.21a-e, 6.21a, c and e followed the expected sequence of peak intensity but exceptions observed for 6.21b and 6.21c, which may be due to the improper mixing. During the blend formation, with the increasing of the percentage of PKM, mainly the number of carbonyl groups (C=O) are increased. Therefore, I & II types of interactions were predominated. From the spectra, it is observed that C=O group peaks (1630-1640 cm^{-1}) broadened as well as the extent of red shift was also remarkable. This may be due to the complex geometry of the macromolecules in PKM. In the case of lower percentage of PKM, the peak of O-H and N-H was remarkably broadened, which indicates the groups are involved with lesser extent of interaction and tried to show their individual identity peak with some degree of overlapping. However, with the increasing of PKM the necessary orientation for the same type of interaction may not be present and both the O-H, N-H groups were effectively involved interactions with C=O groups of PKM, and it is observed as a single enveloped shape peak. Therefore, it may be conclude that most effective interactions observed for ‘e’ compare with ‘a’ since for the C=O group peak of ‘e’ is broadened with the highest degree.

CHAPTER 7

CONCLUSION

In this chapter it divided into two sections, there are conclusion and future work in section 7.1 and 7.2 respectively.

7.1 Conclusion

The adhesive consisting of MUF resin and various types of natural fillers was evaluated for making plywood panel. Hot press temperature and hot press time were investigated in term of enhancing the shear strength of the plywood panel. The shear strength met the minimum industrial requirements of type II plywood at the following variables: hot press temperature at 125 ^{o}C, hot press time at 150 sec and MUF resin viscosity at 55 cp.

In optimization part, processing parameter and fillers of MUF based adhesive was optimized using design expert software (version 6.10, Stat Easy Inc., Minneapolis, USA). The optimum shear strength and formaldehyde emission of plywood bonded with PKM, IF and PS were 1.41 MPa; 1.30 MPa; 1.19 MPa and 0.9199 mg/L; 0.5009 mg/L; 2.1098 mg/L respectively. In addition, the optimum hot press temperature and time of PKM, IF and PS were 129.5 ^{o}C; 133.7 ^{o}C; 130.7 ^{o}C and 170 sec; 159 sec; 186 sec respectively.

The MUF adhesive with various filler content was evaluated for making plywood panel. The processing parameter fixed at 125 ^{o}C and 150 sec, shear strength and formaldehyde emission of plywood panels were investigated. The amount the filler increase until a certain amount the shear strength and formaldehyde emission value reach maximum and minimum respectively. Further increased the amount filler the shear strength and formaldehyde emission value was markedly decreased and increased respectively. This may due to excess of filler usage and the system become highly heterogeneous. Among the natural fillers, plywood bonded with PKM result greatest shear strength and plywood bonded with IF result lowest formaldehyde emission.

In physico-chemical interaction part, functional groups (C=O, -OH and N-H) of PKM after heat treatment was more free compared to PKM without heat treatment. For PKM-MUF blend, hydrogen bond between C=O (PKM) and N-H (MUF) was suggested. For PKM-Wood blend, bond interaction between C=O (wood) and N-H (PKM) was suggested. Furthermore, PKM-Wood-MUF blend, C=O (wood) was suggested in interaction with PKM and MUF because C=O group showed red shift in most of the case. In addition, PKM-Wood-MUF with different amount of PKM, the bonding interaction between C=O (PKM) with O-H and N-H groups effectively involved more as the amount of PKM increase.

In morphology analysis part, SEM micrograph was provided the evidence of distingusih the resin and wood layer. However, the mechanical interlocking information was not provided by the SEM micrograph. Therefore, FESEM was introduced for further investigation. FESEM micrograph was provided evidence of adhesive penetrated into the wood matrix. Besides that, the adhesive distribution within the wood tissues was also detected. However, the PKM was not detected by FESEM. Therefore, LM was choosen to further anlayses the sample. The samples were prepared with different concentration of PKM (0 % to 23 %). The PKM was detected in the LM micrograph and the mechanical interlocking of the PKM, resin and wood tissue was shown in the micrograph. From the LM micrograph, the PKM detetcted was increased as the PKM concentration increase. Moreover, wood crack was observed in mircrograph with 18 % PKM and non-uniform adhesive distribution on the wood surface was observed in micrograph with 23 % PKM. In conclusion, the mechanical interlocking between the wood, resin and PKM was happened. Moreover, excess of PKM will caused the system become highly heterogeneous. Therefore, sufficient amount of PKM used in adhesive formulation is very important.

7.2 Future works

For future works, further study need to do is a thorough understanding of the interaction between the veneer and adhesive by using more technique. Besides that, different particle sizes of natural fillers have to conduct for future work, to determine the particle size effect on the shear strength and formaldehyde emission.

Lastly, the facilities and equipment for preparing the adhesive and manufacturing the plywood may be improved to obtain a more exact result.

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APPENDIX A

Table A.1: Effects of reaction time on viscosity of MUF resin

Reaction time, min	**Viscosity, cp**			
	1st	**2nd**	**3rd**	**Average**
0	0.0	0.0	0.0	0
20	36.0	36.5	33.0	35
70	55.0	53.0	57.0	55
90	76.0	76.0	73.5	75
95	101.0	101.5	98.0	100
100	300.0	280.0	290.0	290

Table A.2: Effects of viscosity on shear strength of MUF resin

Viscosity, cp	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
0	0.00	0.00	0.00	0.00
35	0.38	0.39	0.38	0.38
55	0.00	0.00	0.00	0.00
75	0.62	0.61	0.61	0.61

Table A.2.1: Effects of viscosity,35 cp on shear strength of MUF resin

Viscosity @ 35 cp	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.38	0.37	0.35	0.37
2	0.38	0.40	0.40	0.39
3	0.39	0.42	0.37	0.39
4	0.40	0.39	0.40	0.40
5	0.39	0.38	0.43	0.40
6	0.41	0.42	0.39	0.41
7	0.36	0.36	0.38	0.37
8	0.37	0.38	0.36	0.37
9	0.34	0.35	0.37	0.35
10	0.38	0.38	0.36	0.37
Average				**0.38**

Table A.2.2: Effects of viscosity, 55 cp on shear strength of MUF resin

Viscosity @ 55 cp	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.57	0.59	0.56	0.57
2	0.58	0.60	0.61	0.60
3	0.55	0.55	0.57	0.56
4	0.60	0.60	0.58	0.59
5	0.58	0.58	0.55	0.57
6	0.61	0.61	0.59	0.60
7	0.57	0.56	0.55	0.56
8	0.56	0.53	0.56	0.55
9	0.58	0.61	0.61	0.60
10	0.55	0.55	0.53	0.54
Average				**0.57**

Table A.2.3: Effects of viscosity, 75 cp on shear strength of MUF resin

Viscosity @ 75 cp	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.60	0.62	0.58	0.60
2	0.65	0.66	0.62	0.64
3	0.64	0.63	0.65	0.64
4	0.61	0.61	0.59	0.60
5	0.61	0.59	0.63	0.61
6	0.62	0.63	0.64	0.63
7	0.57	0.56	0.60	0.58
8	0.61	0.58	0.60	0.60
9	0.63	0.64	0.65	0.64
10	0.61	0.60	0.57	0.59
Average	0.62	0.61	0.61	**0.61**

Table A.4: Effects of filler on shear strength of the plywood

Different Filler	**MUF only**	**PKM**	**IF**	**PS**
Shear Strength	0.57	1.45	1.37	1.26

Table A.4.1: Effects of MUF on shear strength of the plywood

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.57	0.59	0.56	0.57
2	0.58	0.60	0.61	0.60
3	0.55	0.55	0.57	0.56
4	0.60	0.60	0.58	0.59
5	0.58	0.58	0.55	0.57
6	0.61	0.61	0.59	0.60
7	0.57	0.56	0.55	0.56
8	0.56	0.53	0.56	0.55
9	0.58	0.61	0.61	0.60
10	0.55	0.55	0.53	0.54
Average				**0.57**

Table A.4.2: Effects of PKM on shear strength of the plywood

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.63	1.61	1.63
2	1.20	1.20	1.25	1.22
3	1.27	1.23	1.25	1.25
4	1.61	1.58	1.63	1.61
5	1.59	1.56	1.55	1.57
6	1.74	1.71	1.71	1.72
7	1.15	1.14	1.21	1.17
8	1.06	1.11	1.10	1.09
9	1.54	1.50	1.50	1.51
10	1.71	1.70	1.67	1.69
Average				**1.45**

Table A.4.3: Effects of IF on shear strength of the plywood

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.21	1.24	1.21	1.22
2	1.43	1.38	1.38	1.40
3	1.32	1.36	1.33	1.34
4	1.44	1.50	1.43	1.46
5	1.40	1.44	1.41	1.42
6	1.42	1.47	1.43	1.44
7	1.25	1.29	1.24	1.26
8	1.43	1.43	1.47	1.44
9	1.28	1.31	1.28	1.29
10	1.42	1.46	1.44	1.44
Average				**1.37**

Table A.4.4: Effects of PS on shear strength of the plywood

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.31	1.34	1.31	1.32
2	1.36	1.37	1.40	1.38
3	1.32	1.31	1.33	1.32
4	1.28	1.29	1.34	1.30
5	1.07	1.05	1.05	1.06
6	1.06	1.10	1.09	1.08
7	1.11	1.10	1.10	1.10
8	1.27	1.30	1.31	1.29
9	1.38	1.40	1.40	1.39
10	1.35	1.32	1.32	1.33
Average				**1.26**

Table A.5: Effects of hot press temperature on shear strength of natural filler at 150 sec

Time, 150 sec	**Temperature, ^{o}C**				
	75	**100**	**125**	**150**	**175**
PKM	0.95	1.24	1.45	1.22	1.05
IF	0.78	0.96	1.37	1.10	0.94
PS	0.70	0.94	1.26	1.05	0.89

Table A.5.1: Shear strength value of PKM at 75 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.03	1.03	1.05	1.04
2	0.95	1.00	0.95	0.97
3	0.95	0.93	0.94	0.94
4	0.84	0.85	0.88	0.86
5	1.07	1.10	1.10	1.09
6	0.98	0.93	0.93	0.95
7	0.86	0.82	0.88	0.85
8	0.85	0.90	0.89	0.88
9	0.95	0.98	0.99	0.97
10	0.94	0.95	0.94	0.94
Average				**0.95**

Table A.5.2: Shear strength value of PKM at 100 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.20	1.20	1.17	1.19
2	1.20	1.17	1.23	1.20
3	1.26	1.29	1.30	1.28
4	1.33	1.32	1.29	1.31
5	1.20	1.17	1.19	1.19
6	1.33	1.30	1.33	1.32
7	1.20	1.22	1.20	1.21
8	1.25	1.24	1.27	1.25
9	1.18	1.21	1.21	1.20
10	1.24	1.25	1.21	1.23
Average				**1.24**

Table A.5.3: Shear strength value of PKM at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.64	1.63	1.61	1.63
2	1.20	1.20	1.25	1.22
3	1.27	1.23	1.25	1.25
4	1.61	1.58	1.63	1.61
5	1.59	1.56	1.55	1.57

6	1.74	1.71	1.71	1.72
7	1.15	1.14	1.21	1.17
8	1.06	1.11	1.10	1.09
9	1.54	1.50	1.50	1.51
10	1.71	1.70	1.67	1.69
Average				**1.45**

Table A.5.4: Shear strength value of PKM at 150 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.20	1.16	1.19	1.18
2	1.18	1.18	1.18	1.18
3	1.23	1.23	1.22	1.23
4	1.23	1.23	1.26	1.24
5	1.21	1.20	1.20	1.20
6	1.19	1.21	1.23	1.21
7	1.20	1.20	1.18	1.19
8	1.24	1.24	1.23	1.24
9	1.26	1.27	1.23	1.25
10	1.25	1.24	1.25	1.25
Average				**1.22**

Table A.5.5: Shear strength value of PKM at 175 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.00	0.99	1.00	1.00
2	1.04	1.03	1.07	1.05
3	1.02	1.03	1.03	1.03
4	1.00	1.03	1.00	1.01
5	1.00	1.04	1.02	1.02
6	1.05	1.04	1.05	1.05
7	1.08	1.09	1.09	1.09
8	1.08	1.08	1.08	1.08
9	1.10	1.07	1.06	1.08
10	1.10	1.08	1.08	1.09
Average				**1.05**

Table A.5.6: Shear strength value of IF at 75 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.82	0.81	0.78	0.80
2	0.80	0.81	0.80	0.80
3	0.75	0.75	0.72	0.74
4	0.74	0.77	0.78	0.76
5	0.74	0.75	0.75	0.75
6	0.74	0.74	0.72	0.73
7	0.79	0.79	0.80	0.79
8	0.79	0.79	0.79	0.79
9	0.80	0.81	0.80	0.80
10	0.79	0.81	0.78	0.79
Average				**0.78**

Table A.5.7: Shear strength value of IF at 100 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.00	0.98	1.03	1.00
2	0.93	0.97	0.96	0.95
3	1.00	1.00	1.00	1.00
4	0.99	1.00	0.99	0.99
5	0.95	0.94	0.93	0.94
6	0.98	0.96	0.97	0.97
7	0.94	0.94	0.94	0.94
8	0.95	0.93	0.94	0.94
9	0.95	0.94	0.95	0.95
10	0.95	0.92	0.97	0.95
Average				**0.96**

Table A.5.8: Shear strength value of IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.21	1.24	1.21	1.22
2	1.43	1.38	1.38	1.40
3	1.32	1.36	1.33	1.34
4	1.44	1.50	1.43	1.46
5	1.40	1.44	1.41	1.42

6	1.42	1.47	1.43	1.44
7	1.25	1.29	1.24	1.26
8	1.43	1.43	1.47	1.44
9	1.28	1.31	1.28	1.29
10	1.42	1.46	1.44	1.44
Average				**1.37**

Table A.5.9: Shear strength value of IF at 150 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.07	1.04	1.08	1.06
2	1.08	1.08	1.08	1.08
3	1.07	1.08	1.07	1.07
4	1.10	1.12	1.12	1.11
5	1.10	1.11	1.10	1.10
6	1.11	1.11	1.12	1.11
7	1.08	1.10	1.06	1.08
8	1.18	1.11	1.15	1.15
9	1.10	1.14	1.13	1.12
10	1.15	1.16	1.15	1.15
Average				**1.11**

Table A.5.10: Shear strength value of IF at 175 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.93	0.96	0.96	0.95
2	1.00	0.97	0.97	0.98
3	1.00	1.01	1.00	1.00
4	0.90	0.90	0.91	0.90
5	0.90	0.90	0.89	0.90
6	0.91	0.91	0.91	0.91
7	0.94	0.95	0.94	0.94
8	0.92	0.88	0.91	0.90
9	0.97	1.00	1.04	1.00
10	0.89	0.93	0.92	0.91
Average				**0.94**

Table A.5.11: Shear strength value of PS at 75 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.75	0.77	0.77	0.76
2	0.69	0.68	0.65	0.67
3	0.67	0.68	0.67	0.67
4	0.68	0.68	0.68	0.68
5	0.70	0.71	0.70	0.70
6	0.68	0.63	0.66	0.66
7	0.70	0.73	0.68	0.70
8	0.75	0.68	0.68	0.70
9	0.75	0.76	0.75	0.75
10	0.70	0.72	0.75	0.72
Average				**0.70**

Table A.5.12: Shear strength value of PS at 100 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.94	0.97	0.94	0.95
2	0.94	0.94	0.93	0.94
3	0.95	0.95	1.00	0.97
4	1.00	0.98	0.98	0.99
5	0.94	0.95	0.94	0.94
6	0.96	1.00	0.93	0.96
7	0.92	0.88	0.90	0.90
8	0.91	0.91	0.96	0.93
9	0.94	0.94	0.92	0.93
10	0.91	0.92	0.90	0.91
Average				**0.94**

Table A.5.13: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.31	1.34	1.31	1.32
2	1.36	1.37	1.40	1.38
3	1.32	1.31	1.33	1.32
4	1.28	1.29	1.34	1.30
5	1.07	1.05	1.05	1.06

6	1.06	1.10	1.09	1.08
7	1.11	1.10	1.10	1.10
8	1.27	1.30	1.31	1.29
9	1.38	1.40	1.40	1.39
10	1.35	1.32	1.32	1.33
Average				**1.26**

Table A.5.14: Shear strength value of PS at 150 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.05	1.02	1.03	1.03
2	1.05	1.03	1.07	1.05
3	1.08	1.09	1.10	1.09
4	1.05	1.01	1.00	1.02
5	1.05	1.05	1.05	1.05
6	1.02	1.02	1.06	1.03
7	1.08	1.06	1.06	1.07
8	1.08	1.07	1.07	1.07
9	1.03	1.03	1.03	1.03
10	1.01	1.01	1.03	1.02
Average				**1.05**

Table A.5.15: Shear strength value of PS at 175 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.90	0.90	0.90	0.90
2	0.91	0.90	0.91	0.91
3	0.87	0.87	0.82	0.85
4	0.85	0.86	0.89	0.87
5	0.92	0.95	0.90	0.92
6	0.90	0.91	0.90	0.90
7	0.88	0.89	0.88	0.88
8	0.89	0.89	0.89	0.89
9	0.84	0.88	0.84	0.85
10	0.87	0.90	0.94	0.90
Average				**0.89**

Table A.6: Effects of hot press time on shear strength of natural filler at 125^{o}C

Temperature, 125 ^{o}C	Time, sec						
	50	**150**	**250**	**350**	**450**	**550**	**650**
PKM	1.13	1.45	1.22	1.06	0.89	0.84	0.69
IF	1.05	1.37	1.13	0.90	0.78	0.73	0.66
PS	0.93	1.26	1.02	0.81	0.70	0.65	0.58

Table A.6.1: Shear strength value of PKM at 125 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.15	1.18	1.15	1.16
2	1.15	1.18	1.13	1.15
3	1.14	1.10	1.10	1.11
4	1.11	1.10	1.10	1.10
5	1.08	1.10	1.13	1.10
6	1.10	1.06	1.07	1.08
7	1.14	1.15	1.15	1.15
8	1.15	1.12	1.12	1.13
9	1.16	1.13	1.14	1.14
10	1.11	1.12	1.14	1.12
Average				**1.13**

Table A.6.2: Shear strength value of PKM at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.63	1.61	1.63
2	1.20	1.20	1.25	1.22
3	1.27	1.23	1.25	1.25
4	1.61	1.58	1.63	1.61
5	1.59	1.56	1.55	1.57
6	1.74	1.71	1.71	1.72
7	1.15	1.14	1.21	1.17
8	1.06	1.11	1.10	1.09
9	1.54	1.50	1.50	1.51
10	1.71	1.70	1.67	1.69
Average				**1.45**

Table A.6.3: Shear strength value of PKM at 125 ℃ and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.26	1.26	1.24	1.25
2	1.22	1.20	1.20	1.21
3	1.20	1.20	1.17	1.19
4	1.25	1.25	1.26	1.25
5	1.25	1.21	1.26	1.24
6	1.20	1.22	1.22	1.21
7	1.17	1.20	1.24	1.20
8	1.27	1.23	1.28	1.26
9	1.17	1.23	1.18	1.19
10	1.18	1.18	1.18	1.18
Average				**1.22**

Table A.6.4: Shear strength value of PKM at 125 ℃ and 350 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.08	1.11	1.12	1.10
2	1.08	1.06	1.06	1.07
3	1.09	1.11	1.11	1.10
4	1.00	1.00	0.99	1.00
5	1.05	1.03	1.03	1.04
6	1.05	1.05	1.05	1.05
7	1.07	1.08	1.08	1.08
8	1.01	1.00	1.05	1.02
9	1.00	1.02	1.05	1.02
10	1.07	1.08	1.07	1.07
Average				**1.06**

Table A.6.5: Shear strength value of PKM at 125 ℃ and 450 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.92	0.91	0.88	0.90
2	0.87	0.87	0.88	0.87
3	0.87	0.86	0.86	0.86
4	0.89	0.90	0.92	0.90
5	0.91	0.91	0.90	0.91

6	0.85	0.85	0.86	0.85
7	0.92	0.95	0.93	0.93
8	0.90	0.88	0.88	0.89
9	0.91	0.90	0.90	0.90
10	0.90	0.90	0.92	0.91
Average				**0.89**

Table A.6.6: Shear strength value of PKM at 125 ℃ and 550 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.88	0.89	0.86	0.88
2	0.88	0.86	0.87	0.87
3	0.85	0.85	0.85	0.85
4	0.87	0.84	0.86	0.86
5	0.83	0.83	0.85	0.84
6	0.81	0.82	0.82	0.82
7	0.88	0.85	0.85	0.86
8	0.79	0.79	0.82	0.80
9	0.81	0.80	0.81	0.81
10	0.81	0.81	0.81	0.81
Average				**0.84**

Table A.6.7: Shear strength value of PKM at 125 ℃ and 650 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.70	0.70	0.70	0.70
2	0.71	0.71	0.70	0.71
3	0.73	0.77	0.74	0.75
4	0.64	0.63	0.67	0.65
5	0.72	0.67	0.70	0.70
6	0.68	0.66	0.65	0.66
7	0.64	0.65	0.65	0.65
8	0.70	0.70	0.68	0.69
9	0.65	0.67	0.66	0.66
10	0.70	0.68	0.69	0.69
Average				**0.69**

Table A.6.8: Shear strength value of IF at 125 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.00	1.00	1.02	1.01
2	1.05	1.05	1.05	1.05
3	1.07	1.08	1.07	1.07
4	0.99	1.00	1.00	1.00
5	0.99	1.03	1.05	1.02
6	1.10	1.08	1.05	1.08
7	1.08	1.09	1.08	1.08
8	1.06	1.04	1.09	1.06
9	1.02	1.03	1.03	1.03
10	1.07	1.07	1.05	1.06
Average				**1.05**

Table A.6.9: Shear strength value of IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.21	1.24	1.21	1.22
2	1.43	1.38	1.38	1.40
3	1.32	1.36	1.33	1.34
4	1.44	1.50	1.43	1.46
5	1.40	1.44	1.41	1.42
6	1.42	1.47	1.43	1.44
7	1.25	1.29	1.24	1.26
8	1.43	1.43	1.47	1.44
9	1.28	1.31	1.28	1.29
10	1.42	1.46	1.44	1.44
Average				**1.37**

Table A.6.10: Shear strength value of IF at 125 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.10	1.09	1.10	1.10
2	1.11	1.10	1.10	1.10
3	1.15	1.15	1.15	1.15
4	1.16	1.18	1.14	1.16
5	1.11	1.11	1.11	1.11

6	1.10	1.10	1.13	1.11
7	1.08	1.10	1.11	1.10
8	1.17	1.18	1.17	1.17
9	1.15	1.17	1.17	1.16
10	1.15	1.14	1.14	1.14
Average				**1.13**

Table A.6.11: Shear strength value of IF at 125 ℃ and 350 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.90	0.90	0.90	0.90
2	0.89	0.91	0.90	0.90
3	0.88	0.89	0.88	0.88
4	0.87	0.90	0.89	0.89
5	0.95	0.90	0.90	0.92
6	0.90	0.92	0.92	0.91
7	0.96	0.95	0.95	0.95
8	0.95	0.97	0.94	0.95
9	0.89	0.88	0.88	0.88
10	0.85	0.86	0.83	0.85
Average				**0.90**

Table A.6.12: Shear strength value of IF at 125 ℃ and 450 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.80	0.77	0.82	0.80
2	0.78	0.75	0.77	0.77
3	0.77	0.76	0.75	0.76
4	0.81	0.84	0.82	0.82
5	0.80	0.80	0.81	0.80
6	0.79	0.78	0.80	0.79
7	0.80	0.80	0.78	0.79
8	0.74	0.76	0.77	0.76
9	0.75	0.74	0.75	0.75
10	0.77	0.77	0.77	0.77
Average				**0.78**

Table A.6.13: Shear strength value of IF at 125 ℃ and 550 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.76	0.77	0.73	0.75
2	0.69	0.71	0.72	0.71
3	0.77	0.74	0.77	0.76
4	0.71	0.70	0.71	0.71
5	0.70	0.70	0.70	0.70
6	0.70	0.71	0.74	0.72
7	0.75	0.79	0.78	0.77
8	0.72	0.72	0.73	0.72
9	0.70	0.70	0.70	0.70
10	0.70	0.70	0.73	0.71
Average				**0.73**

Table A.6.14: Shear strength value of IF at 125 ℃ and 650 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.70	0.71	0.70	0.70
2	0.66	0.67	0.71	0.68
3	0.64	0.66	0.71	0.67
4	0.64	0.65	0.63	0.64
5	0.63	0.63	0.63	0.63
6	0.59	0.58	0.63	0.60
7	0.66	0.66	0.66	0.66
8	0.64	0.64	0.59	0.62
9	0.64	0.67	0.66	0.66
10	0.64	0.72	0.70	0.69
Average				**0.66**

Table A.6.15: Shear strength value of PS at 125 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.90	0.90	0.90	0.90
2	0.94	0.93	0.90	0.92
3	0.94	0.94	0.95	0.94
4	0.95	0.95	0.95	0.95
5	0.91	0.88	0.90	0.90

6	0.88	0.88	0.90	0.89
7	0.93	0.87	0.90	0.90
8	0.93	0.99	0.97	0.96
9	0.91	0.98	0.99	0.96
10	0.96	0.94	0.97	0.96
Average				**0.93**

Table A.6.16: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.31	1.34	1.31	1.32
2	1.36	1.37	1.40	1.38
3	1.32	1.31	1.33	1.32
4	1.28	1.29	1.34	1.30
5	1.07	1.05	1.05	1.06
6	1.06	1.10	1.09	1.08
7	1.11	1.10	1.10	1.10
8	1.27	1.30	1.31	1.29
9	1.38	1.40	1.40	1.39
10	1.35	1.32	1.32	1.33
Average				**1.26**

Table A.6.17: Shear strength value of PS at 125 ℃ and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.00	1.00	1.00	1.00
2	0.98	1.00	0.99	0.99
3	0.99	0.94	0.95	0.96
4	1.07	1.06	1.02	1.05
5	0.99	1.00	1.00	1.00
6	1.04	1.05	1.02	1.04
7	1.03	1.03	1.03	1.03
8	1.06	1.05	1.02	1.04
9	1.06	1.05	1.06	1.06
10	1.03	1.03	1.03	1.03
Average				**1.02**

Table A.6.18: Shear strength value of PS at 125 ℃ and 350 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.80	0.80	0.81	0.80
2	0.79	0.80	0.81	0.80
3	0.82	0.81	0.82	0.82
4	0.86	0.85	0.86	0.86
5	0.80	0.80	0.74	0.78
6	0.77	0.74	0.76	0.76
7	0.80	0.81	0.80	0.80
8	0.75	0.80	0.77	0.77
9	0.86	0.86	0.80	0.84
10	0.86	0.83	0.85	0.85
Average				**0.81**

Table A.6.19: Shear strength value of PS at 125 ℃ and 450 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.68	0.67	0.69	0.68
2	0.66	0.67	0.67	0.67
3	0.70	0.70	0.70	0.70
4	0.72	0.73	0.73	0.73
5	0.71	0.70	0.74	0.72
6	0.72	0.66	0.67	0.68
7	0.70	0.67	0.74	0.70
8	0.64	0.65	0.69	0.66
9	0.72	0.78	0.70	0.73
10	0.71	0.70	0.71	0.71
Average				**0.70**

Table A.6.20: Shear strength value of PS at 125 ℃ and 550 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.63	0.61	0.68	0.64
2	0.69	0.68	0.68	0.68
3	0.66	0.66	0.66	0.66
4	0.62	0.70	0.70	0.67
5	0.63	0.68	0.69	0.67

6	0.68	0.70	0.70	0.69
7	0.69	0.63	0.64	0.65
8	0.60	0.60	0.60	0.60
9	0.57	0.64	0.59	0.60
10	0.60	0.62	0.61	0.61
Average				**0.65**

Table A.6.21: Shear strength value of PS at 125 ℃ and 650 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.54	0.52	0.58	0.55
2	0.59	0.60	0.59	0.59
3	0.60	0.60	0.66	0.62
4	0.57	0.60	0.60	0.59
5	0.57	0.58	0.56	0.57
6	0.60	0.60	0.60	0.60
7	0.55	0.56	0.62	0.58
8	0.55	0.54	0.55	0.55
9	0.55	0.57	0.53	0.55
10	0.60	0.61	0.60	0.60
Average				**0.58**

Table A.7: Effects of filler content on shear strength and formaldehyde emission of the plywood

Temperature, °C Time, sec	**Filler, %**	**Shear Strength, MPa**			**Formaldehyde Emission, mg/L**		
		PKM	**IF**	**PS**	**PKM**	**IF**	**PS**
125 °C, 150 sec	23%	0.92	0.88	0.54	1.2958	0.9784	1.5560
	18%	1.36	1.22	0.82	0.7353	0.5347	1.0410
	13%	1.45	1.33	1.23	1.0057	0.6552	1.1062
	8%	1.14	1.09	1.01	1.2886	0.9391	1.3590
	3%	0.71	0.66	0.60	1.5142	1.2887	1.5080
	0%	0.57	0.57	0.57	1.5780	1.5780	1.5780

Table A.7.1: Shear strength value of MUF (0 % PKM, 0 % IF, 0 % PS) at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.57	0.59	0.56	0.57
2	0.58	0.60	0.61	0.60
3	0.55	0.55	0.57	0.56
4	0.60	0.60	0.58	0.59
5	0.58	0.58	0.55	0.57
6	0.61	0.61	0.59	0.60
7	0.57	0.56	0.55	0.56
8	0.56	0.53	0.56	0.55
9	0.58	0.61	0.61	0.60
10	0.55	0.55	0.53	0.54
Average				**0.57**

Table A.7.2: Shear strength value of 3 % PKM at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.73	0.75	0.76	0.75
2	0.71	0.70	0.70	0.70
3	0.73	0.75	0.73	0.74
4	0.63	0.69	0.70	0.67
5	0.70	0.67	0.70	0.69
6	0.71	0.70	0.70	0.70
7	0.70	0.66	0.68	0.68
8	0.70	0.73	0.70	0.71
9	0.67	0.69	0.73	0.70
10	0.71	0.72	0.71	0.71
Average				**0.71**

Table A.7.3: Shear strength value of 8 % PKM at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.10	1.11	1.14	1.12
2	1.15	1.16	1.20	1.17
3	1.16	1.16	1.16	1.16
4	1.10	1.08	1.11	1.10
5	1.14	1.15	1.13	1.14

6	1.16	1.17	1.16	1.16
7	1.10	1.10	1.10	1.10
8	1.17	1.16	1.14	1.16
9	1.12	1.10	1.15	1.12
10	1.15	1.16	1.15	1.15
Average				**1.14**

Table A.7.4: Shear strength value of 13 % PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.63	1.61	1.63
2	1.20	1.20	1.25	1.22
3	1.27	1.23	1.25	1.25
4	1.61	1.58	1.63	1.61
5	1.59	1.56	1.55	1.57
6	1.74	1.71	1.71	1.72
7	1.15	1.14	1.21	1.17
8	1.06	1.11	1.10	1.09
9	1.54	1.50	1.50	1.51
10	1.71	1.70	1.67	1.69
Average				**1.45**

Table A.7.5: Shear strength value of 18 % PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.35	1.38	1.41	1.38
2	1.34	1.35	1.35	1.35
3	1.36	1.30	1.32	1.33
4	1.34	1.41	1.40	1.38
5	1.30	1.28	1.32	1.30
6	1.35	1.34	1.39	1.36
7	1.37	1.37	1.38	1.37
8	1.35	1.33	1.36	1.35
9	1.38	1.38	1.38	1.38
10	1.39	1.40	1.36	1.38
Average				**1.36**

Table A.7.6: Shear strength value of 23 % PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.00	1.00	0.99	1.00
2	0.87	0.88	0.86	0.87
3	0.91	0.91	0.89	0.90
4	0.94	0.90	0.90	0.91
5	0.90	0.86	0.87	0.88
6	0.88	0.93	0.90	0.90
7	0.96	0.97	0.93	0.95
8	0.93	0.92	0.93	0.93
9	0.94	0.97	0.98	0.96
10	0.91	0.92	0.89	0.91
Average				**0.92**

Table A.7.7: Shear strength value of 3 % IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.70	0.70	0.65	0.68
2	0.67	0.68	0.67	0.67
3	0.70	0.70	0.67	0.69
4	0.70	0.70	0.70	0.70
5	0.65	0.66	0.63	0.65
6	0.67	0.68	0.67	0.67
7	0.60	0.64	0.65	0.63
8	0.68	0.67	0.64	0.66
9	0.63	0.60	0.62	0.62
10	0.66	0.65	0.65	0.65
Average				**0.66**

Table A.7.8: Shear strength value of 8 % IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.10	1.09	1.10	1.10
2	1.15	1.10	1.10	1.12
3	1.06	1.06	1.06	1.06
4	1.05	1.04	1.04	1.04
5	1.05	1.05	1.05	1.05

6	1.05	1.08	1.05	1.06
7	1.15	1.10	1.15	1.13
8	1.10	1.03	1.08	1.07
9	1.15	1.16	1.15	1.15
10	1.15	1.14	1.14	1.14
Average				**1.09**

Table A.7.9: Shear strength value of 13 % IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.15	1.11	1.11	1.12
2	1.16	1.21	1.17	1.18
3	1.09	1.12	1.09	1.10
4	1.23	1.22	1.29	1.25
5	1.45	1.50	1.45	1.47
6	1.48	1.54	1.47	1.50
7	1.28	1.33	1.27	1.29
8	1.61	1.66	1.62	1.63
9	1.43	1.43	1.48	1.45
10	1.30	1.30	1.34	1.31
Average				**1.33**

Table A.7.10: Shear strength value of 18 % IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.25	1.26	1.25	1.25
2	1.20	1.22	1.21	1.21
3	1.20	1.16	1.18	1.18
4	1.15	1.20	1.20	1.18
5	1.20	1.20	1.21	1.20
6	1.18	1.20	1.20	1.19
7	1.25	1.24	1.24	1.24
8	1.24	1.18	1.20	1.21
9	1.25	1.27	1.21	1.24
10	1.25	1.25	1.25	1.25
Average				**1.22**

Table A.7.11: Shear strength value of 23 % IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.86	0.87	0.85	0.86
2	0.88	0.90	0.90	0.89
3	0.88	0.90	0.87	0.88
4	0.91	0.90	0.90	0.90
5	0.90	0.91	0.88	0.90
6	0.93	0.94	0.93	0.93
7	0.87	0.86	0.83	0.85
8	0.90	0.91	0.91	0.91
9	0.82	0.82	0.90	0.85
10	0.84	0.84	0.84	0.84
Average				**0.88**

Table A.7.12: Shear strength value of 3 % PS at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.55	0.57	0.56	0.56
2	0.61	0.65	0.63	0.63
3	0.64	0.64	0.64	0.64
4	0.62	0.64	0.64	0.63
5	0.60	0.58	0.55	0.58
6	0.58	0.57	0.58	0.58
7	0.60	0.60	0.61	0.60
8	0.55	0.55	0.58	0.56
9	0.60	0.65	0.57	0.61
10	0.64	0.64	0.63	0.64
Average				**0.60**

Table A.7.13: Shear strength value of 8 % PS at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.00	1.00	0.99	1.00
2	0.94	0.97	0.98	0.96
3	0.98	1.00	0.97	0.98
4	0.99	1.01	1.00	1.00
5	1.03	1.00	0.97	1.00

6	1.08	1.04	1.03	1.05
7	1.02	1.03	1.03	1.03
8	1.00	1.00	1.00	1.00
9	1.03	1.06	1.06	1.05
10	0.98	1.00	1.05	1.01
Average				**1.01**

Table A.7.14: Shear strength value of 13 % PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.44	1.50	1.46	1.47
2	1.12	1.10	1.07	1.10
3	1.10	1.11	1.11	1.11
4	1.37	1.41	1.36	1.38
5	1.32	1.32	1.33	1.32
6	1.19	1.16	1.14	1.16
7	1.04	1.10	1.08	1.07
8	1.04	1.07	1.08	1.06
9	1.30	1.30	1.27	1.29
10	1.29	1.32	1.30	1.30
Average				**1.23**

Table A.7.15: Shear strength value of 18 % PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.86	0.87	0.83	0.85
2	0.88	0.88	0.88	0.88
3	0.77	0.77	0.75	0.76
4	0.80	0.85	0.80	0.82
5	0.82	0.84	0.84	0.83
6	0.84	0.84	0.85	0.84
7	0.81	0.78	0.80	0.80
8	0.90	0.90	0.85	0.88
9	0.79	0.80	0.81	0.80
10	0.78	0.78	0.77	0.78
Average				**0.82**

Table A.7.16: Shear strength value of 23 % PS at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.60	0.63	0.58	0.60
2	0.55	0.55	0.55	0.55
3	0.54	0.55	0.51	0.53
4	0.51	0.50	0.51	0.51
5	0.57	0.55	0.53	0.55
6	0.54	0.60	0.60	0.58
7	0.51	0.54	0.50	0.52
8	0.51	0.50	0.51	0.51
9	0.55	0.55	0.56	0.55
10	0.49	0.48	0.53	0.50
Average				**0.54**

Table A.7.17: Effects of PKM content on formaldehyde emission of the plywood at 125 ℃ and 150 sec

Temperature, ^{o}C Time, sec	Filler, %	Formaldehyde Emission, mg/L			
		1st	2nd	3rd	Average
125 ^{o}C, 150 sec	23%	1.306	1.2579	1.3235	1.2958
	18%	0.6683	0.7613	0.7762	0.7353
	13%	0.9528	1.0475	1.0167	1.0057
	8%	1.1659	1.2058	1.4942	1.2886
	3%	1.4913	1.5105	1.5409	1.5142
	0%	1.5803	1.5569	1.5969	1.5780

Table A.7.18: Effects of IF content on formaldehyde emission of the plywood at 125 ℃ and 150 sec

Temperature, ^{o}C Time, sec	Filler, %	Formaldehyde Emission, mg/L			
		1st	2nd	3rd	Average
125 ^{o}C, 150 sec	23%	0.9968	1.0392	0.8992	0.9784
	18%	0.5026	0.5411	0.5603	0.5347
	13%	0.6417	0.6739	0.6501	0.6552
	8%	1.0063	0.9259	0.8852	0.9391
	3%	1.2683	1.3085	1.2894	1.2887
	0%	1.5803	1.5569	1.5969	1.5780

Table A.7.19: Effects of PS content on formaldehyde emission of the plywood at 125 ℃ and 150 sec

Temperature, °C **Time, sec**	**Filler, %**	**Formaldehyde Emission, mg/L**			
		1st	**2nd**	**3rd**	**Average**
125 °C, 150 sec	23%	1.5886	1.5393	1.5402	1.5560
	18%	1.0343	1.0097	1.0791	1.0410
	13%	1.0913	1.1598	1.0674	1.1062
	8%	1.3961	1.3902	1.2907	1.3590
	3%	1.5508	1.5339	1.4393	1.5080
	0%	1.5803	1.5569	1.5969	1.5780

Table A.8: Effects of filler on formaldehyde emission of the plywood at 125 ℃ and 150 sec

Temperature, °C **Time, sec**	**Type fillers**	**Formaldehyde Emission, mg/L**			
		1st	**2nd**	**3rd**	**Average**
125 °C, 150 sec	MUF only	1.5803	1.5569	1.5969	1.5780
	PKM	0.9528	1.0475	1.0167	1.0057
	IF	0.6417	0.6739	0.6501	0.6552
	PS	1.0913	1.1598	1.0674	1.1062

Table A.9: Average shear strength and formaldehyde emission of various types of natural fillers.

No.run	**Temperature,x_1 (℃)**	**Pressing Time, x_2 (sec)**	**Average Shear Strength of 10 Specimens of Plywood, Y_1 (MPa)**			**Formaldehyde Emission of Specimens of Plywood, Y_2 (mg/L)**		
			PKM, x_3	**IF, x_3**	**PS, x_3**	**PKM, x_3**	**IF, x_3**	**PS, x_3**
1	100.00	50.00	1.08	0.90	0.91	1.5773	1.0215	2.1502
2	125.00	250.00	1.22	1.11	1.02	0.8524	0.4555	0.7431
3	150.00	50.00	1.12	1.08	0.97	0.9973	0.3785	1.4422
4	100.00	150.00	1.24	0.96	0.94	1.3997	0.9516	1.5774
5	125.00	150.00	1.45	1.36	1.21	1.0283	0.6151	1.2798
6	125.00	50.00	1.13	1.03	0.93	1.1891	0.7374	1.4985
7	100.00	250.00	1.13	0.93	0.87	1.1066	0.6759	1.0002
8	125.00	150.00	1.37	1.37	1.26	0.9809	0.5750	1.1673

9	150.00	250.00	1.11	1.06	0.92	0.5367	0.3383	0.9212
10	150.00	150.00	1.22	1.10	1.05	0.7735	0.3563	1.1513
11	125.00	150.00	1.49	1.33	1.23	1.0080	0.6224	1.4989
12	125.00	150.00	1.49	1.30	1.26	0.8956	0.5275	1.2392
13	125.00	150.00	1.35	1.28	1.19	1.0984	0.6479	1.4489

Table A.9.1: Shear strength value of PKM at 100 ℃ and 50 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.72	0.79	0.80	0.77
2	0.77	0.79	0.85	0.80
3	1.05	1.03	0.98	1.02
4	1.02	0.95	1.00	0.99
5	0.89	0.86	0.80	0.85
6	1.39	1.34	1.33	1.35
7	1.20	1.16	1.14	1.17
8	1.51	1.47	1.44	1.47
9	1.21	1.16	1.15	1.17
10	1.15	1.22	1.15	1.17
Average				**1.08**

Table A.9.2: Shear strength value of PKM at 100 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.04	1.05	0.97	1.02
2	1.26	1.33	1.34	1.31
3	1.27	1.24	1.28	1.26
4	1.10	1.10	1.15	1.12
5	1.34	1.30	1.31	1.32
6	1.43	1.40	1.39	1.41
7	1.20	1.23	1.18	1.20
8	1.15	1.12	1.16	1.14
9	1.56	1.57	1.51	1.55
10	1.00	1.03	1.05	1.03
Average				**1.24**

Table A.9.3: Shear strength value of PKM at 100 ℃ and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.05	1.10	1.06	1.07
2	1.11	1.14	1.10	1.12
3	1.07	1.08	1.14	1.10
4	1.22	1.20	1.18	1.20
5	1.05	1.10	1.04	1.06
6	1.11	1.14	1.09	1.11
7	1.20	1.20	1.24	1.21
8	1.10	1.09	1.14	1.11
9	1.13	1.08	1.10	1.10
10	1.15	1.15	1.17	1.16
Average				**1.12**

Table A.9.4: Shear strength value of PKM at 125 ℃ and 50 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.22	1.20	1.18	1.20
2	0.99	0.94	0.92	0.95
3	1.00	0.98	1.01	1.00
4	0.99	1.02	1.02	1.01
5	1.38	1.35	1.36	1.36
6	1.24	1.23	1.27	1.25
7	1.33	1.37	1.37	1.36
8	1.06	1.09	1.11	1.09
9	1.08	1.06	1.10	1.08
10	1.06	1.05	0.99	1.03
Average				**1.13**

Table A.9.5: Shear strength value of PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.63	1.61	1.63
2	1.20	1.20	1.25	1.22
3	1.27	1.23	1.25	1.25
4	1.61	1.58	1.63	1.61
5	1.59	1.56	1.55	1.57

6	1.74	1.71	1.71	1.72
7	1.15	1.14	1.21	1.17
8	1.06	1.11	1.10	1.09
9	1.54	1.50	1.50	1.51
10	1.71	1.70	1.67	1.69
Average				**1.45**

Table A.9.6: Shear strength value of PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.25	1.19	1.21	1.22
2	1.43	1.39	1.39	1.40
3	1.36	1.32	1.33	1.34
4	1.47	1.48	1.44	1.46
5	1.40	1.45	1.40	1.42
6	1.43	1.47	1.42	1.44
7	1.27	1.27	1.24	1.26
8	1.43	1.47	1.43	1.44
9	1.27	1.30	1.28	1.28
10	1.42	1.45	1.46	1.44
Average				**1.37**

Table A.9.7: Shear strength value of PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.59	1.65	1.63
2	1.21	1.20	1.25	1.22
3	1.24	1.24	1.27	1.25
4	1.55	1.56	1.59	1.57
5	1.58	1.61	1.63	1.61
6	1.64	1.60	1.60	1.61
7	1.15	1.14	1.21	1.17
8	1.64	1.60	1.64	1.63
9	1.49	1.48	1.55	1.51
10	1.72	1.70	1.66	1.69
Average				**1.49**

Table A.9.8: Shear strength value of PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.64	1.60	1.65	1.63
2	1.75	1.72	1.74	1.74
3	1.27	1.25	1.23	1.25
4	1.70	1.72	1.74	1.72
5	1.42	1.43	1.47	1.44
6	1.55	1.55	1.60	1.57
7	1.42	1.45	1.40	1.42
8	1.25	1.20	1.21	1.22
9	1.40	1.40	1.43	1.41
10	1.52	1.51	1.48	1.50
Average				**1.49**

Table A.9.9: Shear strength value of PKM at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.23	1.25	1.27	1.25
2	1.31	1.36	1.34	1.34
3	1.39	1.37	1.44	1.40
4	1.40	1.43	1.40	1.41
5	1.32	1.32	1.30	1.31
6	1.28	1.27	1.32	1.29
7	1.40	1.45	1.41	1.42
8	1.24	1.27	1.25	1.25
9	1.38	1.43	1.38	1.40
10	1.42	1.44	1.40	1.42
Average				**1.35**

Table A.9.10: Shear strength value of PKM at 125 ℃ and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.10	1.12	1.09	1.10
2	0.87	0.89	0.93	0.90
3	1.23	1.27	1.24	1.25
4	0.94	0.96	0.96	0.95
5	1.26	1.27	1.30	1.28

6	1.07	1.08	1.11	1.09
7	1.59	1.59	1.57	1.58
8	1.67	1.66	1.63	1.65
9	1.11	1.10	1.14	1.12
10	1.28	1.30	1.27	1.28
Average				**1.22**

Table A.9.11: Shear strength value of PKM at 150 ℃ and 50 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.90	0.91	0.94	0.92
2	1.13	1.11	1.11	1.12
3	0.89	0.88	0.92	0.90
4	1.15	1.16	1.19	1.17
5	1.30	1.29	1.26	1.28
6	1.07	1.08	1.12	1.09
7	0.96	0.94	0.95	0.95
8	1.00	1.01	1.03	1.01
9	1.12	1.16	1.13	1.14
10	1.60	1.57	1.57	1.58
Average				**1.12**

Table A.9.12: Shear strength value of PKM at 150 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.29	1.29	1.33	1.30
2	1.27	1.28	1.32	1.29
3	1.29	1.26	1.26	1.27
4	1.15	1.15	1.20	1.17
5	1.16	1.19	1.17	1.17
6	0.82	0.86	0.83	0.84
7	1.22	1.19	1.18	1.20
8	1.58	1.54	1.53	1.55
9	1.27	1.23	1.24	1.25
10	1.17	1.13	1.14	1.15
Average				**1.22**

Table A.9.13: Shear strength value of PKM at 150 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.88	0.89	0.92	0.90
2	0.88	0.84	0.83	0.85
3	0.93	0.89	0.87	0.90
4	1.33	1.30	1.30	1.31
5	1.35	1.32	1.30	1.32
6	1.38	1.35	1.34	1.36
7	0.88	0.93	0.89	0.90
8	1.20	1.14	1.16	1.17
9	1.30	1.27	1.26	1.28
10	1.14	1.13	1.15	1.14
Average				**1.11**

Table A.9.14: Shear strength value of IF at 100 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.89	0.88	0.93	0.90
2	1.11	1.07	1.08	1.09
3	1.14	1.11	1.10	1.12
4	0.66	0.69	0.70	0.68
5	0.75	0.76	0.79	0.77
6	0.74	0.69	0.70	0.71
7	0.64	0.64	0.67	0.65
8	0.87	0.83	0.82	0.84
9	1.09	1.04	1.04	1.06
10	1.16	1.13	1.13	1.14
Average				**0.90**

Table A.9.15: Shear strength value of IF at 100 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.14	1.11	1.10	1.12
2	1.36	1.40	1.34	1.37
3	1.08	1.11	1.08	1.09
4	0.84	0.90	0.91	0.88
5	0.84	0.88	0.88	0.87
6	0.80	0.71	0.71	0.74
7	0.98	1.00	0.94	0.97
8	0.97	1.00	0.99	0.99
9	0.69	0.70	0.66	0.68
10	0.90	0.90	0.86	0.89
Average				**0.96**

Table A.9.16: Shear strength value of IF at 100 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.70	0.74	0.69	0.71
2	0.99	1.00	0.96	0.98
3	1.20	1.15	1.16	1.17
4	0.77	0.82	0.79	0.79
5	0.72	0.75	0.73	0.73
6	0.96	0.95	0.94	0.95
7	0.99	1.00	0.96	0.98
8	1.00	1.01	1.03	1.01
9	1.10	1.08	1.08	1.09
10	0.85	0.89	0.88	0.87
Average				**0.93**

Table A.9.17: Shear strength value of IF at 125 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.29	1.28	1.25	1.27
2	0.77	0.82	0.80	0.80
3	1.08	1.07	1.01	1.05
4	1.00	1.03	1.03	1.02
5	0.96	0.90	0.90	0.92

6	1.00	1.05	1.00	1.02
7	1.15	1.18	1.15	1.16
8	1.30	1.30	1.35	1.32
9	0.98	1.05	1.00	1.01
10	0.73	0.80	0.72	0.75
Average				**1.03**

Table A.9.18: Shear strength value of IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.94	0.88	0.89	0.90
2	1.95	2.00	1.96	1.97
3	1.58	1.63	1.59	1.60
4	1.02	0.99	0.99	1.00
5	1.07	1.11	1.11	1.10
6	1.45	1.49	1.46	1.47
7	1.57	1.60	1.60	1.59
8	1.24	1.26	1.24	1.25
9	0.93	0.97	0.94	0.95
10	1.73	1.76	1.73	1.74
Average				**1.36**

Table A.9.19: Shear strength value of IF at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.21	1.24	1.21	1.22
2	1.43	1.38	1.38	1.40
3	1.32	1.36	1.33	1.34
4	1.44	1.50	1.43	1.46
5	1.40	1.44	1.41	1.42
6	1.42	1.47	1.43	1.44
7	1.25	1.29	1.24	1.26
8	1.43	1.43	1.47	1.44
9	1.28	1.31	1.28	1.29
10	1.42	1.46	1.44	1.44
Average				**1.37**

Table A.9.20: Shear strength value of IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.15	1.11	1.11	1.12
2	1.16	1.21	1.17	1.18
3	1.09	1.12	1.09	1.10
4	1.23	1.22	1.29	1.25
5	1.45	1.50	1.45	1.47
6	1.48	1.54	1.47	1.50
7	1.28	1.33	1.27	1.29
8	1.61	1.66	1.62	1.63
9	1.43	1.43	1.48	1.45
10	1.30	1.30	1.34	1.31
Average				**1.33**

Table A.9.21: Shear strength value of IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.40	1.37	1.36	1.38
2	1.07	1.14	1.09	1.10
3	1.15	1.17	1.22	1.18
4	1.22	1.22	1.27	1.24
5	1.27	1.33	1.27	1.29
6	1.12	1.15	1.16	1.14
7	1.39	1.45	1.41	1.42
8	1.37	1.41	1.37	1.38
9	1.41	1.42	1.47	1.43
10	1.39	1.43	1.39	1.40
Average				**1.30**

Table A.9.22: Shear strength value of IF at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	1.36	1.41	1.37	1.38
2	1.42	1.42	1.46	1.43
3	1.22	1.25	1.21	1.23
4	1.28	1.30	1.35	1.31
5	1.27	1.33	1.28	1.29
6	1.10	1.11	1.15	1.12
7	1.05	1.07	1.13	1.08
8	1.39	1.40	1.45	1.41
9	1.14	1.19	1.13	1.15
10	1.39	1.41	1.44	1.41
Average				**1.28**

Table A.9.23: Shear strength value of IF at 125 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.97	1.00	0.96	0.98
2	0.98	1.05	1.00	1.01
3	0.96	0.99	1.00	0.98
4	1.13	1.17	1.13	1.14
5	1.10	1.11	1.14	1.12
6	1.00	0.97	0.96	0.98
7	1.28	1.30	1.35	1.31
8	1.00	1.05	0.99	1.01
9	1.10	1.15	1.11	1.12
10	1.48	1.43	1.42	1.44
Average				**1.11**

Table A.9.24: Shear strength value of IF at 150 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	**2nd**	**3rd**	**Average**
1	0.93	0.98	0.93	0.95
2	1.33	1.28	1.30	1.30
3	0.86	0.90	0.89	0.88
4	1.21	1.24	1.21	1.22
5	1.23	1.27	1.24	1.25

6	1.14	1.08	1.09	1.10
7	0.90	0.87	0.94	0.90
8	0.90	0.88	0.91	0.90
9	1.12	1.11	1.15	1.13
10	1.22	1.19	1.24	1.22
Average				**1.08**

Table A.9.25: Shear strength value of IF at 150 °C and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.16	1.20	1.15	1.17
2	1.19	1.19	1.23	1.20
3	1.10	1.05	1.03	1.06
4	1.10	1.11	1.13	1.11
5	1.46	1.49	1.49	1.48
6	0.83	0.85	0.84	0.84
7	0.80	0.78	0.76	0.78
8	1.31	1.33	1.35	1.33
9	0.84	0.82	0.80	0.82
10	1.26	1.24	1.25	1.25
Average				**1.10**

Table A.9.26: Shear strength value of IF at 150 °C and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.11	1.15	1.11	1.12
2	1.03	1.04	1.03	1.03
3	1.18	1.17	1.15	1.17
4	1.10	1.05	1.04	1.06
5	1.12	1.15	1.15	1.14
6	1.10	1.15	1.11	1.12
7	1.05	1.02	1.02	1.03
8	1.08	1.10	1.10	1.09
9	0.90	0.85	0.86	0.87
10	1.00	0.99	1.03	1.01
Average				**1.06**

Table A.9.27: Shear strength value of PS at 100 ℃ and 50 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.96	1.00	0.97	0.98
2	0.97	0.95	0.93	0.95
3	0.85	0.90	0.86	0.87
4	0.86	0.87	0.87	0.87
5	0.84	0.86	0.90	0.87
6	0.94	0.96	0.94	0.95
7	0.81	0.84	0.81	0.82
8	0.95	0.97	0.94	0.95
9	0.85	0.88	0.88	0.87
10	0.99	0.98	0.98	0.98
Average				**0.91**

Table A.9.28: Shear strength value of PS at 100 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.75	0.78	0.75	0.76
2	0.72	0.71	0.71	0.71
3	0.74	0.70	0.68	0.71
4	0.85	0.84	0.83	0.84
5	1.30	1.30	1.33	1.31
6	1.00	0.96	0.97	0.98
7	0.98	0.99	0.98	0.98
8	1.12	1.16	1.13	1.14
9	1.13	1.07	1.08	1.09
10	0.92	0.91	0.88	0.90
Average				**0.94**

Table A.9.29: Shear strength value of PS at 100 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.81	0.85	0.80	0.82
2	0.88	0.85	0.88	0.87
3	0.99	0.97	0.96	0.97
4	0.90	0.90	0.94	0.91
5	0.86	0.83	0.83	0.84
6	0.96	0.97	1.00	0.98
7	0.80	0.77	0.76	0.78
8	0.75	0.76	0.80	0.77
9	0.86	0.85	0.85	0.85
10	0.91	0.90	0.94	0.92
Average				**0.87**

Table A.9.30: Shear strength value of PS at 125 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.90	0.94	0.91	0.92
2	0.96	1.00	0.97	0.98
3	0.88	0.87	0.85	0.87
4	1.02	1.01	1.05	1.03
5	0.88	0.88	0.85	0.87
6	1.08	1.05	1.05	1.06
7	0.82	0.84	0.86	0.84
8	0.90	0.86	0.86	0.87
9	0.96	0.97	1.00	0.98
10	0.83	0.87	0.83	0.84
Average				**0.93**

Table A.9.31: Shear strength value of PS at 125 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.02	1.05	1.02	1.03
2	1.28	1.26	1.30	1.28
3	1.00	1.00	1.03	1.01
4	1.33	1.30	1.30	1.31
5	1.02	1.01	1.05	1.03

6	1.03	1.01	1.05	1.03
7	1.24	1.24	1.27	1.25
8	1.37	1.36	1.36	1.36
9	1.24	1.24	1.25	1.24
10	1.55	1.51	1.51	1.52
Average				**1.21**

Table A.9.32: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.46	1.50	1.45	1.47
2	1.05	1.08	1.05	1.06
3	1.07	1.07	1.10	1.08
4	1.16	1.15	1.15	1.15
5	1.45	1.46	1.50	1.47
6	1.47	1.45	1.48	1.47
7	1.10	1.10	1.11	1.10
8	1.11	1.11	1.11	1.11
9	1.39	1.38	1.36	1.38
10	1.32	1.32	1.33	1.32
Average				**1.26**

Table A.9.33: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.44	1.50	1.46	1.47
2	1.12	1.10	1.07	1.10
3	1.10	1.11	1.11	1.11
4	1.37	1.41	1.36	1.38
5	1.32	1.32	1.33	1.32
6	1.19	1.16	1.14	1.16
7	1.04	1.10	1.08	1.07
8	1.04	1.07	1.08	1.06
9	1.30	1.30	1.27	1.29
10	1.29	1.32	1.30	1.30
Average				**1.23**

Table A.9.34: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.31	1.34	1.31	1.32
2	1.36	1.37	1.40	1.38
3	1.32	1.31	1.33	1.32
4	1.28	1.29	1.34	1.30
5	1.07	1.05	1.05	1.06
6	1.06	1.10	1.09	1.08
7	1.11	1.10	1.10	1.10
8	1.27	1.30	1.31	1.29
9	1.38	1.40	1.40	1.39
10	1.35	1.32	1.32	1.33
Average				**1.26**

Table A.9.35: Shear strength value of PS at 125 ℃ and 150 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	1.00	1.02	1.02	1.01
2	1.30	1.26	1.26	1.27
3	1.01	1.02	1.00	1.01
4	1.02	1.05	1.02	1.03
5	1.07	1.13	1.14	1.11
6	1.40	1.35	1.34	1.36
7	1.24	1.25	1.26	1.25
8	1.13	1.12	1.12	1.12
9	1.33	1.39	1.39	1.37
10	1.37	1.39	1.40	1.39
Average				**1.19**

Table A.9.36: Shear strength value of PS at 125 ℃ and 250 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.02	1.05	1.03	1.03
2	1.30	1.27	1.28	1.28
3	0.88	0.90	0.90	0.89
4	0.93	0.99	0.94	0.95
5	1.14	1.20	1.14	1.16
6	1.00	0.95	1.00	0.98
7	0.91	0.91	0.94	0.92
8	1.14	1.14	1.20	1.16
9	0.95	0.93	0.98	0.95
10	0.85	0.86	0.90	0.87
Average				**1.02**

Table A.9.37: Shear strength value of PS at 150 ℃ and 50 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	0.86	0.90	0.86	0.87
2	0.86	0.83	0.83	0.84
3	0.86	0.88	0.88	0.87
4	0.85	0.88	0.88	0.87
5	1.16	1.16	1.20	1.17
6	0.88	0.83	0.85	0.85
7	0.85	0.97	0.89	0.90
8	1.18	1.18	1.23	1.20
9	0.95	1.00	1.00	0.98
10	1.15	1.11	1.11	1.12
Average				**0.97**

Table A.9.38: Shear strength value of PS at 150 ℃ and 150 sec

No	Shear Strength, Mpa			
	1st	2nd	3rd	Average
1	1.05	1.01	1.02	1.03
2	1.18	1.19	1.24	1.20
3	0.85	0.80	0.81	0.82
4	1.00	0.96	0.99	0.98
5	1.18	1.14	1.20	1.17

6	1.05	1.06	1.08	1.06
7	1.18	1.15	1.19	1.17
8	1.12	1.13	1.16	1.14
9	1.07	1.04	1.08	1.06
10	0.87	0.88	0.87	0.87
Average				**1.05**

Table A.9.39: Shear strength value of PS at 150 ℃ and 250 sec

No	**Shear Strength, Mpa**			
	1st	**2nd**	**3rd**	**Average**
1	0.83	0.87	0.83	0.84
2	0.94	0.94	0.97	0.95
3	0.94	0.90	0.92	0.92
4	0.90	0.90	0.90	0.90
5	0.94	0.91	0.90	0.92
6	0.92	0.88	0.90	0.90
7	1.00	1.02	1.00	1.01
8	0.99	1.00	1.01	1.00
9	0.89	0.88	0.85	0.87
10	0.93	0.91	0.85	0.90
Average				**0.92**

Table A.9.40: Formaldehyde emission value of PKM at various time and temperature

Temperature,x_1 (℃)	**Pressing Time, x_2 (sec)**	**Formaldehyde Emission of Specimens of Plywood, Y_2 (mg/L)**			
		1st	**2nd**	**3rd**	**Average**
100	50	1.5434	1.5652	1.6234	1.5773
	150	1.3598	1.2376	1.6016	1.3997
	250	0.9392	1.1866	1.1939	1.1066
125	50	1.2303	1.1284	1.2085	1.1891
	150	1.0171	1.0276	0.9792	1.0080
	150	0.8837	0.9273	0.8758	0.8956
	150	1.1185	1.0775	1.0992	1.0984
	150	0.9714	1.0138	0.9571	0.9808
	150	1.0275	1.0186	1.0389	1.0283
	250	0.9403	0.7712	0.8456	0.8524
150	50	1.0486	0.9606	0.9828	0.9973
	150	0.7442	0.7509	0.8253	0.7735
	250	0.5292	0.5262	0.5547	0.5367

Table A.9.41: Formaldehyde emission value of IF at various time and temperature

Temperature, x_1 (℃)	Pressing Time, x_2 (sec)	Formaldehyde Emission of Specimens of Plywood, Y_2 (mg/L)			
		1st	2nd	3rd	Average
	50	1.0215	1.0553	0.9877	1.0215
100	150	0.9065	0.9268	1.0215	0.9516
	250	0.6291	0.6679	0.7306	0.6759
	50	0.7442	0.7645	0.7036	0.7374
	150	0.6251	0.629	0.6132	0.6224
	150	0.5269	0.5171	0.5386	0.5275
125	150	0.6475	0.6678	0.6283	0.6479
	150	0.5721	0.5641	0.5887	0.5750
	150	0.6196	0.6246	0.6011	0.6151
	250	0.4803	0.4465	0.4397	0.4555
	50	0.4194	0.3915	0.3247	0.3785
150	150	0.3788	0.3721	0.318	0.3563
	250	0.3977	0.3112	0.3059	0.3383

Table A.9.42: Formaldehyde emission value of PS at various time and temperature

Temperature, x_1 (℃)	Pressing Time, x_2 (sec)	Formaldehyde Emission of Specimens of Plywood, Y_2 (mg/L)			
		1st	2nd	3rd	Average
	50	2.1376	2.2659	2.0472	2.1502
100	150	1.5958	1.4371	1.6994	1.5774
	250	0.9686	0.9821	1.0498	1.0002
	50	1.4557	1.4557	1.5842	1.4985
	150	1.5879	1.5491	1.3598	1.4989
	150	1.4591	1.1278	1.1307	1.2392
125	150	1.3998	1.3898	1.5572	1.4489
	150	1.0972	1.1471	1.2577	1.1673
	150	1.2392	1.1513	1.4489	1.2798
	250	0.7183	0.6845	0.8266	0.7431
	50	1.4669	1.4176	1.4421	1.4422
150	150	1.0719	1.1717	1.2102	1.1513
	250	1.0119	0.9007	0.8511	0.9212

APPENDIX B

Publication:

Journal

Huei Ruey Ong, Reddy Prasad, Md. Maksudur Rahman Khan and Md. Najmul Kabir Chowdhury, 2011. Effect of Palm Kernel Meal as Melamine Urea Formaldehyde Adhesive Extender for Plywood application : Using a Fourier Transform Infrared Spectroscopy (FTIR) Study. *Applied Mechanics and Materials*, Vols. 121-126, pp 493-498. DOI:10.4028/www.scientific.net/AMM.121-126.493

Patent

PI 2011001946-D.M. Reddy Prasad, Rosli Yunus, Maksudur Rahman Khan, **Ong Huei Ruey** and Awang Bono. An Improved Adhesive Composition.

Research Award:

Silver Medal in PECIPTA 2011, International Conference and Exposition on Inventions of Higher Learning/ Invigorating Innovation in the New Economic Model, Kuala Lumpur Convention Centre (KLCC), Kuala Lumpur, Malaysia, 13th -15th September 2011, for the invention titled "Green and Cost Effective Adhesive using Melamine Urea Formaldehyde (MUF) Resin and Natural Fillers".

Silver Medal in CITReX 2011, Creation, Innovation, Technology & Research Exposition, Universiti Malaysia Pahang, Pahang, Malaysia, 13th -14th April 2011, for the invention titled "Formulation of Melamine Urea Formaldehyde Resin (MUF) with Various Types of Filler as Adhesive".