OPTIMIZATION AND CHARACTERIZATION OF MELAMINE UREA FORMALDEHYDE (MUF) BASED ADHESIVE WITH WASTE RUBBER POWDER (WRP) AS FILLER

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SUPERVISOR'S DECLARATION

"I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Bachelor of Chemical Engineering"

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STUDENT'S DECLARATION

I declare that this thesis entitled "Optimization and Formulation of Melamine Urea Formaldehyde (MUF) with Waste Rubber Powder (WRP)" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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LIST OF ABBREVIATIONS

EVA	Ethylene Vinyl Acetate
FE	Formaldehyde Emission
FTIR	Fourier Transform Infrared spectroscopic
JAS	Japanese Agriculture Standard
LVL	Laminated Veneer Lumber
MF	Melamine Formaldehyde
MUF	Melamine Urea Formaldehyde
OSB	Oriented Strand Board
PF	Phenol Formaldehyde
PMDI	Diphenylmethane Diisocyanate
PVA	Polyvinyl Alcohol
PVAc	Polyvinyl Acetate
RSM	Research Surface Methodology
RTV	Room Temperature Vulcanizing
SEM	Scanning Electron Microscopic
WRP	Waste Rubber Powder
UF	Urea Formaldehyde
UV/V	Ultra-violet Visible Spectrophotometer

LIST OF SYMBOLS

˚C	Degree Celsius
%	Percentage
MPa	Mega Pascal
USD	United States Dollar
RM	Ringgit Malaysia
Tons	Tonnes
$	Dollar
pH	Power of Hydrogen
˚F	Degree Fahrenheit
g/cm^3	Gram per centimeter cube
µm	Micro meter
mm	Millimeter
M	Molarity
V	Volume
mL	Milli-Liter
g	Gram
h	Hour
cP	Centipoises
wt.	Weight
s	Second

OPTIMIZATION AND CHARACTERIZATION OF MELAMINE UREA FORMALDEHYDE (MUF) BASED ADHESIVE WITH WASTE RUBBER POWDER (WRP) AS FILLER

ABSTRACT

Fillers are added in adhesive formulation to minimize the utilization of resin in wood based products. Waste Rubber Powder is being used as wood adhesive filler in order to change the research work from waste to wealth. In this work, Melamine Urea Formaldehyde (MUF) resin was produced in the laboratory and waste rubber powder was subjected to chemical modification by using oxidizing agents such as 20% nitric acid, 30% hydrogen peroxide and acetone solution were added to the Melamine Urea Formaldehyde (MUF) resin in identifying the best chemically modified waste rubber powder for interior plywood manufacturing using a laboratory press. Most of the plywood adhesives are formaldehyde based, which are not environmental friendly due to the formaldehyde emission, formaldehyde is considered as a carcinogenic agent. Due to the formaldehyde emission issue, plywood export to Europe and United State had been decreased. Therefore, the formaldehyde emission from the plywood is reduced. This work demonstrates the effect of filler at shear strength, water resistant and formaldehyde performance. Response surface methodology (RSM) software was used for identification of the optimum temperature and pressing time for wood adhesive performance. The optimum parameters investigated in this experiment was in the temperature range from 100 to 175°C at fixed pressing time at 150sec while in the time range from 50 to 450s at fixed prssing temperature at 125˚C. It was found that chemically modified waste rubber powder with 20% nitric acid had better plywood shear strenght, water resistant and formaldehyde emmision performance compared with other oxidizing agents solution. The optimum shear strength and formaldehyde emission performance of WRP was obtained by using pressing temperature 171.60˚C and time 269.27s was 1.37MPa and 0.7315mg/L. This work proved that extender is an important in enhancing the wood performance for wood adhesive. The sufficient amount of filler will increase the shear strength and decrease the formaldehyde emission of wood adhesive.

PENGOPTIMUMAN DAN PENCIRIAN MELAMINE UREA FORMALDEHYDE (MUF) DENGAN SISA SERBUK GETAH SEBAGAI PENGISI

ABSTRAK

Pengisi ditambah dalam formulasi pelekat untuk meminimumkan penggunaan resin dalam produk berasaskan kayu. Bahan buangan seperti sisa serbuk getah telah dimanfaatkan melalui kerja penyelidikan ini dengan menggunakannya sebagai pengisi pelekat kayu. Dalam kajian ini, Melamine Urea Formaldehyde (MUF) resin telah dihasilkan di dalam makmal dan serbuk getah sisa telah mengalami pengubahsuaian kimia dengan menggunakan agen pengoksidaan seperti asid nitrik 20%, hidrogen peroksida dan larutan 30% aseton telah ditambah kepada Melamine Urea Formaldehyde (MUF) resin untuk mengenal pasti sisa getah kimia diubahsuai serbuk terbaik untuk pembuatan papan lapis dalaman dengan menggunakan mesin penekan suhu makmal. Kebanyakan pelekat papan lapis adalah berasaskan bahan tidak mesra alam, formaldehid yang merupakan agen karsinogenik. Disebabkan isu pelepasan formaldehid, eksport papan lapis ke Eropah dan Amerika Syarikat telah menurun. Oleh itu, pelepasan formaldehid daripada papan lapis dikurangkan. Selain itu, kesan pengisi pada prestasi kekuatan ricih dan pelepasan formaldehid papan lapis telah dikaji. Perisian 'Response Surface Methodology (RSM)' telah digunakan untuk mengenal pasti suhu dan masa menekan optimum untuk prestasi pelekat kayu. Parameter optimum dikaji dalam eksperimen ini adalah dalam lingkungan suhu 100-175 ° C pada masa yang tetap menekan iaitu 150sec dan dalam lingkungan masa dari 50 hingga 450s pada suhu menekan tetap pada 125 ˚ C. Sebagai hasilnya, keputusan sisa kimia diubahsuai serbuk getah dengan asid nitrik 20% mempunyai kekuatan ricih papan lapis, kalis air dan pelepasan formaldehid yang baik berbanding dengan lain-lain agen larutan pengoksidaan. Kekuatan ricih dan pelepasan formaldehid sisa serbuk getah yang optimum telah diperolehi dengan menggunakan suhu dan masa menekan 171.60 ˚ C dan 269.27s masing-masing adalah 1.37MPa dan 0.7315mg / L. Kerja ini membuktikkan bahawa pengisi adalah penting dalam meningkatkan prestasi kayu untuk pelekat kayu.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Forest based industry can be divided into five sectors such as wood working industry, pulp and paper industry, paper and board converting industry, graphic and furniture industry. The conversion of trees into useful consumer products and building materials are the wood processing method. The applications of woodworking industries are to supply basic products such as sawn goods, wood panels and builders' carpentry for construction, internal decoration and packaging (pallets; European Commission, 2008). Malaysia is one of the world's largest exporters of tropical hardwood logs and sawn timber and is also a major exporter of tropical plywood, veneer and moldings. In fact, Malaysia is a top exporter of wood products with the revenue of over USD10billion in 2006 (Statistical Dept. of Malaysia, 2007) and exports of plywood amounted to RM20.5 billion in 2010 (MTIB, 2010).

The demand for wood based adhesive increase day by day in wood based industry because most of them are petrochemical based adhesive. The thermosetting and thermoplastic resins are the mainly used resin in wood industry. Urea Formaldehyde (UF), Melamine Urea Formaldehyde (MUF), Melamine Formaldehyde (MF) and Phenol Formaldehyde (PF) are some examples of thermosetting resins while polyvinyl acetate (PVAc), Polyvinyl Alcohol (PVA), and Ethylene Vinyl Acetate (EVA) are some commonly used thermoplastic resins (Ong, *et.al.* 2011). Melamine Urea Formaldehyde (MUF) is one of the mostly used and class of amino resin adhesive. The advantages of MUF adhesives are their initial water solubility which tenders them eminently suitable for bulk and relatively inexpensive production, hardness inflammability, good thermal properties, absence of colors in cured polymers and easily adaptability to a variety of curing conditions. Thermosetting amino resins produced from urea are built by condensation polymerization. The types of thermosetting are resorcinol formaldehyde, urea formaldehyde, phenolics, polyesters, anaerobic resins, polysulfide and room temperature vulcanizing (rtv) silicons (Dinwoodie, 1983; Pizzi, 1983).

Melamine urea formaldehyde condensate (MUF resins) based adhesives are employed in the wood processing industry and in other manufactures industries. The disadvantage of formaldehyde emission from MUF bonded wood product is carcinogenic effects. However, adhesives with a declared lower formaldehyde emission which are produced in a lower molar ratio of formaldehyde to urea (approx. 1.2:1) in the reaction mixture and further addition of approx. 5% urea to the adhesive is recommended to actual curing of adhesive film (Pizzi & Mittal, 1994; Marutzky & Pizzi, 1989). The major reasons formaldehyde emission from MUF bonded wood

products are unreacted formaldehyde in the MUF resins, released formaldehyde during the condensation reaction between methylol groups and emitted formaldehyde from the hydrolytic degradation of the cured resin (Ko, 1976, Tomita, 1980).

Adhesive is a substance capable of holding at least two surfaces together in a strong and permanent manner. Adhesive is one of the important materials applied on wood-based industry. Pizzi (1994) stated that during the last decades, there were many researches and development in wood-based industry on adhesives has shown successful result. Adhesives play a central role in wood-based panel production. Generally, adhesives are manufactured by compounding a base resinous material with fillers and hardener.

Filler which used in this research is waste rubber powder (WRP). WRP is the product of used tires. Applications of the filler are to increase viscosity, control rheology and reduce raw material cost. The pours wood surface consists of small holes. The filler in the adhesive is 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 also used to reduce the penetration of resin into the small holes of the wood (Pizzi, 1994).

The aim of the research is to compare the MUF based adhesive with filler and the effect of filler on bonding strength and formaldehyde emission performance. Besides that, optimization of processing condition also will be studied.

1.2 Problem Statement

Wheat flour is the industrial common used filler, whereas waste rubber powder (WRP) as the product of the used tires, it can used to replace the wheat flour. WRP available abundance in Malaysia and it's cheap. The research work indirectly leads to waste to wealth. Moreover, formaldehyde emission from the wood composite poses a hazard to human health because it is a human carcinogen. The WRP applied as filler for adhesive in wood composite can lower the formaldehyde emission. Besides that, WRP can reduce the usage of MUF resin in adhesive and directly it reduces the amount of formaldehyde emission from wood composite.

1.2 Objectives

The objectives of this research are as following:

- To study the optimization and characterization of MUF adhesive with WRP filler with different processing parameter (pressing time and temperature).
- To study the effect of filler at shear strength and water resistant performance
- To study the effect of filler at formaldehyde emission of plywood.

1.3 Scope of research

The scope of this research is to study the effect of filler on shear strength and formaldehyde emission. Apart from that, the optimization of the different processing conditions (pressing time and temperature) conducted. Characterization of WRP have been investigated.

1.4 Rationale and Significance

Introduced new filler which taken from waste (WRP) proves with better performance on shear strength and formaldehyde emission performance.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of wood adhesives

Wood adhesives are essential components of development and growth of wood composites. In 2011, the worldwide wood adhesive consumption was 13.3 million tons and total sale value reached $6.1 billion [Sellers, 2011]. Since 2011 the global wood composite output has increased steadily which means an increasing consumption of wood adhesives. Wood adhesives can be broadly classified as synthetic-based and natural-material-based adhesives.

2.2 Synthetic based Adhesives

There are two types of synthetic based resins which are thermosetting and thermoplastic resins. These resins are differentiated by their chemical structure and response of heat (Li Kai Cheng, 2009).

2.2.1 Thermosetting Resin

Thermosetting resins are cross-linked while heating and cannot return to their original chemical structure as it's in cooling process. The raw uncured resin molecules are cross-linked through a catalytic chemical reaction. The chemical reaction which takes place in this reaction is exothermic reaction and the resin creates strong bonds one to another and change state form liquid to solid. The examples of thermosetting resins are urea formaldehyde (UF), melamine formaldehyde (MF), melamine urea formaldehyde (MUF), phenol formaldehyde (PF) and others such as polyurethanes, epoxy resins, and isocyanates resins are used in the wood composite manufacturing (Li Kai Cheng, 2009).

2.2.1.1 Urea Formaldehyde (UF) Resins

Urea formaldehyde resin is produced approximately 1 million metric tons annually. UF resin is used by forest products industry more than 70% in variety of purposes (White, 1995). The resin is used in the production of an adhesive for bonding particleboard (61% of urea formaldehyde used by the industry), medium-density fiberboard (27%), hardwood plywood (5%), and laminating adhesive for bonding (7%), for example, furniture case goods, overlays to panels, and interior flush doors. Urea formaldehyde resins are the example of the thermosetting resins which referred to as amino resins (William, 1991; Updegraff, 1990). Urea formaldehyde resins comprise about 80% of the amino resins produced worldwide. The remainder of this class of resins is melamine formaldehyde resins, except for

minor amounts of resins that are produced from other aldehydes or amino compounds, or both.

Amino resins are often used to modify the properties of other materials (William, 1991; Updegraff, 1990). For example, these resins are added during the processing of such products like textile fabrics to impart permanent press characteristics; automobile tires to improve the tear strength; especially of wet paper; and alkyds and acrylics to improve their cure.

Urea formaldehyde resins are majorly used as adhesive by the wood industry because of low cost, ease of use under a wide variety of curing conditions, low cure temperatures, water solubility, resistance to microorganism and to abrasion, hardness, excellent thermal properties, and lack of color, especially of the cured resin. The advantage of UF resin is highly reactive, clear glue line, short hot-pressing time, aqueous system, cold tack ability, no flammability and low price. Meanwhile, the disadvantage of urea formaldehyde resin compared to other thermosetting wood adhesives is lack of resistance to moist conditions with combination of heat. These conditions encourage to a reversal of the bond-forming reactions and the release of formaldehyde. This situation lead to narrow the usage of urea formaldehyde resins for interior use, particleboard and MDF. The overexposure to formaldehyde from urea formaldehyde may lead to carcinogen effects.

2.2.1.2 Melamine Formaldehyde (MF) Resins

MF resin is also one of the thermosetting adhesives in wood industry. MF is looks lighter in colour compare to other types of resin and it's also have acceptable water resistance characteristics. The applications of MF are primarily used wood adhesives for exterior and semi-exterior plywood and particleboard, and for finger joints. In addition, MF commonly used for impregnating paper sheets which used as the backing in making plastic laminates.

The reaction between melamine and formaldehyde are almost similar as the reaction between urea and formaldehyde where first is the addition reaction and then continue by condensation reaction. However, the addition between formaldehyde to melamine reaction is occurs more easily compare to the addition of formaldehyde to urea addition and the residual of formaldehyde is lower in MF resin (Pizzi, 1983). The reason the residual of formaldehyde is lower in MF resin because melamine is added into UF resin as formaldehyde scavenger. The good stability of the symmetrical triazine ring makes the MF resin resistance to water when the resin has been cured to the insoluble cross-linked state (Skeist, 1990). The limitation of MF adhesive is melamine is more expensive than urea. Usually, melamine will be added to UF resin to make melamine urea formaldehyde (MUF) adhesive.

2.2.1.3 Melamine Urea Formaldehyde (MUF) Resins

Melamine urea formaldehyde (MUF) is a synthetic resin belongs to the amino resin family. There are many authors been studied on 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 opinion about the co-condensation reaction between melamine and urea during the MUF resin synthesis (Ong, *et. al.* 2011). At present, melamine-urea-formaldehyde resins (MUF) are used most commonly for production of wood composites, for exterior and semi exterior wood panels and for the preparation and bonding of both low- and high-pressure paper laminates and overlays (Pizzi, 1994).

Melamine fortified UF resins and MUF resins can be manufactured in a variety of ways, for example:

(i) By condensation of melamine, urea, and formaldehyde in a multistep reaction (Georgia Pacific Resin, 1996).

(ii) By mixing of an MF resin with a UF resin according to the desired composition of the resin (Maylor, 1995).

(iii) By addition of melamine in various forms (pure melamine, MF/MUF powder resin) to a UF resin during the application of the glue mix.

(iv) Melamine also can be added in the form of melamine salts such as acetates, formats or oxalates (Weinstabi, Binder, Gruber and Kantner, 2001), which decompose in the aqueous resin mix only at higher temperature.

The characteristic of MUF resin is higher water resistance compare to UF (Skeist, 1990). The MUF resin produced has unique characteristics and properties, which in many ways are very different from the properties of MF or UF resin (Pizzi,

1994). Various MUF resin formulations have different properties, performance and durability. The important properties of MUF resin include the shelf life, solubility in water and curing period are formulated according to its applications. MUF resin formulations are built up from a combination of several factors. Among the important factors are the reaction period for each stage, the efficiency of controlling the pH and the temperature throughout the process, the mole ratio of formaldehyde to urea/melamine and the number of stages in which amino compound is reacted. The combination and variation of these factors produce different resin shelf life, degree of solubility in water and curing periods (Sandler et al, 1994). However, balancing all of these factors to obtain satisfactory properties for specific applications is rather difficult due to the interactions among the factors. For example, improving resin solubility may increase the curing period (Vaughn et al., 1999). On the other hand, shortening the resin-curing period may produce an unstable resin (Tutin 1998). In enhancing unbaked tile properties (Noraini, 2001; Hirdawati, 2001 and Hartini 2001), thermosetting resin with good shelf life, high solubility in water and shorter curing period at room temperature are desirable. MUF resin has the potential to be used in unbaked tiles since it also a thermosetting resin with high solubility in water and good physical properties such as being resistance to scratch, heat, stain, water and chemicals.

Previously, researches to produce MUF resin with good stability and higher solubility in water have been reported. Nevertheless, the resulting formulation does not have a satisfactory amount of melamine or urea. For example, in Breyer et al. 1997 and Shieu et al. 1985, the amount of melamine is between 2-10%. This percentage is too low for any visible chemical, scratch and stain resistant properties

from the melamine. In Heger 1982, the melamine content reaches 40% of the total resin weight, while urea comprises of only a more 3% of total resin weight. Addition of urea is used only as a means to reduce the free formaldehyde emission. Hence, the percentage of urea present is too low for the resin to be economical. Since all of these formulations also require considerable curing period, thus, higher temperature is needed to help enhance the curing process (Bono, *et. al*. 2003).

2.2.1.4 Phenol Formaldehyde (PF) Resins

The reaction between phenol and formaldehyde produce Phenol Formaldehyde (PF) resin. According to the pH value of catalyst used to produce PF resin, can be divided into resole and novolac resins.

Usually for resole resin a molar excess of formaldehyde is being used in the presence of basic catalyst. The excess formaldehyde attacks the *ortho*- and *para*-positions of phenol to form methylol phenol. As a result, a sufficient number of methlol groups remain reactive to complete the polymerization. Therefore, no addition of excess formaldehyde is needed and the resin can cure by elevated temperature.

The reaction between phenol and formaldehyde in the presence of acidic catalyst can produce novolac resin. At first methylol phenol derivatives are formed and further react with additional phenol to create methyelene bridge at either the *ortho*- and *para*- positions of phenolic aromatic ring and the reaction terminated when the formaldehyde reactant is exhaust.

The applications of PF resins are commonly used in softwood plywood, oriented strand board (OSB) and laminated veneer lumber (LVL) because they are good in water and weather resistance. The disadvantage of PF resin is it has dark glue lines which are not desirable for interior or decorative applications (USDA, 2010).

2.2.1.5 Isocyanate Resins

Isocyanates are refer to the compound which contains isocyanates group (-N=C=O). The isocyanate group highly reactive with reactive hydrogen compounds such as amino and hydroxyl groups at room temperature. Nowadays, diphenylmethane diisocyanate (pMDI) resins commonly used in wood based industries. PMDI is the combination of the monomeric diphenylmethane diisocyanate and Methyelene Bridge polyatomic polyisocyanates (Pizzi *et. al*. 1994).

The advantages of pMDI resin are ability to form adhesive bonds in the presence of high moisture content and rapid curing. Mainly pMDI used in OSB production and the limitations of this resin are very hazardous and more expensive than UF and PF resins (Wilson, 1981).

2.2.2 Thermoplastic Resins

Thermoplastic resins are polymers that can soften or melt when heated, and solidify when cooled down. The softening and solidifying behaviors are reversible; hence, thermoplastic polymers can be melted and solidified many times without

degradation (Eckelman, 1997). The advantages of thermoplastic resin are higher in impact resistance compare to thermosetting composites and thermoplastic composites are able to reform and reshape at room temperature. However, there are some disadvantages in thermoplastic resin where the thermoplastic resin is naturally in a solid state, it is much more difficult to impregnate reinforcing fibre. The resin must be heated to the melting point, and pressure is required to impregnate fibres, and the composite must then be cooled under this pressure. This is a complex reaction (Johnson, 2012).

2.2.2.1 Poly (vinyl acetate) (PVAc) Resins

PVAc is one of the thermoplastic resins where softening when the temperature is raised to a particular level and hardening again when cooled. They are prepared by emulsion polymerization of vinyl acetate and other monomers in water under controlled conditions. PVAc resin is commonly known as 'white glue'. The advantage of odourless, non-flammable and obtain long curing time (Roger, 2000). The application of PVAc resin is commonly used in veneering, edge bending and joining in furniture production (Roger, 2000).

2.2.2.2 Hot Melt Resins

Hot melt adhesives are thermoplastic and lack high resistance to solvents and moisture, and are prone to creep. Hot-melt adhesive are sold in pelleted, chunk or stick form, which is melted and applied in molten form at temperatures of 350 - 400˚F. The adhesives cure by chilling. While they are not accepted as structural or

semi-structural adhesives, future developments may offer more durable glue bond suitable for construction.

2.3 Adhesives from natural resources

2.3.1 Animal adhesives

Animal glues are made up from animal hide, connective tissues and bones. They are also known as collagen derivatives. Animal glues are essentially a protein-based adhesive (Pourdier, 1948). Animal glue was once most commonly used to glue the wood for thousands of years until it was replaced by synthetic adhesives in the 20th century due to the properties of their many undesirable properties such as poor moisture resistance, susceptibility to biological degradation, and due to the price which is quite high (Salzberg, 1962). Animal adhesives are still applied in high-quality furniture and critical applications such as pianos.

2.3.2 Casein-based adhesives

Casein is held together by calcium ions and hydrophobic interactions which exist in between the molecules. Casein adhesive viscosity and consistency can be varied by several protein denaturants such as sulfur compounds, formaldehyde donors or metal salts complex (Salzberg, 1962; Sutermeister, *et.al.* 1939). Casein was the first adhesive used for structural wood composites. Now casein is used in the

door skin bonding with linseed oil added to improve the surface qualities (Sutermeister, *et.al.* 1939).

2.3.3 Blood-based adhesives

Blood is very sensitive adhesive based on heat, resulting in a very short hot-pressing curing time (Gossett, 1959). At present, the blood of animals, in the form of solid powder, used as a vital ingredient for foaming adhesive in the production of industrial and structural plywood (Eichholz, 1907). However, the blood of animals tends to degrade rapidly and have a limited number of suppliers (Hojilla-Evangelista, 2002).

2.3.4 Tannin-based adhesives

There are two types of tannins: hydrolysable tannins and condensed tannins. Hydrosable tannins composed of simple phenols and sugar esters with gallic and digallic acids whereas condensed tannins are chemically and economically important in making adhesives and resins. (Pizzi, *et.al*,1983). Tannin extracts generally have high viscosity so that a series of acid or alkali treatment needed to adjust the viscosity of tannin-based adhesive to make exterior-grade particleboard (Pizzi, 1978). In North American wood composites industry, tannin-based adhesives are rarely used because it is one of the limited resources, but in the southern hemisphere they have been widely used.

2.3.5 Lignin-based adhesives

Lignin is one of the main components of wood and it is the second most a natural polymer in the world. Lignin is mainly recovered as a waste product in pulp mills. Although lignin composed of phenyl propane units, it is actually a very complex polymer and does not respond as easily as phenol molecules. Other work focused on partial replacement of phenol by lignin in making PF resins. It has been found that methylolated lignin can replace up to 30% PF in making plywood under regular hot-press conditions without giving a negative impact on the adhesive strength (Tahir, 1990). At this time, some modified lignin is used for partial replacement of phenol.

2.3.6 Soy-based adhesives

Soy-based adhesive has been widely used in the production of wood composites (Yamakawa, 1998). However, wood composite panels bonded with soy-based adhesives have a relatively poor strength, poor water-resistance, and poor biological stability, and requires a long press times for their production. These weaknesses led to their replacement by petroleum-based adhesives. As discussed earlier, the petroleum-based adhesives have their own problems such as formaldehyde emissions and heavy reliance on petroleum and natural gas. With the lack of world oil reserves and growing concerns about the environment and public health, soy-based adhesive gain interest in recent years gradually.

2.4 Filler

Filler is a type of relatively non-adhesive substances which is added to an adhesive binder to improve its working properties, permanence, strength, or other qualities. Filler is added into adhesive to minimize the adhesive cost and lower the resin dissipates into the wood. One of the advantages of filler application is to fulfill the tiny hole and pore on the board surface in order to avoid weak bonding formation between adhesive and board (Jackson, 1976). Filler mainly can be divided into organic and inorganic filler.

2.4.1 Organic Filler

Organic filler is compounded with carbon chain. The examples of organic fillers are from natural sources such as soy bean meal, palm kernel meal, jatropha meal, rubber meal, almond shell flour, animal fibre, wood fibres and flour, kenaf fibres, sago, rice starch, cornstarch, henequen fibres, and pineapple-leaf fibres (Supri, *et.al* 2009). The advantages of organic filler are low in cost, low density and renewable nature (Janigova, *et. al*. 2000). The organic fillers caused enhancements in the rigidity and thermo mechanical resistance of the matrix in a way that was rather similar to the one observed for the inorganic filler. In organic filler a reduction in impact strength is observed (Mantia, 2005). Another characteristic of organic filler is its low in specific gravity (Zurale, 1998). Many different types of organic fillers can be added into polyethylene, polypropylene and other thermoplastic polymers. The addition of fillers into wood products will affect the mechanical, thermal, and water absorbent properties of the wood products.

2.4.2 Inorganic Filler

Inorganic filler is absence in carbon chain. Thermoplastic and thermosetting wood adhesives based industries using inorganic filler traditionally (Zurale, 1998). Inorganic fillers are inexpensive materials used to increase the density, smoothness and other properties of wood adhesive. Inorganic fillers or mineral fillers, such as clay, calcite, aragonite and talc, are inexpensive materials that are frequently used in wood industry. Fillers not only reduce the cost of wood adhesive, but also frequently impart performance improvements that might not otherwise be achieved by the reinforcement and resin ingredients alone. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. Also, filled resins shrink less than unfilled resins, thereby improving the dimensional control of molded parts. Important properties, including water resistance, weathering, surface smoothness, stiffness, dimensional stability and temperature resistance, can all be improved through the proper use of fillers. The thermosetting resin segment of the composite industry has taken advantage of the properties of fillers for many years. More recently, the thermoplastic industry has begun to make widespread use of inorganic fillers. Breakthroughs in chemical treatment of fillers that can provide higher filler loadings and improved laminate performance are accelerating this trend (ACMA, 2003).

2.4.2.1 Waste Rubber Powder as filler

The rate of waste tire rubber has increased day by day with rapid development of vehicles in the last decades (Shanmugharaj, Kim and Ryu, 2007).

The accumulation of large quantities of waste tire has brought serious environment problems. The waste tire rubber is ground into a powder, which is the main method to utilization and recycling of waste tire rubber in large scale. Waste rubber powder (WRP) filled polymer partially retains the cost reduction and process ability of polymers, with improvement in the impact resistance. Reuse or recycling of these waste tires becomes an important social subject and considerable efforts have been devoted to find new applications for waste tires (Li, et al., 2004). The WRP used as fillers and property modifiers in thermoplastic, elastomer, and thermoset blends.

However in most cases, the addition of WRP into polymer matrices have deleterious effect on the physical properties of finished products, even at low rubber contain. This is due to the poor matrix-filler adhesion and lack of reactive sites on WRP surface. In order to overcome this problem, modification of the WRP seems to be required various surface treatments such as high energy irradiation, chlorination, chemical grafting and so on (Shanmugharaj, et al., 2005).

2.5 Hardener

There are lots hardener used as curing agents in the resins adhesive. These are boric acid, phosphoric acid, acid sulphates, ammonium salts and many others. However, the most widely used products in industry are still ammonium chloride or ammonium sulphate. The driving force in the use of these salts as hardeners is their capacity to release acid, which decrease the pH of the resin and thereby accelerates curing. Ammonium chloride is a better hardener than hydrochloric acid, as the latter

produces weaker joints. Ammonium chloride is used to regulate pot life and rate of curing. The factors used to regulate the curing resin is by varying the concentration of the hardener in the resin, by changing the relative proportions of acid and salt and by changing the type of acid or salt composing the hardener (Pizzi, 1983).

2.6 Wood in Wood Gluing

The main three parameters such as wood, adhesive, and processing conditions are important in wood-based panels industry. One of the parameter woods involves several factors. Bonded wood often described as a chain of several links while the strength of an adhesive bond depends on various parameters. There are strength of glue line and its behaviour against stresses; influence of humidity, wood preservatives added; wood properties and mechanical properties of the wood material. Hence, wood surface and its interface with bond line play a very important role in wood-based panels industry.

A great variety of wood species are used as raw materials in the wood-based industry. The choice of the wood species used is often determined by the availability and the cost of raw material. Wood size and shape also some factors needed to consider in the wood choosing. The strength of a bond in a wood panel increases with the value of wood density for the range of 0.7 to 0.8g/cm^3. Above the density a decrease of the bond strength occurs. The performance and properties of wood-based panels are strongly influenced by the properties of the wood used. Thus, wood anisotropy and heterogeneous nature, the variability of its properties, and its

hygroscopicity have to be taken into consideration in all bonding processes (Lchmann, 1974).

The main parameters that influence the surface tension of the adhesive, when on the substrate, and therefore the possible bond strength are:

(i) Wood species (Scheiki and Dunky, 1996; Kazayawoko, et al., 1997; Kazayawoko, Neumann, and Balatinecz, 1997).

(ii) Roughness of the surface (Shupe, Hse, and Wang, 1998).

(iii) Cutting direction (radial/tangential) (Scheiki and Dunky, 1996; Kazayawoko, et al., 1997).

(iv) Early wood, latewood (Scheiki and Dunky, 1996; Shupe, et al., 1998).

(v) Direction of the spreading of the droplet during measurement of the contact angle (along or lateral to the direction of the fibers) (Shen, Nylund and Rosenholm, 1998).

(vi) Wood moisture content (Elbez, 1985).

(vii) Type of adhesives: UF resins (Scheiki and Dunky, 1996); PF resins (Shupe, et al., 1998).

2.7 Applications

Adhesive based on MUF condensates resin are mainly used in wood-based panels industry and other various industrial manufactures mainly for application from aqueous system like non-inflammable systems with relatively low production cost, for easily adapting to various curing conditions, for their cured films processing

good thermal properties and lacking sharp coloration (Langmaier, Sivarova, Mladek and Kolomaznik, 2004). Besides that, MUF resins have great commercial importance and are easy to be manufactured at low prices, especially as adhesives for metal, plastic and wood products (Que, Furuno, Katoh and Nishino, 2007; Guru, Tekeli, and Bilici, 2006). The other applications are MUF resins are used in furniture and joinery industry, including the manufacture of hollow-core doors. Besides that, MUF resins also applicable as sand core binders (Pizzi, 1994).

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

In order to achieve the objectives and the scope of research, several materials, experimental procedures or methodologies used in this project were explained with more detailed in this section. The chemicals and methods used in this study are depending exactly on the research needed by considering all factors. The materials and methodology used in this study are referred from literature studies.

3.2 Materials

The materials which were used in this study for the wood adhesive preparation are formaldehyde 37% solution, urea and melamine. Waste rubber powder (WRP) was purchased from local supplier. Materials for production of type II plywood was red-meranti veneer 300x300x3.3mm, it was provided by Shin Yang

Chemical Sdn.Bhd. The chemicals used to treat WRP are 65% nitric acid, 30% hydrogen peroxide and acetone.

3.3 Waste rubber powder (WRP) preparation

Waste Rubber Powder (WRP) was purchased from the local supplier. The Waste Rubber Powder was dried in oven for 16 hours. After that, the WRP was grinded with a shaker grinder and sieved by using sieving machine to obtain 100µm of WRP fine powder.

3.4 Treatment of waste rubber powder (WRP)

3.4.1 Treatment of waste rubber powder (WRP) with 20% nitric acid

Firstly, 65% concentrated nitric acid diluted into 20% nitric acid by using $M_1V_1 = M_2V_2$ formulae. Then, the waste rubber powder (WRP) was treated with 20% nitric acid. 100g of the WRP was placed in a500-ml beaker in an ice bath. Then, the oxidizing agent was introduced onto the WRP drop wise with continuous stirring until complete immersion of the waste rubber powder. The reaction mixture was heated to 100°C for about 3 hours with good stirring. The beaker containing the reaction mixture was covered and then left for 24 hours at room temperature. The treated WRP was washed thoroughly with distilled water until a neutral solution was obtained. The waste rubber powder (WRP) was then dried in oven at 60^oC for 16

hours. The waste rubber powder was grinded with shaker grinder and sieved by using sieving machine to obtain 100µm of WRP fine powder. Infrared spectroscopic analysis was carried out by using FTIR (Yehia, et al, 2003).

3.4.2 Treatment of waste rubber powder (WRP) with 30% hydrogen peroxide

Waste Rubber Powder (WRP) was treated with 30% hydrogen peroxide. 100g of the WRP was placed in a500-ml beaker in an ice bath. Then, the oxidizing agent was introduced onto the WRP drop wise with continuous stirring until complete immersion of the waste rubber powder. The reaction mixture was mixed to room temperature for good stirring. The beaker containing the reaction mixture was covered and then left for 24 hours at room temperature. The treated WRP was washed thoroughly with distilled water until a neutral solution was obtained. The waste rubber powder (WRP) was then dried in oven at 60^{o}C for 16 hours. The waste rubber powder was grinded with shaker grinder and sieved by using sieving machine to obtain 100µm of WRP fine powder. Infrared spectroscopic analysis was carried out by using FTIR (Yehia, et al, 2003).

3.4.3 Treatment of waste rubber powder (WRP) with acetone

The waste rubber powder will undergo oil extraction by using acetone in a soxhlet extractor for 10 hrs. It is repeated three times to ensure the oil was fully removed. The oil free waste rubber powder (WRP) was then dried in oven at 60^{o}C for 16 hours. The waste rubber powder was grinded with shaker grinder and sieved

by using sieving machine to obtain 100µm of WRP fine powder. Fourier Transform Infrared spectroscopic analysis was carried out by using FTIR (Fan, et al, 2011).

3.5 Melamine urea formaldehyde (MUF) based resin preparation

The main materials used to produce MUF resin are formaldehyde, melamine and urea. The formalin (37%) is poured into a three-necked flask, followed by melamine, $urea_1$ and sorbitol. Adjust the pH of the mixture to 8.5-9.0. The temperature of the mixture rose until it reaches 80^oC. Refluxing is continued until the end point is reached. Finally $urea_2$ is added upon achieving 60^oC. The resin is then cooled down to ambient room temperature and transferred to plastic container for further testing (Bono et. al, 2006, 2007).Finally, the viscosity of MUF resin checked by using Brookfield viscometer. The viscosity ensured between the range of 50 -60 cP.

3.6 Optimization and formulation of MUF based adhesive.

Resin often compound with filler and hardener (NH_4Cl) to produce adhesive which apply in plywood production. Filler helps in fills the hole on the veneer surface and reduce the resin usage in plywood industry. Meanwhile, it acts as viscosity control agent to control adhesive viscosity and minimize the plywood manufacture cost. The greater formulated adhesive with WRP as filler will increase the bonding strength between adhesive and veneer and reduce the production cost of

plywood. The parameter are pressing time, temperature of hot press process will be optimized.

3.6.1 Wood performance test (shear strength test)

The shear strength of type II plywood was determined by bonding test according to the Japanese Agriculture Standard (JAS) for structural plywood (Japanese Agriculture Standard for plywood, 2003) Total of ten plywood test pieces (25x80 mm) were tested for every trial plywood panel produced. Prior to the test, the test pieces were soaked in a hot water bath at 60˚C for 3 hours and followed by soaking it at cold water bath room temperature. Once the test pieces reached cold state, then it was used for shear strength test. Test was conducted using universal testing machine while the plywood test pieces were wet (Ong et. al, 2012).

3.6.2 Formaldehyde emission test

The formaldehyde emission test use to check the concentration of formaldehyde release from the plywood. The plywood specimen will placed in desiccators with small amount of distill water. The distill water will absorb the formaldehyde release from the plywood and the distill water sample will used to check the formaldehyde concentration by using UV/V spectrophotometer (JAS, 2003).

3.6.3 Water resistance test

The water resistance was determined by immersion delaminating test (soaking test). This test also adopted from the Japanese Agriculture Standard (JAS) for structural plywood. Here, six if plywood test pieces with size 75mm x 75mm were immersed in hot water bath at 70°C for 2 hours and followed of drying in the oven at 60°C for 3 hours. After the drying procedure, test pieces were inspected for the delaminating. The plywood produced here will be considered fail if any of the test piece delaminated (Bono, et al., 2010).

3.6.4 Experimental design

The experimental design was conducted using Response Surface Methodology (RSM). The effect of two independent variables of temperature and pressing time for the hot-press plywood were investigated.

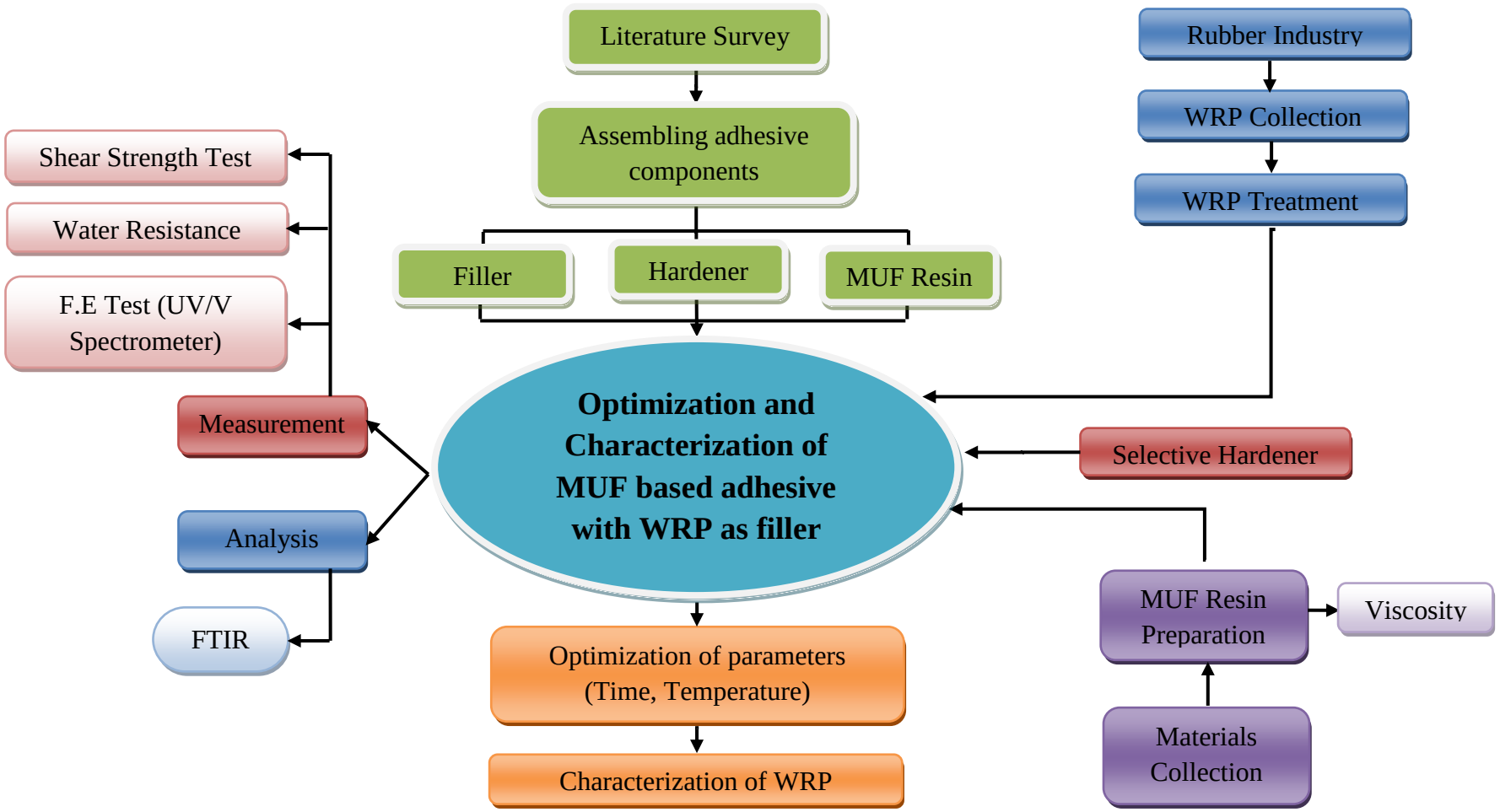

Figure 3.1 Flow chart of optimization and characterization of MUF based adhesive with WRP as filler

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This study is carried out to investigate the effect of hot-press temperature, hot-press time, optimization of processing parameter (temperature and pressing time), various composition of waste rubber powder (WRP) in wood adhesive and various modified waste rubber powder (WRP) in wood adhesive value by shear strength, water resistance, formaldehyde emission and Fourier Transform Infrared (FTIR) analysis of plywood and WRP based wood adhesive.

4.2 Effect of hot-press temperature on the mechanical properties and formaldehyde emission of the plywood

4.2.1 Shear strength

Effects of hot-press temperature on the shear strength of plywood panels are shown in Figure 4.1. At all hot-press temperatures studied, the shear strength exceeded the minimum industrial requirement of 0.7MPa (horizontal dashed line, Figure 4.1) for plywood. According to the standard, any plywood panel having the shear strength less than 0.7 MPa is considered fail. The average shears strength value significantly increased by 27.4% when hot-press temperatures were raised from 100 to 125°C. Moreover, the average shears strength value increase by 29.9% when hot-press temperatures were raised from 125 to 150°C. However, the average shears strength value significantly decreased by 16.8% when hot-press temperatures were raised from 150 to 175°C. The function of the hot-pressing in plywood production is to provide the necessary heat and pressure for the curing the adhesive, and consolidating the discrete particles into a solid board. During the hot-pressing, the heat is transferred from surface to core so the core temperature is generally lower than that of the surface temperature. Full curing of an adhesive can be accomplished by increasing hot-press temperature at a fixed hot-press time. However, if the hot-press temperature was higher than that needed for full curing of the adhesive at a fixed hot-press time, mechanical properties of resultant plywood panel would either remain the same or decreased due to the partial degradation of MUF adhesives and wood particles (Youngquist, 1999). Therefore, hot-press temperature should be optimized. At a fixed hot-press time of 150s, it appeared that the adhesive was

already fully cured at 150°C and further increase in the hot-press temperature significantly decrease the shear strength value. Besides that, filler also plays its role in increasing temperature of the curing adhesive. In addition to adding fillers, other variables can be altered in the adhesive to reduce residual stresses and many studies have been performed to measure factors that affect shear strength. Increasing the cure temperature increases the residual stress (Chair, *et.al*. 2003). Meanwhile, the value of shear strength decrease after 175˚C because the melting point of waste rubber powder is within the range of 160 -180˚C where within this temperature the waste rubber powder began to degrade in MUF resin and the internal bonding between MUF resin and WRP filler increase. As a result, interaction between veneer and adhesive reduce (WRAP, 2008). With the shear strength test considered, 150°C appeared maximum hot-press temperature and was used for subsequent investigations.

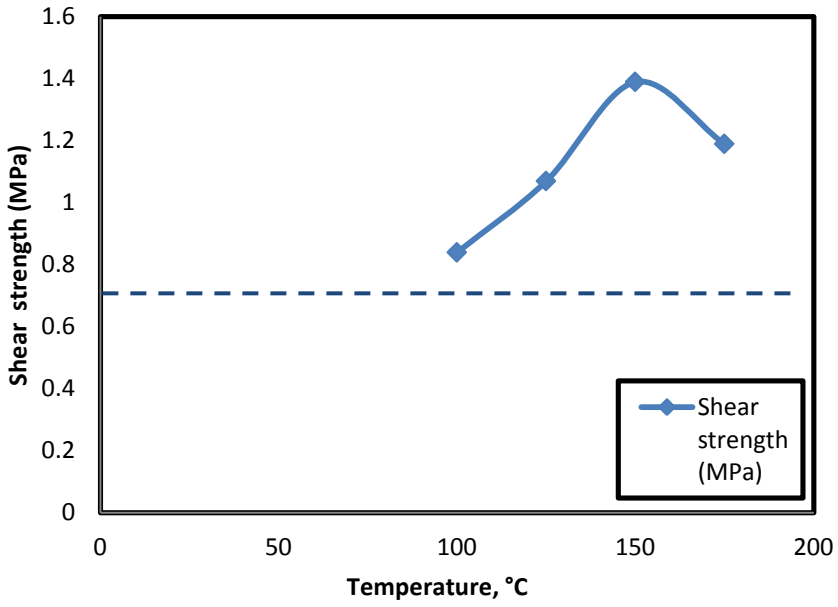

Figure 4.1 Effect of hot-press temperature on the shear strength of plywood using waste rubber powder based wood adhesive. [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press time 150s. Data are the average shear strength of ten specimen plywood (MPa)]

4.2.2 Water resistance

Effects of hot-press temperature on the water resistance of plywood panels are shown in Table 4.1. The maximum delamination permitted in any one glue line is 1% of the total glue line length, i.e 0.075mm. From the result obtained, wood specimens delaminated at temperatures of 100 and 175 ˚C where the number of failure specimen are 3 and 2 out of 6 total specimen respectively. This delaminating test is related with shear strength test (Walfrod, 2010). Since the adhesive is not fully cured at the temperature of 100˚C, the interaction between veneer and adhesive is low and the wood specimens are delaminated. However, the optimum curing adhesive of the wood panels are fall in the range of temperature 125 - 150˚C. Therefore, the overall plywood test for the both temperatures is pass. Meanwhile, there are 2 wood specimens delaminated at the temperature of 175˚C. This situation happens because, the melting point of the waste rubber powder is within the range of 160 -180˚C where within this temperature the waste rubber powder began to degrade in MUF resin and the internal bonding between MUF resin and WRP filler increase. As a result, interaction between veneer and adhesive reduce.

Table 4.1 Water resistance performance of plywood using waste rubber powder based wood adhesive

Temperature, °C	Delaminating test (No. of failure/ total specimen)	Overall plywood test: Pass (P) or Fail (F)
100	3/6	F
125	0/6	P
150	0/6	P
175	2/6	F

4.2.3 Formaldehyde emission

Figure 4.2 shows the effect of processing parameters on the formaldehyde emissions of plywood panels bonded with the waste rubber powder with MUF adhesive. The formaldehyde emissions decreased as the hot press temperature increased from 100˚C to 175˚C. An elevated hot press temperature improved the extent of cure of the adhesive and reduced the residual free formaldehyde in the cured adhesive (Gao et.al., 2011).

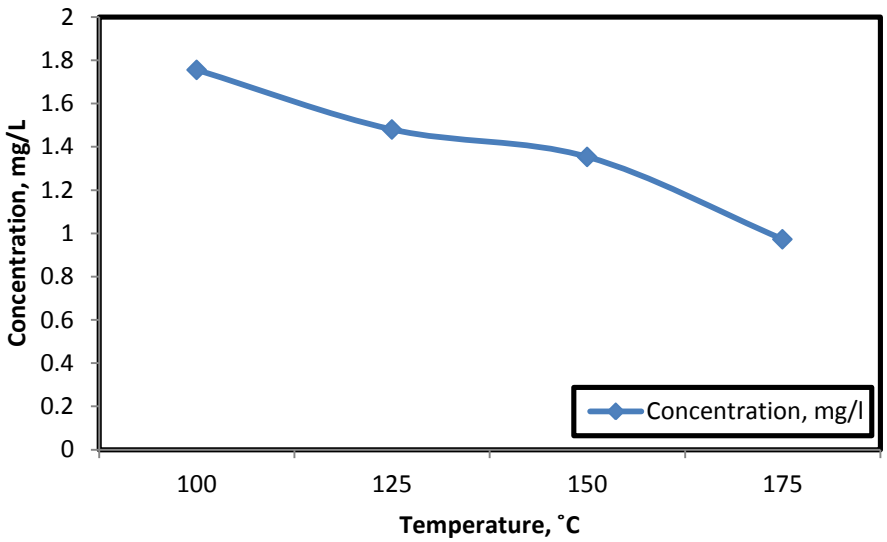

Figure 4.2 Effect of hot-press temperature on the formaldehyde emission of plywood using waste rubber powder based wood adhesive. [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press time 150s. Data are the average formaldehyde emission of ten specimen plywood (MPa)]

4.3 Effect of hot-press time on the mechanical properties and formaldehyde emission of the plywood

4.3.1 Shear strength

Effects of hot-press time on the shear strength of plywood are shown in Figure 4.3. The shear strength significantly increased when the hot-press time was raised from 50 to 250s. However, the shear strength markedly decreased when the hot-press time was increased from 250 to 450s. The shear strength at most of hot-press times tested met the minimum industrial requirement (horizontal dashed line, Figure 4.3) except for hot-press time at 50s. According to the standard, any plywood panel having the shear strength less than 0.7 MPa is considered fail. According to Lambuth (2003), the hot-press time for initiation of curing of adhesive at constant hot-press temperature 125˚C is start from 75s. This is the reason why, woo d panel at hot-press time at 50s is failed. Full curing of an adhesive can be accomplished by increasing hot-press time at a fixed hot-press temperature. However, if the long hot-press time was longer than that needed for full curing of the adhesive, mechanical properties of resultant plywood panels would either remain the same or decreased due to the partial degradation of adhesives and wood particles (Youngquist, 1999). Therefore, hot-press time should be optimized. At a fixed hot-press temperature of 125°C, it appeared that the adhesive was already fully cured at the hot-press time of 250s. The decreased shear strength value at the hot-press time of 450s over 250s implied that the hot-press time of 450s was too long (Figure 4.3).

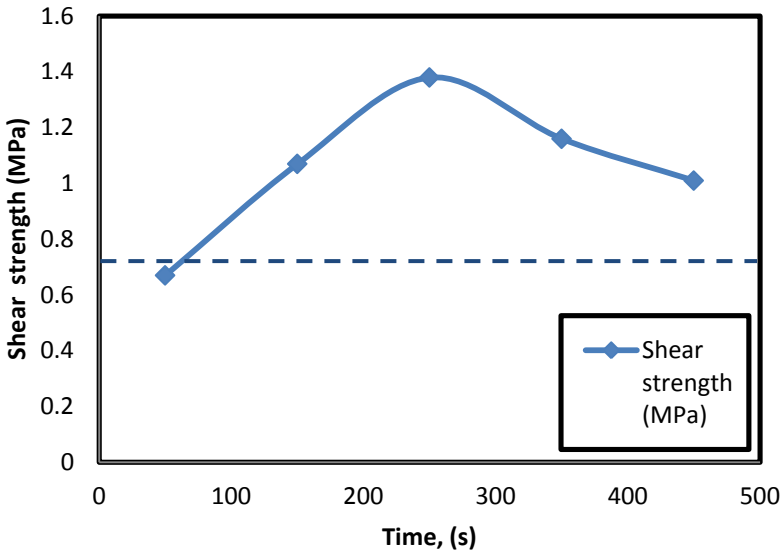

Figure 4.3 Effect of hot-press time on the shear strength of plywood using waste rubber powder based wood adhesive. [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press temperature 125˚C. Data are the average shear strength of ten specimen plywood (MPa)]

4.3.2 Water resistance

Effects of hot-press time on the water resistance of plywood panels are shown in Table 4.2. The maximum delamination permitted in any one glue line is 1% of the total glue line length, i.e 0.075mm. From the result obtained, wood specimens delaminated at time of 50, 350 and 450 s where the number of failure specimen are 3, 2 and 2 out of 6 total specimen respectively. This delaminating test is related with shear strength test (Walfrod, 2010). Since the adhesive is not fully cured at the time of 50s, the interaction between veneer and adhesive is low and the wood specimens are delaminated. However, the optimum curing adhesive of the wood panels are fall in the range of time 150 – 250 s. Therefore, the overall plywood test for the both time is pass. Meanwhile, there are 2 and 3 wood specimens delaminated at the time of 350 and 450 s respectively. This situation happens because, the long hot-press time was longer than that needed for full curing of the adhesive, mechanical properties of

resultant plywood panels would either remain the same or decreased due to the partial degradation of adhesives and wood particles (Youngquist, 1999).

Table 4.2 Water resistance performance of plywood using waste rubber powder based wood adhesive

Time, s	Delaminating test (No. of failure/ total specimen)	Overall plywood test: Pass (P) or Fail (F)
50	3/6	F
150	0/6	P
250	0/6	P
350	2/6	F
450	5/6	F

4.3.3 Formaldehyde emission

The hot press time curves showed that the effects of hot press time from 50 to 450 s on formaldehyde emissions of plywood bonded by waste rubber powder with MUF adhesive were decrease. The higher curing adhesive time showed that lower the formaldehyde emissions of plywood. A lower level of curing adhesive time brought more free formaldehyde into plywood to increase the formaldehyde emissions (Gao et.al., 2011).

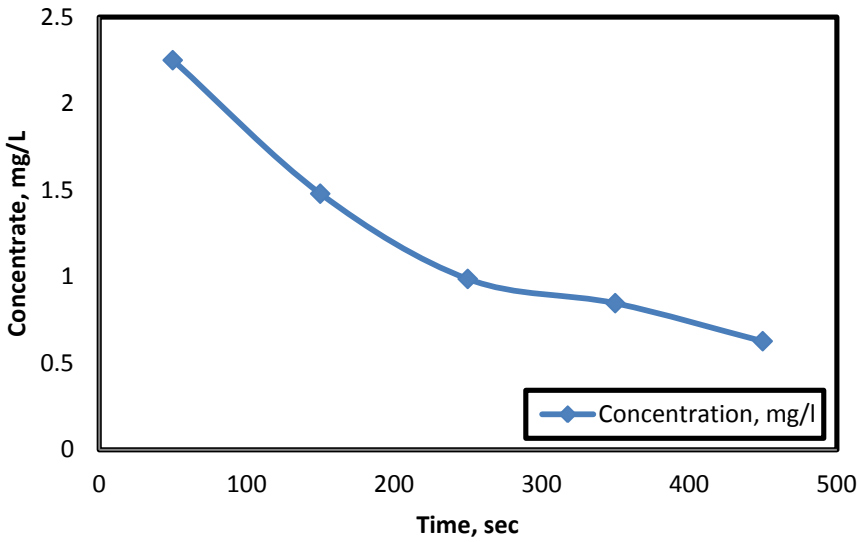

Figure 4.4 Effect of hot-press time on the formaldehyde emission of plywood using waste rubber powder based wood adhesive. [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press temperature 125˚C. Data are the average formaldehyde emission of ten specimen plywood (MPa)]

4.4 Optimization of melamine urea formaldehyde (MUF) with waste rubber powder (WRP)

Initial range of temperature between 125 to 175˚C and pressing time around 150 to 350s were selected for the experiment. However, the experimentation at the lower ranges of temperature and pressing time were impossible to evaluate the results. This is due to the veneers failed to meet the industrial requirements. In addition, the experiment for the above pressing time 350 s was also found to be failed. This due to the interaction between veneer and core adhesive is weaker and the core adhesives degrade after 250s. As concluded that, the suitable range of temperature 125^{o}C to 175^{o}C and the pressing time is 150s to 350s for the experimental study.

Table 4.3 Average shear strength and formaldehyde emission performance of hot-press temperature and time for waste rubber powder (WRP)

No. of run	Temperature, x_1(˚C)	Pressing Time, x_2 (s)	Shear strength, Y_1 (MPa)	Formaldehyde, Y_2 (mg/L)
1	125	150	1.07	1.4798
2	150	250	1.52	1.0347
3	175	150	1.19	0.9723
4	150	250	1.48	1.1173
5	150	350	1.34	1.0084
6	175	350	1.22	0.5762
7	150	150	1.39	1.3531
8	125	250	1.38	0.9873
9	125	350	1.16	0.8473
10	150	250	1.4	1.2955
11	175	250	1.32	0.6438
12	150	250	1.45	1.0851
13	150	250	1.5	1.1793

4.4.1 Development of regression model equation

A polynomial regression equation was developed by using three level factorial designs 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 is given in Table 4.3. The shear strength and formaldehyde emission of MUF adhesive with WRP was found from 1.07 MPa to 1.52 MPa and 0.58mg/L to 1.48mg/L respectively.

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 formaldehyde emission performance of plywood, quadratic models was suggested by the software and selected due to higher order polynomial. The final empirical models in term of coded factors for shear strength and formaldehyde emission performance (Y_1) and (Y_2) is shown in Equation 1 and Equation 2 respectively:

$$Y_1 = 1.48 + 0.020x_1 + 0.012x_2 – 0.16x_1^2 – 0.15\ x_2^2 – 0.015\ x_1\ x_2 \quad (1)$$

$$Y_2 = 1.13 – 0.19\ x_1 – 0.23\ x_2 – 0.27\ x_1^2 + 0.094\ x_2^2 + 0.059\ x_1\ x_2 \quad (2)$$

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. The R^2 value for the equation (1) and (2) was 0.8945 and 0.9255 respectively. This indicated that 89.45% of the total variation in the shear strength and 92.55% of total variation in the formaldehyde

performances of the plywood. The closer the R^2 value to unity, the better the model will give predicted values which are closer to the actual values for the response. The R^2 of 0.8945 for Eq. 1 and 0.9255 for Eq. 2 were considered relatively high, indicating that there was good agreement between the experimental and the predicted shear strength and formaldehyde emission performance of plywood from this model.

Table 4.4 Analysis of variance (ANOVA) for response surface quadratic model for shear strength of plywood

Source	Sum of Squares	DF	Mean square	Value	Prob > F	Comment
Model	0.214684	5	0.042937	11.87219	0.0026	significant
x_1	0.0024	1	0.0024	0.66361	0.4421	
x_2	0.000817	1	0.000817	0.225812	0.6491	
Y_1	0.071622	1	0.071622	19.80377	0.0030	
Y_2	0.058901	1	0.058901	16.28624	0.0050	
x_1x_2	0.0009	1	0.0009	0.248854	0.6332	
Residual	0.025316	7	0.003617			
Lack of Fit	0.016516	3	0.005505	2.502438	0.1983	not significant
Pure Error	0.0088	4	0.0022			

Table 4.5 Analysis of variance (ANOVA) for response surface quadratic model for formaldehyde emission of plywood

Source	Sum of Squares	DF	Mean square	Value	Prob > F	Comment
Model	0.741759	5	0.148352	17.38926	0.0008	significant
x_1	0.209851	1	0.209851	24.59803	0.0016	
x_2	0.314325	1	0.314325	36.84411	0.0005	
Y_1	0.20332	1	0.20332	23.83244	0.0018	
Y_2	0.024341	1	0.024341	2.853126	0.1350	
x_1x_2	0.013971	1	0.013971	1.637659	0.2414	
Residual	0.059719	7	0.008531			
Lack of Fit	0.019405	3	0.006468	0.641791	0.6272	not significant
Pure Error	0.040314	4	0.010078			

4.4.2 Statistical analysis

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. From the Table 4.4 and Table 4.5, the model F-values are 11.87 and 17.39 respectively and Prob. < 0.0026 and Prob. < 0.0008 implied that this models were significant. In this case, x_1, x_2 and x_1x_2 were insignificant to the response from Table 4.4 whereas x_1, x_2, and x_1x_2 were significant to the response in Table 4.5. 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. Figure 4.5 and Figure 4.6 show the predicted values versus the experimental values for shear strength and formaldehyde emission performance. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the models developed were successful in capturing the correlation between operating parameter to the response. Figure 4.7 and Figure 4.8 shows the three dimensional response surface which was constructed to show the effect of pressing time and temperature of filler on the plywood shear strength and formaldehyde emission performance.

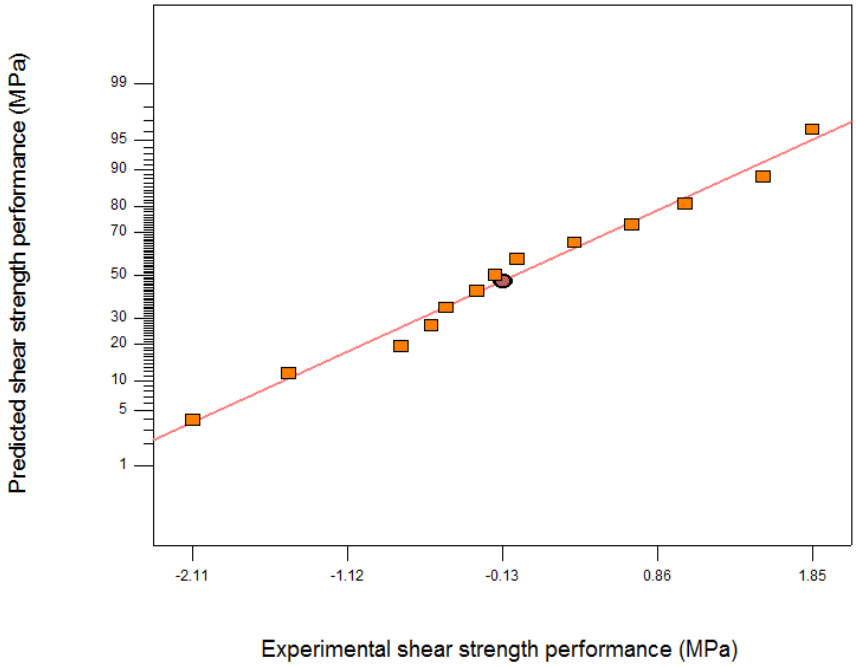

Figure 4.5 Predicted versus experimental shear strength performance (MPa)

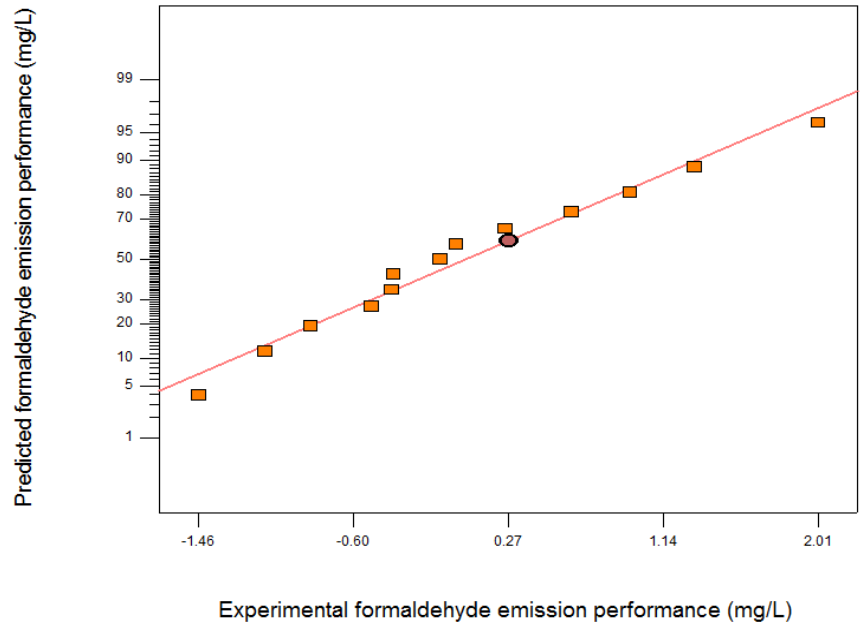

Figure 4.6 Predicted versus experimental formaldehyde emission performance (MPa)

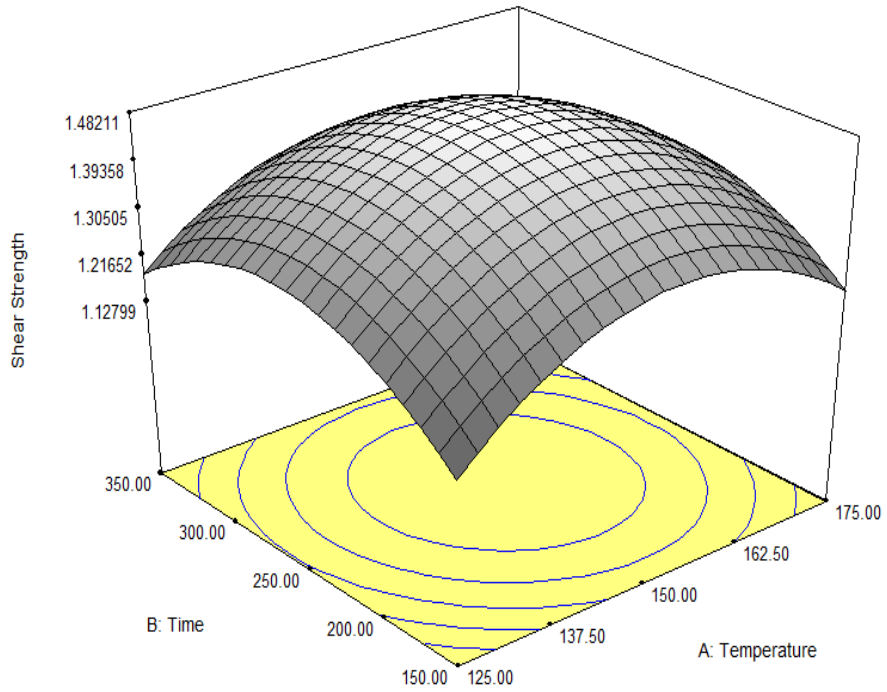

Figure 4.7 Design expert plots for shear strength performance

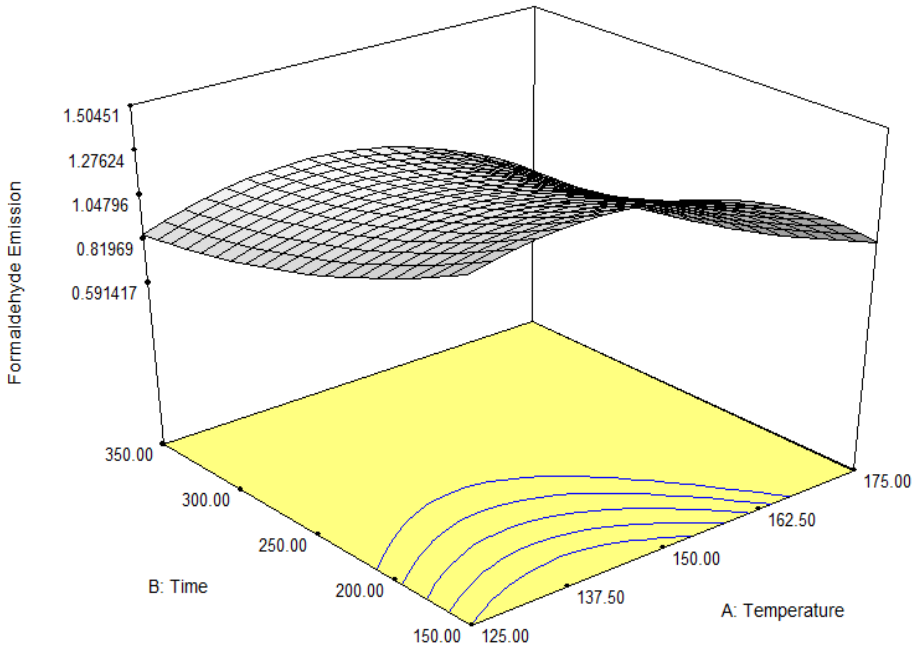

Figure 4.8 Design expert plots for formaldehyde emission performance

4.4.3 Process Optimization

Three level factorial has been used to optimize the parameters affecting the shear strength and formaldehyde emission performances response. In this optimization analysis, the target criteria were set as maximum values for shear strength and minimum values for formaldehyde emission while the values for variables were set in the ranges being studied. The predicted and experimental results of shear strength and formaldehyde emission obtained at optimum conditions are shown in Table 4.6. The optimum shear strength and formaldehyde emission performance of WRP were obtained by using pressing temperature 171.6^{o}C and time 269.18s was 1.37 MPa and 0.7315mg/L. It was observed that the experimental values obtained were in good agreement with the value calculated from the models, with relatively small errors, which only 1.46% and 3.72% for shear strength and formaldehyde emission of WRP respectively.

Table 4.6 Model validation

Pressing temperature x_1 (˚C)	Pressing time x_2 (s)	Shear strength performance (MPa)			Formaldehyde emission (mg/L)		
		Predicated	Experimental	Error (%)	Predicated	Experimental	Error (%)
171.60	269.27	1.37	1.32	3.65	0.7315	0.7052	3.60

4.5 Effect of various composition of waste rubber powder (WRP) in wood adhesive on the mechanical properties and formaldehyde emission of the plywood

4.5.1 Shear strength

Effects of various composition of waste rubber powder (WRP) in wood adhesive on the shear strength of plywood panels are shown in Figure 4.9. The average shear strength value decreased when the adhesive usage was reduced from 13 to 8 wt.% and then further decreased when the composition of WRP in wood adhesive usage was further reduced from 8 to 5 wt.%. The average shear strength value significantly decreased again when the composition usage of WRP in wood adhesive was further increased from 13 to 23 wt. %. The average shear strength values at all composition of WRP in wood adhesive tested exceeded the minimum industrial requirement (horizontal dashed line, Figure 4.9) except for 0 and 5wt. % composition. In average shear strength value at composition of 0 and 5 wt. % of WRP in wood based adhesive did not meet the industrial requirement because in 0 and 5wt. % of WRP there is no and very less filler compounded in the adhesive (Pizzi, 1994). The amount of resin decrease when the amount of filler of WRP in wood based adhesive increase, therefore the average values of shear strength decrease. The main function of filler is to fill up the small holes in plywood whereas excess filler composition may cause excess filler appear on the surface of core adhesives and the interaction between veneer and core adhesive decrease. This is the reason why, the shear strength value decrease from 18 to 23 wt% composition. The amount of composition of WRP in wood based adhesive decrease meanwhile the

amount of resin increase. However, the values of shear strength decrease because filler in the adhesive is used to fill up all small holes at the surface of wood to prevent or to reduce the formation of stronger bonding. Therefore, at optimum hot-press temperature and time, the optimum amount of composition of WRP in wood based adhesive is 13 wt. %.

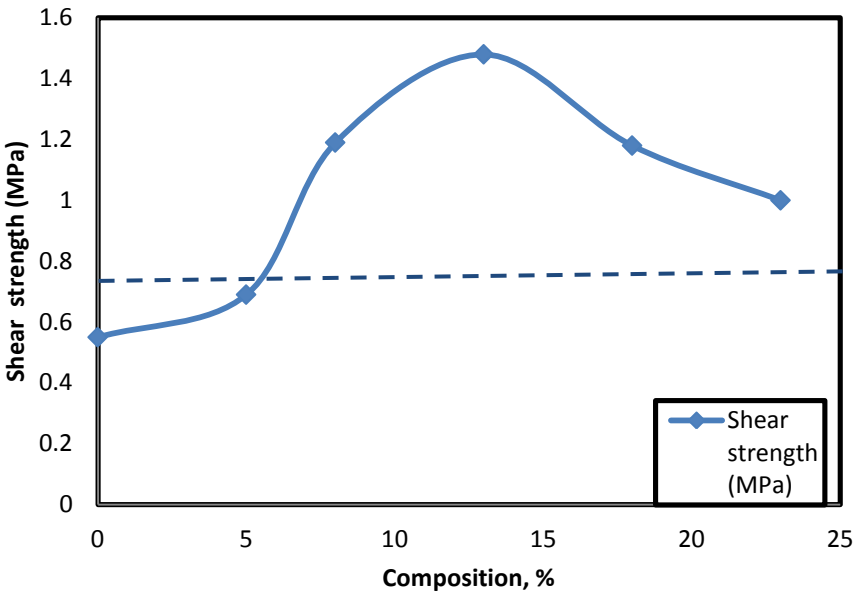

Figure 4.9 Effect of various composition of waste rubber powder (WRP) in wood adhesive on the shear strength of plywood. [hot-press temperature 172°C; hot-press time270s. Data are the average shear strength of ten specimen plywood (MPa)]

4.5.2 Water resistance

Effects of various composition of waste rubber powder (WRP) on the water resistance of plywood panels are shown in Table 4.7. The maximum delamination permitted in any one glue line is 1% of the total glue line length, i.e 0.075mm. From the result obtained, wood specimens delaminated at composition of 0, 5, and 8wt.% where the number of failure specimen are 6, 5 and 3 out of 6 total specimen respectively. This delaminating test is related with shear strength test (Walfrod,

2010). Since the composition of filler is not sufficient for 0, 5 and 8wt%, the physical bonding between the veneer and adhesive is weaker. Therefore, the three types of composition of WRP of wood specimens failed. However, when the composition weight percentage increase from 13 to 23 wt%, the overall plywood test for particular specimens pass because the physical bonding between the veneer and adhesive is getting stronger due to the more composition of WRP as filler. Therefore, the interaction between veneer and core adhesive increase as the composition percentage of WRP is increase.

Table 4.7 Water resistance performance of plywood using various composition of waste rubber powder (WRP) in wood adhesive

Composition, %	Delaminating test (No. of failure/ total specimen)	Overall plywood test: Pass (P) or Fail (F)
0	6/6	F
5	5/6	F
8	3/6	F
13	0/6	P
18	0/6	P
23	0/6	P

4.5.3 Formaldehyde emission

The curves showed that the effects of various compositions from 0wt. % to 23 wt. % of WRP on formaldehyde emissions of plywood bonded with MUF adhesive were decrease. The higher composition of filler used, the lower the emission of formaldehyde. Fillers of both organic and inorganic origins contribute to rheological control of the fluid system, particularly in reducing the spreading and penetrating of the adhesive out from wood. (Frihart, *et. al.* 2009). Due to that, at optimum hot-pressing temperature and time the higher composition of WRP,

penetration of formaldehyde from wood is less to environment because the filler will fill in the holes or gaps between the veneer and core adhesive. As s result, the formaldehyde finds hard to emit from plywood. This significantly proves that higher the composition of filler, lower the formaldehyde emission.

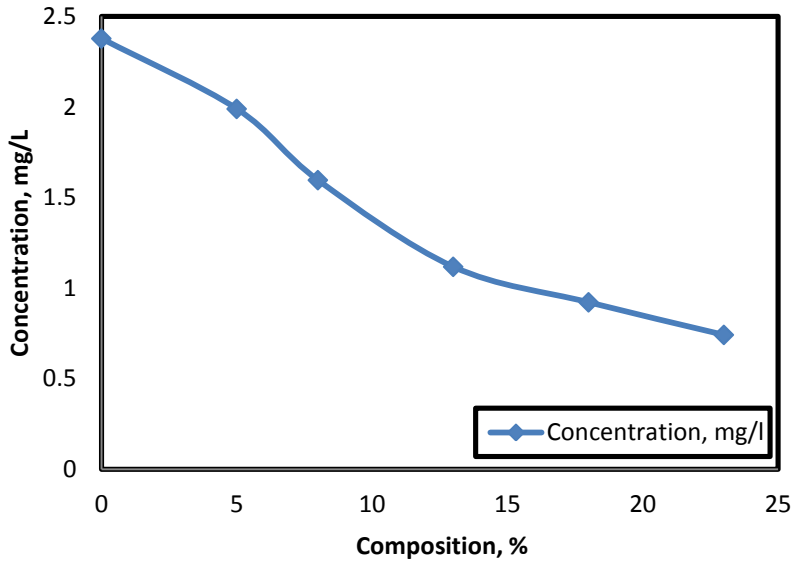

Figure 4.10 Effect various composition of WRP on the formaldehyde emission of plywood using MUF wood adhesive. [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press temperature 172˚C, hot-press time 270s. Data are the average formaldehyde emission of ten specimen plywood (MPa)]

4.6 Effect of various treated and untreated waste rubber powder (WRP) in wood adhesive on the mechanical properties and formaldehyde emission of the plywood

4.6.1 Shear strength and formaldehyde emission

Effect of various treated waste rubber powder (WRP) in wood adhesive on the shear strength of plywood are showed in and Figure 4.11. The first treatment of WRP is with 20% nitric acid, second treatment is with 30% Hydrogen Peroxide with WRP, and the following treatment is with acetone and WRP and finally untreated or pure WRP. The average value of shear strength of the 20% nitric acid with WRP was significantly higher than that of other treated WRP components. The average shear strength value of the treated WRP with 30% Hydrogen Peroxide and acetone was statistically the same while the untreated WRP shows the least shear strength. The average shear strength values of all treated and untreated WRP met the minimum industrial requirement (horizontal dashed line, Figure 4.11). Results from Figure 4.11 confirmed that treatment of WRP with 20% nitric acid was higher than others because the rheumatic characteristics and physic-mechanical properties at room temperature are optimum. On the other hand, the creation of new functional groups because of chemical oxidation increases the values of average shear strength (Yehia, et al. 2003). As the average shear strength value increases while the average formaldehyde emission for treated and untreated WRP is decrease. This shows that interaction between the veneer and core adhesive is higher for treated WRP and therefore less formaldehyde is emitting from plywood. According to Figure 4.11, higher the values of shear strength of wood panels obtain lower the formaldehyde

emission. As a result, WRP treated with 20% HNO_3 plywood specimen which obtain higher shear strength and lower formaldehyde emission considered that it can be applicable in wood based industry.

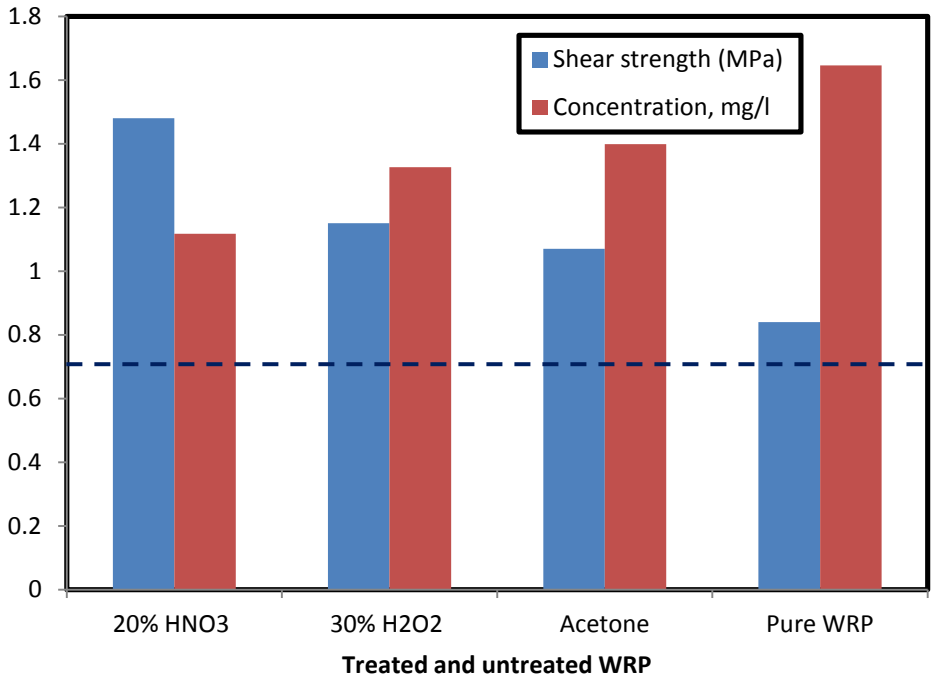

Figure 4.11 Effect of various treated and untreated waste rubber powder (WRP) in wood adhesive [surface adhesive usage (dry basis on wood particles), 13wt%; hot-press temperature 172˚C, hot-press time 270s. Data are the average shear strength and formaldehyde emission of ten specimen plywood (MPa)]

4.6.2 Water resistance

Effects of treated and untreated waste rubber powder (WRP) on the water resistance of plywood panels are shown in Table 4.8. The maximum delamination permitted in any one glue line is 1% of the total glue line length, i.e 0.075mm. From the result obtained, wood specimens delaminated for treated WRP such 30% H_2O_2, acetone and untreated WRP where the number of failure specimen are 3, 2 and 3 out

of 6 total specimen respectively. This delaminating test is related with shear strength test (Walfrod, 2010). This significantly shows that interaction between the veneer and core adhesive is weak or less due to the less interaction between MUF resin and WRP. This statement's justification is proved in FTIR analysis section.

Table 4.8 Water resistance performance of plywood using various treated waste rubber powder (WRP) in wood adhesive

Treatment of WRP	Delaminating test (No. of failure/ total specimen)	Overall plywood test: Pass (P) or Fail (F)
20% HNO_3	0/6	P
30% H_2O_2	3/6	F
Acetone	2/6	F
Pure WRP	3/6	F

4.7 FTIR analysis

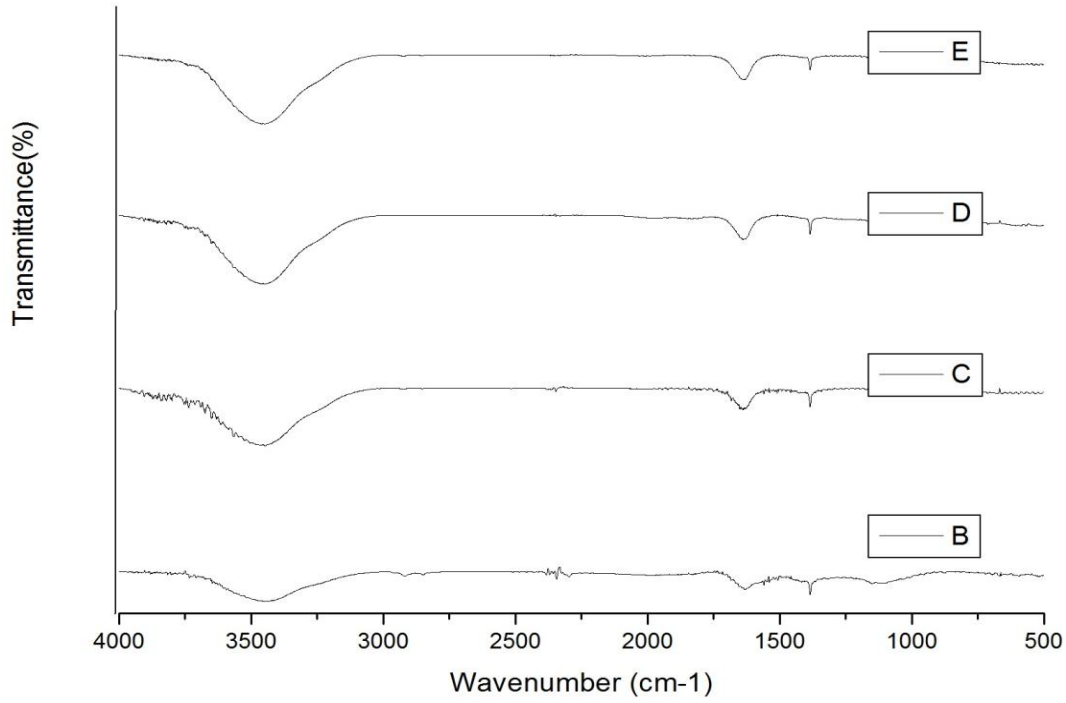

Figure 4.12 FTIR spectra of WRP with and without treatment

The FTIR spectra of E, D, C and B indicates the untreated WRP, acetone + WRP, 30% H_2O_2 + WRP and 20% HNO_3 + WRP respectively are shown in Figure 4.12. As shown in Figure 4.12, the spectra of WRP with and without treatment are closely matching at characteristic peaks of a broad band peaks of a hydrogen bonded O-H and N-H groups at 3500 -3300, the peaks at 2930 - 2918, 2853 -2849 cm^{-1} correspond to the C-H asymmetric and symmetric stretching vibration of CH_2 respectively. The peaks at 1638cm^{-1} is attributed to C=O stretching due to partial oxidation during the grinding of waste rubber powder. The peaks of WRP treated with 20% HNO_3 at 1565 cm^{-1} may due to the benzene ring skeleton vibration and a shoulder formed at 1424 cm^{-1} which lead to the deformation of saturated C-H bond (Long, et.al. 2012). The peak at 1149 cm^{-1} corresponds to the stretching of C-O bond of tertiary alcohol. The FTIR spectrum analysis provided that broad bands at 3500 –

3300 cm^{-1} correspond to the hydrogen bonded O-H and N-H groups while the peaks at 1638 cm^{-1} is corresponding to C=O stretching. It is noted that in Figure 4.12, two spectra are more or less same without some expectations, and these expectation are observed that after WRP treated with 20% HNO_3, where the peaks for stretching vibration of N-H and C=O groups are shifted from 3441 cm^{-1} and 1633 cm^{-1} to 3447cm^{-1} and 1638cm^{-1} respectively. As a result, a certain amount of red shift observed for both the groups which indicating the existence of interactions (Ong, *et. al*., 2011). Therefore, WRP treated with 20% HNO_3 is ready to interact with MUF resin. Meanwhile there is less and almost no change between untreated WRP and WRP treated with 30% H_2O_2 and acetone treatment whereas there are more red shifts occurs between WRP and 20% HNO_3 which allows interaction from resin. Therefore, 20%HNO_3 treated WRP is chosen for further analysis in this study.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study on the optimization and formulation of melamine urea formaldehyde (MUF) with waste rubber powder (WRP) as filler on the effect of hot-press temperature, hot-press time, various compositions of WRP and treated and untreated WRP in wood adhesive value by shear strength, formaldehyde emission, water resistance and Fourier Transform Infrared (FTIR) analysis. In addition, optimization of hot-press temperature and hot-press time conducted by using RSM software. Through analysis of the response surface, pressing temperature and different types of extenders imposed the greater effect on the shear strength and formaldehyde emission performance. The optimum shear strength and formaldehyde emission performance of WRP was obtained by using pressing temperature 171.60˚C and time 269.27s was 1.37MPa and 0.7315mg/L. It was observed that the experimental value obtained by were in good agreement the value calculated from the models, with relatively small errors. Besides that, this work presented that

extender is an important in enhancing the wood performance for wood adhesive. The sufficient amount of filler will increase the shear strength and decrease the formaldehyde emission of wood adhesive (Ong, *et.al*. 2011).

5.2 Recommendations

To improve the performance of wood adhesive, there are some recommendations. Firstly, in the preparation of MUF resin, the viscosity of MUF will be over range. Therefore, it is recommended that in the preparation of MUF resin consistently monitor the temperature and pH. Secondly, in the treatment of WRP, there will be hazardous smoke will be release. Due to that, it is necessary to run the experiment in fume hood and wear personal protective equipment (PPE). Thirdly, the hot-press molding machine has some problem where it takes some time to release the plywood sample. In conjunction, release the sample from the machine earlier 12 s in order to obtain accurate result. Besides that, most of results from UV/Vis spectrometer are varied. In order to reduce the error, it is suggested that calibrate UV/Vis spectrometer each time going to use and take 3 readings and obtain the average. This research can be improved by formulating the MUF resin in order to get the optimization results. In addition, interaction between veneer, resin and filler can be study by using scanning electron microscopic (S.E.M) and light microscopic.

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APPENDIX A

EFFECT ON MECHANICAL PROPERTIES OF MUF WITH WRP

A.1 Effect of hot-press temperature on the mechanical properties of the plywood

Table A.1 Average shear strength performance of plywood using waste rubber powder based wood adhesive

Temperature, °C	100	125	150	175
Run	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)
1	0.80	0.78	1.37	1.17
2	0.66	1.35	1.22	1.25
3	0.92	1.30	1.45	1.42
4	0.90	0.97	1.42	1.05
5	0.75	0.92	1.47	1.04
6	0.97	0.97	1.42	1.07
7	0.65	1.02	1.45	1.20
8	1.09	1.30	1.42	1.18
9	1.09	1.17	1.18	1.29
10	0.58	0.95	1.48	1.19
Average	0.84	1.07	1.39	1.19

A.2 Effect of hot-press time on the mechanical properties of the plywood

Table A.2 Average shear strength performance of plywood using waste rubber powder based wood adhesive

Time,(s)	50	150	250	350	450
Run	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)
1	0.69	0.78	1.47	1.53	1.20
2	0.77	1.35	1.32	1.20	0.94
3	0.67	1.30	1.22	1.12	0.90
4	0.68	0.97	1.57	1.17	0.92
5	0.73	0.92	1.27	1.40	0.80
6	0.53	0.97	1.35	0.88	0.95
7	0.61	1.02	1.47	0.83	1.25
8	0.81	1.30	1.15	1.15	0.97
9	0.68	1.17	1.33	1.37	1.27
10	0.56	0.95	1.60	0.90	0.92
Average	0.67	1.07	1.38	1.16	1.01

A.3 Effect of various composition of waste rubber powder (WRP) in wood adhesive on the mechanical properties of the plywood

Table A.3 Average shear strength performance of various composition of waste rubber powder (WRP) in wood adhesive on plywood

Composition, %	0	5	8	13	18	23
Run	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)
1	0.50	0.67	1.30	1.15	1.18	0.99
2	0.53	0.69	1.22	1.40	0.97	1.07
3	0.58	0.71	1.30	1.55	1.32	1.15
4	0.43	0.65	1.20	1.52	1.25	0.74
5	0.63	0.70	0.93	1.67	1.27	0.94
6	0.43	0.69	0.97	1.48	1.10	0.99
7	0.56	0.71	1.25	1.50	1.14	0.84
8	0.61	0.73	1.20	1.55	1.17	1.15
9	0.65	0.68	1.33	1.44	1.19	1.10
10	0.63	0.65	1.17	1.50	1.18	1.05
Average	0.55	0.69	1.19	1.48	1.18	1.00

A.4 Effect of various treated waste rubber powder (WRP) in wood adhesive on the mechanical properties of the plywood

Table A.4 Average shear strength performance of various treated waste rubber powder (WRP) in wood adhesive on plywood

Treatment of WRP	20% HNO_3	30% H_2O_2	Acetone	Pure WRP
Run	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)	Bonding strength (MPa)
1	1.15	1.22	1.00	0.90
2	1.40	0.95	1.05	0.84
3	1.55	1.20	1.09	0.88
4	1.52	1.21	0.97	1.12
5	1.67	1.07	1.07	0.75
6	1.48	1.19	1.10	0.70
7	1.50	1.08	1.04	0.80
8	1.55	1.13	0.95	0.75
9	1.44	1.21	1.25	0.80
10	1.50	1.25	1.19	0.88
Average	1.48	1.15	1.07	0.84

APPENDIX B

FTIR ANALYSIS RESULTS

B.1 WRP

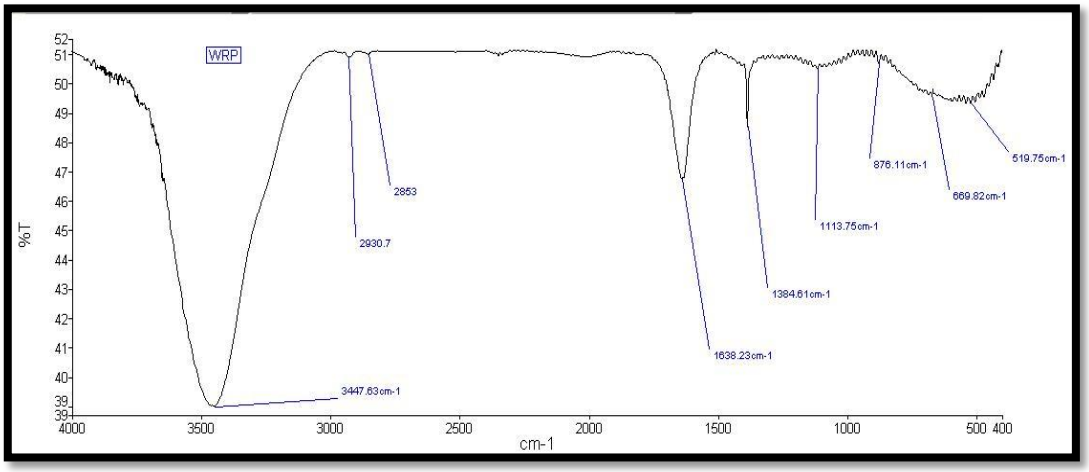

Figure B.1 FTIR spectra of WRP

B.2: Acetone + WRP

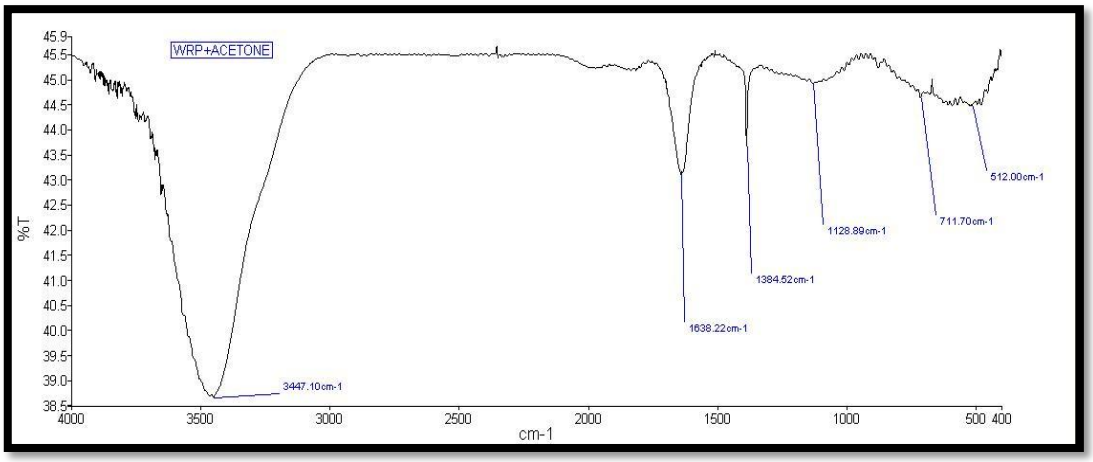

Figure B.2 FTIR spectra of Acetone + WRP

B.3: 30% H_2O_2 + WRP

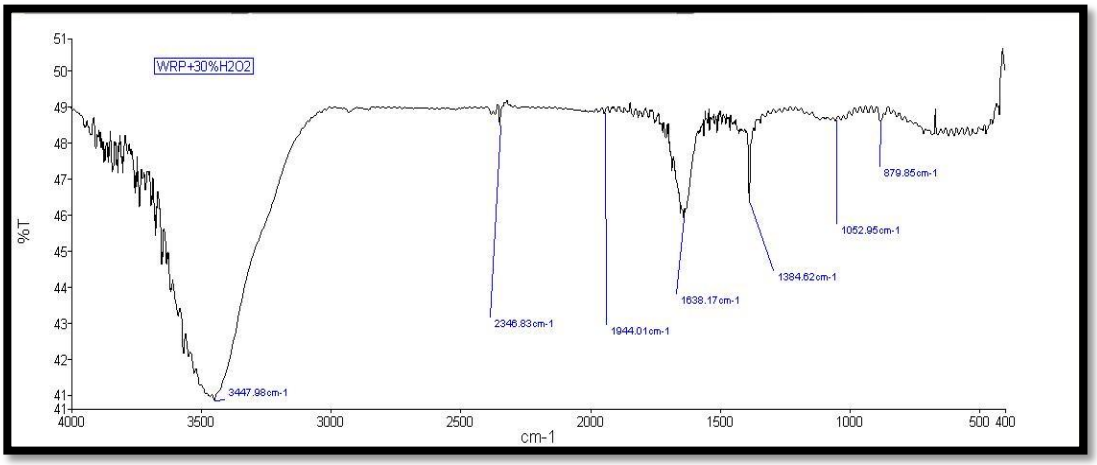

Figure B.3 FTIR spectra of 30% H_2O_2 + WRP

B.4: 20% HNO_3 + WRP

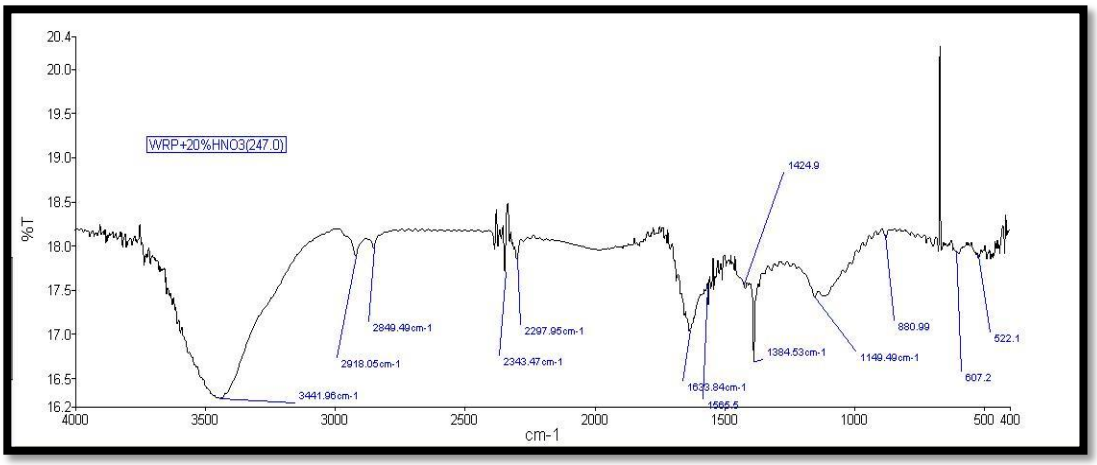

Figure B.4 FTIR spectra of 20% HNO_3 + WRP