CHAPTER ONE

INTRODUCTION

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1.1 General Overview

Formaldehyde (HCHO) is the simplest aldehyde. It consists of only one carbon chain bonded with hydrogen and oxygen molecules (American Chemistry Council, 2010). It occurs naturally in most living systems in the environment and is produced industrially through various chemical reactions, primarily by partial oxidation and dehydrogenation of methanol, using metallic catalysts (Pt, Cu & Ag) in an air stream. It is also eliminated as a by-product in the photo-degradation of dissolved organic matter as well as through the photo-oxidation of hydrocarbons in the atmosphere (WHO, 2000; 2002; Wang *et al*., 2004; Patty, 2008; Roffael, 1993). Formaldehyde easily vaporises and converts into a gaseous state at room temperature. It comes from one of the largest families of chemical compounds called volatile organic compounds (VOCs).

As an important chemical compound with multiple applications, formaldehyde is widely used in the construction, educational, environmental, health and pharmaceutical sectors with a large scale production of about 12 million tonnes (IARC, 1998). The figure has increased to around 29 million tonnes in 2010 as presented in a new market research report (www.prweb.com). The wood industry, particularly in respect of construction, is the single largest consumer of formaldehyde based resin, accounting for over 62% of global formaldehyde demands (Tang *et al*., 2009). This includes commonly used plastics: urea formaldehyde, melamine formaldehyde and phenol formaldehyde resins as wood adhesive in the manufacture of composite wood products (CWPs) like plywood, particleboard, medium density fibreboard and oriented strand board (IARC, 1995; Bohm *et al*., 2012).

Of the composite wood products, plywood shows the most similar physical properties to solid wood. It has a wood like appearance and consists of equivalent density, ranging between 400 kg/cm^3 to 800 kg/cm^3, with more excellent dimensional stability (USTIC, 2008; FPL, 2006). Plywood has better resistance to cracking, shrinkage, twisting or warping and higher degree of strength (Wong & Kozark, 2008). It is stronger than other fibreboards (particleboard, medium density fibreboard and oriented strand board) and sometimes even better than solid wood with its multiple bonding construction. It forms cross-lamination of veneers, running perpendicular to each other with formaldehyde based resin mixed with filler, extenders and inorganic salt acting as hardeners. However, as a result of its fabrication, it emits higher formaldehyde if compared to solid wood because the glue layers as well as the wood itself contribute to the emission. Plywood can be classified into two types according to the glue category, the exterior type is weather and boiled proof (WBP) plywood that is normally laminated with phenol formaldehyde or sometimes by polymethylene diisocyanate (pMDI) resin. Urea formaldehyde and melamine formaldehyde resin bonded plywood are moisture resistance (MR) and they are classified as interior type with higher formaldehyde emission.

The main focus in current research is the plywood glued with urea formaldehyde, which is the most widely used adhesive as a result of its strong bond-ability, rapid curing and relative low cost. Potentially, the emissions of VOCs can arise from each of the materials that compose the panels but the focus is on formaldehyde as a result of the allergenic, hazardous and adverse effects of exposures if compared to other VOCs (Sugaya *et al*., 2004). Formaldehyde is a colourless gas with strong, pungent and suffocating odour at room temperature (Yamato *et al*., 2005). It has been found to produce nasal carcinomas after chronic (long term) exposure of 5.6 ppm to14.1 ppm in rats (Kim & Kim, 2005). The other toxic effects of formaldehyde in experimental animals include irritation, cytotoxity and cell proliferation in the upper respiratory tract (IARC, 2004). For human beings, this chemical compound is a potential risk factor for health. A concentration of more than 0.1 ppm in air can be irritating to the eyes, nose and mucous membranes, resulting in watery eyes, headaches and a burning sensation in the throat following acute inhalation (EPA, 1988; WHO, 1989). Chronic inhalation, however, converts formaldehyde to formic acid in human body, leading to a rapid increase in blood acidity, difficulty in breathing, respiratory tract, hypothermia and coma or death (EPA, 1988; WHO, 1989).

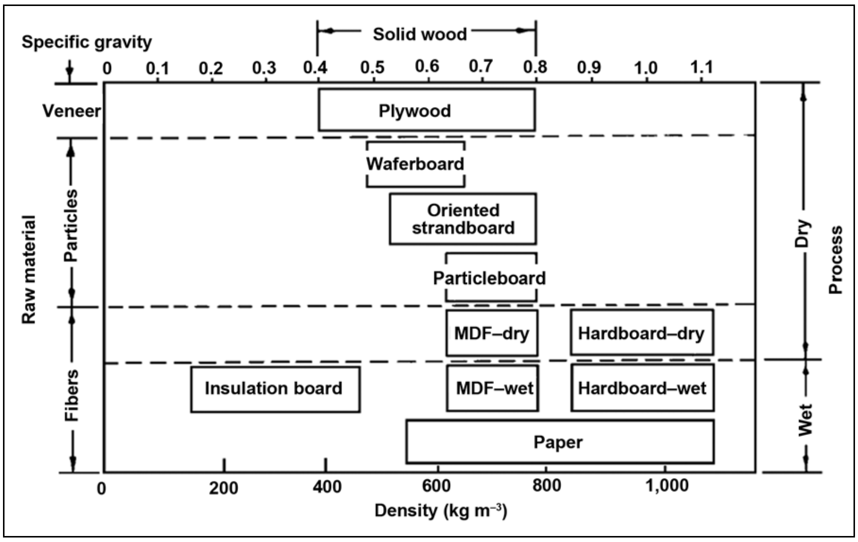

Figure 1.1: Classification of wood composite panels by particle size, density and process (FPL, 2010).

As a result of previous research, the Japanese Government amended the building standard law to comply with the JAS-Mark quality system. In July 2010, the US President signed the Formaldehyde Standards for CWP Act into law simultaneous with the implementation of the California Air Resources Board Phase I and Phase II regulations. In between, the European Union executed the CE-Marking in compliance with the European Standards that has the status of a British Standard, together with the Australia/ New

Zealand Standard (AS/NZS 1859), Chinese National Standard (CNS 1349) and International Organisation for Standardisation (ISO 12460-1, ISO 12460-3 & ISO 12460-4) in monitoring the formaldehyde emission problem. Obviously, formaldehyde emission is a major concern in the wood industry around the world.

1.2 Problem Statement

The declaration of formaldehyde from 'reasonably anticipated to be a carcinogen in humans for nasopharyngeal cancer' (IARC, 2004) has attracted world attention. Short term exposure causes immediate irritation to the visual and respiratory tract. At high concentrations and longer durations of exposure, it is considered to have mutagenic, teratogenic and carcinogenic effects on humans (Takeuchi *et al*., 2007). The affected groups are not limited to workers handling the chemical and secondary users who exposed to the intermediate manufacturing process but also the final consumers, the public, who are exposed to the formaldehyde based products. Most people spend approximately 80% of their daily time indoors, where the chemical concentration is clearly higher than outdoors (Baumann *et al*., 1999). Formaldehyde fumes can enter indoor air from plywood, which has been an important resource of renewable building, construction and also furnishing materials over the past several decades and will continue to play its role in the future. Thus, formaldehyde emission has become an important factor in evaluating the effects of CWPs on the environment and human health.

The demand for formaldehyde in wood resin remains strong and world consumption has been forecast to grow at an average annual rate of 4.0% from 2009 to 2014 (Bizzari, 2010) as no suitable substitute has been discovered for this organic compound. Therefore, it is essential to study, investigate and further determine the factors affecting its emission.

Unlike solid wood, plywood disintegrates if it becomes wet. Although the effect of moisture content (MC) on the formaldehyde emission in plywood, particleboard and medium density fibreboard has been investigated (Myers, 1983; Aydin & Colakoglu, 2005; Kim & Kim, 2005), no further discussion compares the effects of static moisture content and the dynamic moisture content. In addition, it is seldom that plywood samples are bonded by veneers with various combination of moisture content. In the current study, the moisture content has been scheduled in a large combinations probability to examine the attributes of each layer's moisture content on its respective formaldehyde emission.

In addition to the exogenic influences (temperature, relative humidity, air exchange value, etc), the endogenic factors (wood species, production control, binder, etc) were found to have a significant effect on the liberation of formaldehyde (Roffael, 2006). Although formaldehyde comparison has been conducted using different wood species, several works were found to be limited to solid wood (Meyer & Boehme, 1997 and WQI, 2004). Nowadays, solid wood has been replaced by plywood or other CWPs for better quality performance with less energy (logs) consumption. Softwood is the most popular species to be selected in the investigation of the effects of wood species on formaldehyde emissions. Although some studies have been conducted on hardwoods, these mainly focused on temperate timber from Europe and New Zealand, and we did not find much discussion on tropical hardwoods. Tropical plywood is always made of mixed wood species found in the South-East Asia region, mainly from Malaysia and Indonesia. Tropical plywood is superior to softwood plywood in terms of its density, strength, evenness of layers and high quality. It is usually a highly preferable choice for construction purposes in America, Japan, Middle East, Korea, the United Kingdom and many other markets around the world. Therefore, the formaldehyde studies of tropical hardwood in the current work could help to control and further monitor the emission problem globally.

Scientists and researchers have primarily focused on developing methods to characterise plywood with respect to their formaldehyde releases. The existing methods include desiccators, chamber, perforator and gas analysis utilising spectrophotometric analyses. These methods have been established in last few decades with the longer test duration and larger sample size as the remained drawbacks (Yung & Lo, 2012; 2013). Therefore, the methodology to evaluate formaldehyde emission needs attention and revolution. In present research works, the liquid-liquid extraction (LLE) and solid phase micro-extraction (SPME) methods are introduced besides the conventional test methods. LLE is the preferred chromatographic method for air quality evaluation (EPA Method 556) where there is considerable hazardous chemical waste. The SPME is a more advance and efficient technique, which consumes smaller sample size as well as possessing rapid extraction with easier operation procedures (Ouyang & Pawliszyn, 2006). Together with the adoption of higher accuracy chromatographic analyses, more promising results were expected from the SPME method. The variety of testing methods to comply with different standards (Table 1.1) for the determination of formaldehyde emission could result in contradiction among distributors, importers, fabricators, retailers as well as wood product users. It becomes difficult to compare the results obtained as no equalisation is found. For this reason, method correlations are used as a supportive solution to standardise the formaldehyde values obtained from different parts of the world; similarly with the application of standard international unit (SI).

The replacement of formaldehyde based resin with alternative substitutes should be achievable but it requires a longer evaluation interval and further confirmation of its effectiveness in order to gain acceptance from users. In the current investigation, the formaldehyde accounted for is from both the wood itself and the resin adhering to the wood layers. Therefore, the minimisation of formaldehyde emission is discussed after the factors affecting emission are identified together with the application of more advance analysis technology. In addition, the minimisation treatments could even 'rescue' the already manufactured plywood products that give off higher formaldehyde emission.

Table 1.1 Formaldehyde emission standards for plywood panels in different regions

Country	**Standards and correspondence methods**	**Regulations**	**Limits**
Japan	JAS 233: 2003 (08) Desiccator	JAS F4 star	0.3 mg/L
	JIS A 1901 (2009) Small chamber	JIS F4 star	5 µg/(h.m^2)
US	ASTM E1333-10 Large chamber	CARB PII	0.05 µg/mL
	ASTM D6007-02 Small chamber	CARB PI	0.08 µg/mL
Europe	EN 717-1: 2004 Chamber	CE E1	0.1 ppm
	EN 717-2: 1994 Gas analysis	CE E2	3.5 mg/(h.m^2)

Ref: Japanese Ministry of Agriculture, Fisheries and Forestry; Japanese Industrial Standards Committee; American Society for Testing and Material; European Committee for Standardization

1.3 Research Objectives

The present research focuses on three main objectives. First and foremost, the factors that affect the emission of formaldehyde are determined. The findings led to an intensified interest to investigate the most to the least important factors. These factors include moisture content and wood species, which includes colour appearance, pH and also percentage of porosity. Further works were carried out to show the compatibility of SPME with the standard methods, and the improved sensitivity of measurement through chromatographic analysis. In addition, comparisons were carried out by establishing correlations between the SPME method and the existing standard methods for formaldehyde quantitative analysis.

The third part to be evaluated is the efficiency of the minimisation treatments to reduce the formaldehyde emission. Both physical and chemical solutions will be adopted where the bonding strength and bending stiffness remain unaffected. Besides effectiveness and stability performance, other factors, such as cost, manpower, ease of controlling and the pollution issue caused by improper chemical waste discharge system in the post treatment process will also be considered. The current research objectives are as summarised below:

1. Evaluation of factors affecting formaldehyde emission of plywood panels
2. Comparison of SPME method with standard methods in quantitative analysis
3. Minimisation of formaldehyde emission from plywood panels

1.4 Factors Affecting Formaldehyde Emission

Water or moisture has an important influence on wood and occupies approximately 50% of its weight. When green wood dries, free water is the first to go, followed by hygroscopic water bound to the wood cell walls through the hydrogen bond at the fibre saturation point. Wood products like plywood tend to gain moisture in response to an elevation of relative humidity (Hartley, 2001; Meyer, 1986). Their moisture content is expressed as a ratio of the mass of water per unit mass of oven dry wood (Hartley, 2001). Moisture content is one of the factors that have a high impact on the formaldehyde emitted from plywood and also on its finished products, such as flooring underlay, wall panels, shelves, cabinets and other commonly found renovation materials.

As a hygroscopic substance, plywood adsorbs or desorbs water at each level of its manufacturing process including peeling, drying, glue laminating and finally thermal bonding. The relationship between the wood moisture content and formaldehyde emission is resulted by the release of the formaldehyde retained in the aqueous phase of the wood due to its affinity for water (Meyer, 1986). When the plywood specimens are exposed to the water reservoir in the desiccators, the on-going hydrolysis of cured resin and the unbound formaldehyde after thermal pressing both contribute to the emission. The vapour of formaldehyde builds in concentration and is collected by the water reservoir because of its hydrophilic structure. In real life, the same phenomenon occurs; more formaldehyde is emitted from plywood panelling or furniture, especially in indoor environments with pronounced humidity. Hence, many researchers agree that formaldehyde emission is correlated with the dynamic moisture content, which is affected by the relative humidity of the atmosphere in the surroundings (Meyer, 1986; Roffael *et al*., 2010; Roffael, 2006) as well as the static moisture content (Weigl *et al*., 2009; Aydin *et al*., 2006).

For the production of low formaldehyde emission panels, sometimes the drying temperature is increased to boost the drying rate. At 175°C and sometimes up to 240°C, the lignin, containing dried wood fibres, undergoes condensation and the dried wood shrinks (Aydin *et al*., 2006). The shrinkage is further exacerbated by the increase in drying interval, which causes both energy waste and wood material loss. More fuel is required to generate steam or heating energy for the purpose of prolonged drying. Therefore, the improved process has to determine the ideal moisture content of plywood and also the veneer's initial moisture content to ensure that the inherent toxicity of formaldehyde could be controlled while preserving the fine structure of the wood material and minimising the waste of energy.

In terms of timber wood species, plywood is classified into two major types - hardwood and softwood - which could be further divided into a variety of species depending on the origin of the wood and also its chemical compositions (Nguila Inari *et al*., 2010). The majority of species grow in the tropical areas of the world (Friis & Balslev, 2005). As there is considerable variation from one species to another, the tropical hardwood species have to be studied in more detail. The formaldehyde emissions mainly results from the glue bonding the veneers together. Hence, the emission should be equivalent if the plywood is manufactured using a resin belonging to the same group with an unchanged glue mix formula. However, noticeable differences of formaldehyde emission from the plywood are obtained, especially panels constructed from different species of wood.

The wood colour, pH, density and porosity help to differentiate the wood species studied in response to their influence on the emission of formaldehyde. The extractives in wood consist of oils, fats, resin and colouring matter (Horvath, 2005). The colouring matter could be the main substance that interacts with light to give wood colour because neither cellulose nor hemicelluloses absorb light in the visible region. The colour variation exists because of the diverse species due to differences in the composition of the wood components. For the purpose of this research, the two common colours of reddish and yellowish are selected.

Wood is a polymer consisting of 40% to 50% cellulose, 20% to 35% hemicelluloses (polysaccharides), 15% to 30% lignin together with some extractives (Horvath, 2005). The majority of the components are water soluble and tend to form a solution, suspension or mixture. The chemical combinations differ quantitatively and qualitatively across the variety of species. Therefore, the pH varies with different wood species (Wengert, 1998). As expected, the woods exhibited pH with an acidic level and the rate of reaction, polymerisation or cure time is greatly affected by the changes in the pH of the wood (Wengert, 1998). Therefore, pH is a critical factor in the glue bonding process, and, subsequently, affects the emission of formaldehyde, especially when the acid-curing urea formaldehyde resin was used in the current study.

The structure of hardwoods is much more complex and contains vessel elements or pores that softwoods do not have (Jones, 2010). It was also found that the density or porosity is an important physical wood property that controls the formaldehyde emission and appears to be a diffusion controlled process (Christensen *et al*., 1981). Wood density is defined as the index of void volume - the amount of empty spaces comprising cell cavities and intercellular spaces (Usta, 2003). Porosity, however, is the fractional void volume of wood. In relation to its use as a crude indicator for estimating the bond-ability, the porosity of a great variety of wood species is study to predict the formaldehyde emission and the off gassing rate.

1.5 Methodologies of Formaldehyde Determination

The formaldehyde for CWPs is measured using a variety of methods, which initially depend on the product type in response to the suitability of testing parameters. In addition, it also considers the climate and other geographical factors of different countries that contribute to the development of methodology. Formaldehyde released from plywood is commonly determined using a chamber or desiccator in the United States and Asia-Pacific regions while, in Europe, gas analysis is the preferred method. The perforator and flask method are frequently used for particleboard and medium density fibreboard.

The desiccator (DC) is a popular quality control method in the wood industry. There are three significant international regulations concerning the dessicator method for the determination of formaldehyde for wood products. The reaction between chromotropic acid (4, 5-dihydroxynaphthalene-2, 7-disulphonic acid, CA) and formaldehyde with sulphuric acid as a strong acidic media forms a purple colour solution known as chromogen. The obtained absorption spectrum of the chromogen is counter checked using a spectrophotometer at 580 nm. Another commonly used dessicator method with longer conditioning interval (24 hours) complied with JIS 1460, JAS 233: 2008 and ISO 12460-4: 2008. The formaldehyde released is determined based on the *Hantzch* reaction where the formaldehyde reacts with the ammonium ions and acetyl acetone (pentane-2, 4-dione, AA) to yield the yellowish diacetyldihydrolutidine (3, 5-diacetyl-1, 4-dihydrolutidine, DDL). The qualitative test is then carried out at a wavelength of 412 nm of the spectrophotometer. In addition, a small chamber (SC) has been adopted in many standard test methods, such as ASTM D6007-02, EN-717-1, JIS A 1901 and ISO 12460-1. These test methods measure the formaldehyde under defined circulation within the chamber. The sodium hydrogen sulphite is used as an impinge solution and the quantity of formaldehyde is determined in accordance with the chromotropic acid test procedure illustrated above.

The liquid-liquid extraction (LLE) is modified from the US Environmental Protection Agency Method 556 (EPA Method 556), and *O*-(2, 3, 4, 5, 6 pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) is used as the derivatisation agent to form formaldehyde-oxime. The oxime derivative is extracted into hexane and then analysed chromatographically. In order to improve method sensitivity, SPME coupled with the chromatographic analytical method is proposed. The SPME was first invented by Pawliszyn, J. in 1990. It is a simple and solvent-less extraction technology. In SPME, formaldehyde is first derivatised prior to the headspace being extracted and then analysed by gas chromatography in combination with a mass spectrophotometer (GC/MS). Further works of comparison will be carried out to establish the correlation between the SPME and the existing methods: desiccator, small chamber and liquid-liquid extraction.

1.6 Formaldehyde Minimisation Solutions

The phenol formaldehyde appears to give lower formaldehyde emissions (below 0.3 mg/L, recognised by JAS) whereas soy-based resins virtually eliminate the emission (below 0.05 µg/mL, recognised by CARB). Together with the 'no formaldehyde added', polyurethane should be the most suitable substitute. However, the phenols, epichlorohydrin and methylene diphenyl diisocyanate or aromatic diisocynate used by resin manufactures are allergen and sensitizers that present health risk issues (NIOSH, 1994a; NIOSH, 1994b). Taking into account any potential added costs associated with the implementation of the alternatives, which might require a longer glue setting time or higher energy demand, is of course included in the product price and burdens the development of such alternatives.

Therefore, we focus on the minimisation of formaldehyde emission from urea formaldehyde bonded plywood targets for a promising reduction, while also preventing the deterioration of air quality from other hazardous or hazardous risk substitutes. Besides the edges, the surface veneer also serves as a medium of formaldehyde off gassing to the atmosphere. Thus, it is important to investigate the elevation of surface veneer thickness and its influence on the emission of formaldehyde. It is also known as physical or pre-treatment as no changes are involved in the reaction mechanism. Apart from that, the methodologies to reduce the emission of formaldehyde from the plywood through chemical post treatment could be a better alternative. Post treatment enables the treatment of the finished product or pressed panel without changing the manufacturing process. In addition, it should not mar the surface appearance of the treated board in respect of colour and the pH to ensure no risk of delaminating for any additional sheet lamination by the final users.

1.7 Summary

Plywood is a heterogeneous material and its formaldehyde emission depends on several factors. The physical properties of the wood itself have a significant effect on the emission of formaldehyde from the plywood. Therefore, it is important to further investigate the influences of moisture content, colour appearance, pH and porosity of a particular wood species. In response to the new carcinogenic declaration of formaldehyde, a more comparable analysis method is required as the world pursues low level formaldehyde emission wood products. The versatile SPME is introduced and implemented for better validation. The rate at which emission levels decrease is not constant but diminishes with the treatment applied. Therefore, it can be inferred that both physical and chemical treatments enhance the minimisation of formaldehyde.