

CHAPTER TWO

LITERATURE REVIEW

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2.1 Moisture Content and Formaldehyde Emission

The effects of moisture content (MC) on formaldehyde emission in plywood are mainly attributed to the use of amino-plastic resin especially the urea formaldehyde resin as the main binder in the wood based industry (Roffael *et al.*, 2010; Meyer, 1986). This is particularly true because of the presence of a proportion of the non-reacted formaldehyde, resulting in free formaldehyde and the emission from the breakdown of cured urea formaldehyde resin through hydrolysis (Roffael *et al.*, 2010; An *et al.*, 2010). A lot of literatures have been carried out focusing on relationship of formaldehyde emission with moisture content in wood based products (Roffael *et al.*, 2010; Roffael, 2006; Aydin *et al.*, 2006; Wolcott, 1996; Myers, 1983).

The changes of formaldehyde value at different relative humidity, from 30% to 65% and then 80% has been analysed (Roffael *et al.*, 2010; Roffael, 2006). In fact, the wood moisture content is greatly affected by the relative humidity and temperature of surroundings despite of the current water content in the wood (William & TenWolde, 1999). The increase in humidity drives moisture content of the sample boards to a higher level. The boards being acclimatised to higher moisture content emit larger amounts of formaldehyde in an equilibrium conditions. Hence, the formaldehyde declined of about 60% with responds to the moisture content reduction, from 10% to 4%, as measured by both of the perforator and chamber methods (Roffael *et al.*, 2010). In an earlier study, the formaldehyde emission of plywood has been correlated with its moisture content in two experiments (Mayu *et al.*, 2001). Both results were measured using the JIS 1460-Desiccator

method, indicated that more formaldehyde had been released from plywood with greater moisture content, into the air with higher relative humidity.

Besides the fresh manufactured wood products, the used wooden materials were also being investigated. The effect of temperature and humidity on formaldehyde emissions from wood samples collected from temporary housing units supplied by the US Federal Emergency Management Administration has been studied (Parthasarathy *et al.*, 2010). The results showed that the increase in humidity has contributed to an increase in formaldehyde emission. The correlation coefficient between the relative humidity and emission factor was found to be greater than 0.98. Before that, some building materials have been evaluated for their formaldehyde emission (Osanyintola *et al.*, 2006). As wooden products, they are hygroscopic in nature, and, therefore they can accumulate and release formaldehyde as the moisture content varies. The rises or drops of wood moisture content were found very dependent on the changes of indoor humidity.

Five European species solid wood were tested for their formaldehyde emission (Meyer & Boehme, 1997). In accordance with the chamber method, the highest value was discovered for the green oak (9 ppb). It dropped to 4 ppb as the moisture content reduced to 8%. The emission values in dry state are 1 to 2 units higher than those in the green state with exception of oak wood. In the gas analysis method, formaldehyde emission decreased as moisture content reduced to approximately 8%. The measurement using perforator method indicated the similar declination except for the pine species solid wood.

Apart from that, the emission of formaldehyde in the poplar and spruce plywood was found to decrease with the increases of wood moisture content (Aydin *et al.*, 2006). As the

product exits the press, vapours that may include resin especially formaldehyde was facilitates by higher moisture content and then being released in coincide. Equilibrium moisture content of plywood panels decreased with increasing veneer drying temperature, which enhance the emission of formaldehyde (Aydin & Colakoglu, 2005). In addition, the nearly zero formaldehyde emission was obtained after 20 minutes of excessively press time for particleboard with higher moisture content. The accuracy and precision of the hot press formaldehyde collection system was greater than 95% (Wolcott *et al.*, 1996).

The majority of previous works were focused on how relative humidity alters the moisture content of wood particle, which contributes to the formaldehyde emissions. It has been observed in several studies that the increases of moisture content have greater enhancement to the emission of formaldehyde. However, some emphasised that the greater moisture content could cause less emission in the wood products. Therefore, there is no final confirmation formed but the close relationship has been evidenced and further stimuli the author's interest to determine the condition where positive response of the increase in formaldehyde emission to the elevation of the wood moisture content. The moisture content is known to give significant influences to the emission of formaldehyde in wood products. But it has not been widely studied whether similar moisture content changes in the surface veneer or inner core of the plywood has more influence to the formaldehyde emission. Therefore, the dependency of formaldehyde emission to the variation of moisture content for both inner and outer veneers of plywood is being investigated in the current study.

2.2 Wood Species and Formaldehyde Emission

The factors which may influence the formaldehyde emissions need to be identified and quantified with respect to its possible health effects. Some previous investigations had

indicated that wood naturally emits diminutive but still detectable formaldehyde (Weigl *et al.*, 2009; Roffael, 2006; Meyer & Boehme, 1997). Hence, the issue of formaldehyde emission is no longer solely focused on adhesives systems used for bonding the plywood panel. It could be related to the influences of the individual wood species too.

The influences of wood species to particleboard is taken into account instead of other factors, such as the specific gravity, shelling ratio and pressures (Nemli & Ozturk, 2005). The particleboard made from higher amount of *beech* (*Fagus orientalis Lipsky*) particle, consist of lower formaldehyde content than the *pine* panels (*Pinus nigra Arn. Subst. Pallasiana (Lamb.) Holmboe*). In fact, the acetic acid that was released simultaneous from hot pressing behaves as the formaldehyde scavenger (Nemli & Ozturk, 2005). The significant effect of the wood species to the formaldehyde emission has been shown by the *beech* wood, which contains more acetic acid than the *pine*.

The widely used hardwood species in Spain wood processing factories such as *ceiba* (*Ceiba pentandra Gaertn*), *beech* (*Fagus silvatica L.*), *ilomba* (*Pycnathus angolensis Exall*) and *okume* (*Aucoumea klaineana Pierre*) has been studied (Martinez & Belanche, 2000). Among the tested species, formaldehyde present in *ilomba* plywood gave the highest emission, followed by the *beech*, *ceiba* and *okume* plywood using the gas analysis method. The similar sequence of ranking was obtained in terms of the formaldehyde content, for the same batch of plywood samples. Statistical techniques and analysis were employed to further explain the differences.

Although the initial objective of a previous work (Colak & Colakoglu, 2004) studied the effectiveness of borax and boric acid for formaldehyde reduction, the variation of

formaldehyde released from different wood species was discovered. The emission value of the *alder* plywood was found higher than the *beech* panels due to the different structures between these wood species, which determines the emission path of the formaldehyde molecule. Furthermore, it has been reported that the emission of formaldehyde increased in proportional with the reduction of wood density among three different wood species: *larch*, *meranti* and *sugi* (Ishikawa *et al.*, 2009).

Other than that, softwood species such as *Norway spruce* (*Picea abies* (Karst.) L.) and *Scots pine* (*Pinus sylvestris* L.) as well as hardwood species such as *European oak* (*Quercus* sp.), *European beech* (*Fagus sylvatica* L.) and *poplar* (*Populus* sp.) have been tested (Weigl *et al.*, 2009). With some modification to the perforator standard condition, the *pine* showed the highest formaldehyde content (0.54 mg/100g) compared to the rest of the hardwood species (0.27-0.36 mg/100g). A significant difference between mature and juvenile wood were also reported. Of the *beech*, *poplar* and *pine*, the matured wood consists of higher formaldehyde than the juvenile wood of the same species, respectively. In contrast was as performed by the *oak* and *spruce* wood. Generally, the coniferous species have greater formaldehyde contents than the hardwood species (Weigl *et al.*, 2009).

A range of studies has been commissioned with several solid woods: *radiata spruce*, *redwood*, *chestnut*, *larch*, *radiata pine*, *swamp gum*, *macrocarpa* and *douglas* (WQI, 2004). The main objective of the consortium of New Zealand forest sector research agency was to identify the level of formaldehyde emission from solid *pinus radiata*, with a view to documenting how it stacks up against other species. By using the Japanese method, different emission level of formaldehyde among the wood species was noticed. In earlier stage, the emission of formaldehyde emission in *beech* was the lowest (0.16 mg/100 g)

followed by *spruce*, *pine*, *douglas-fir* and *oak* in an ascending trend (Meyer & Boehme, 1997). These results indicated clearly that the individual wood species differ from each other in relation to their formaldehyde emission. It can be inferred that the temperate solid wood contains and emits native formaldehyde although in the absent of adhesion.

Majority of literatures discussed the influence of the wood structure and its physical properties to the mechanical performance (Modzel *et al.*, 2011; Konnerth & Gindl, 2006; Gindl *et al.*, 2005). These influences are rarely related to the wood chemical respond in terms of the formaldehyde emission behaviour, especially for the domestic tropical hardwood species although Malaysia is one of the six largest global wood product suppliers (USTIC, 2008). It was noticed that very few researchers have correlated the wood properties to the phenomenon of formaldehyde emission. In the current investigation, the formaldehyde accounted is from the wood itself besides the resin adheres to the wood layers. Therefore, the colour intensity, pH, density and porosity of the wood are studied in more details also for predicting the emission of formaldehyde.

2.3 Formaldehyde Evaluation Methodology

Formaldehyde emissions of composite wood products (CWPs) are usually evaluated by different methodologies compiled with existing standards that implemented by different countries and regions as the major wood panel manufacturer or as the users. In the middle of 1970, the 24 hours desiccator (DC) test with static measurements was first developed in Japan and then standardised to 2 hours by the American in 1983. Both methods are widely used within the North America and Asia-Pacific region, such as Australia, Indonesia, Japan, Korea, Malaysia and New Zealand until now. Meanwhile, the dynamic chamber method was constituted as the primary method to characterise board's emission because it

is modelled similar to an actual home. Thus, the emission value obtained was closely related to the real formaldehyde level. The 1 m³ chamber method however was implemented by the Technical Committee 89 of the International Standardization Organization as the reference method for the formaldehyde emission measurement and comparisons. The perforator method is more reliable in Europe as it measures the board's formaldehyde contents instead of its emission.

Different testing parameters and specific conditions have resulted in difference results. Therefore, the relationship among methods was studied and the correlations were discussed by some researchers. The formaldehyde emission of CWPs measured by using European standards (EN 717-1 Chamber, EN 717-2 Gas analysis, EN 717-3 Flask method and EN 120 Perforator) and Japanese test methods (JAS 233 Desiccator and JIS A1901 Small chamber) were compared (Risholm-Sundman *et al.*, 2007). Of the same panel, the flask values were always higher than others as a result of large ratio difference of open edge area to the surface area. Besides that, the testing conditions such as temperature, relative humidity, air exchange rate, pre-treatment conditions and edge sealing effects which changes substantially further contribute to the variations.

There are many other research works evaluate the existing methods besides as illustrated in the section 2.1 and 2.2. Formaldehyde emission of particleboard and plywood were also evaluated by using a large chamber (28.4 m³) and the desiccator-acetyl acetone (DC-AA) methods (Que & Furuno, 2007). They obtained the almost equivalent results using the chamber and DC-AA method at an unequal loading ratio between the particleboard (0.52 m²/m³) and the plywood (1.05 m²/m³). This could be due to the material transport phenomenon between the board and air. The driving force at any one time was

determined by the magnitude of the concentration difference from the maximum possible value at a zero air change per hour (Que & Furuno, 2007; Myers & Nagaoka, 1981). Furthermore, the linear regression analysis of the chamber and the correspondence DC-AA results gave the correlation coefficient of 0.97 to 0.99. The empirical correlations between the 1 m³ chambers with DC-AA methods have been established again for the particleboard and the plywood (Park *et al.*, 2011). The formaldehyde emission evaluated by the chamber method corresponding to about 2% of the DC-AA method was reported. In particular, the DC-AA values were highly statistically correlated with the chambers and resulting in regression coefficient of 0.92. In addition, a good correlation was obtained in a resin molar ratio study using the perforator, desiccators and chamber methods (Que *et al.*, 2007b).

The methodology to evaluate formaldehyde emission has drawn many researchers' concern. It is therefore not surprising that several new methods have been proposed such as the calorimetric type passive flux sampler, annular denuder, field and laboratory emission cell (Shinohara *et al.*, 2011). Both the passive flux sampler and the annular denuder using 2, 4-dinitrophenyl hydrazine to collect the atmospheric formaldehyde, subsequently inspected via visual observation and analysed through the high pressure liquid chromatography (HPLC) with ultraviolet (UV) spectrophotometry detection respectively. In earlier stage, the field and laboratory emission cell has been used together with the desiccator lid as emission cell in a comparison study. They were proposed to compare with 1 m³ chamber method besides the use of closed container methods such as the flask and the desiccator (Risholm-Sundman & Wallin, 1999). The field and laboratory emission cell collects the emitted formaldehyde on a 2, 4-dinitrophenyl hydrazine coated filter for HPLC analysis. The desiccator lid however acts as an alternative of the field and laboratory emission cell. Both of them well correlated to the chamber value, given a regression

coefficient of about 0.9. In contrast, the correlation with the chamber method was poor for both the flask and desiccator methods. The conditioning time have to be maintained in a standardised way to obtain more comparable results (Risholm-Sundman & Wallin, 1999).

The formaldehyde evaluation methodologies study have been established by many researchers as stated in above and most of them were focusing on the traditional methods comparison. Newer method such like passive flux sampler and annular denuder however measure low concentration of atmospheric formaldehyde. The field and laboratory emission cell and desiccator lid methods (Risholm-Sundman & Wallin, 1999) that found applicable to wood products are specialty for curve surface or material with single side of exposure in usual. Therefore, a wide range coverage extraction technology by optimising the solid phase micro-extraction (SPME) is suggested in the current research. The SPME is a reliable and fast extraction alternative for liquid-liquid extraction (LLE) (Pawliszyn, 1997). Several researchers have discussed the use of the SPME but the formaldehyde analyses were limited to food, cosmetics and biological specimens (Iglesias *et al.*, 2007; Rivero & Topiwala, 2005; Deng *et al.*, 2004; Pacenti *et al.*, 2010). In addition, the use of SPME was found more common in food, drugs, forensic and pharmaceutical area (Howard *et al.*, 2005; Iglesias *et al.*, 2007; Myung *et al.*, 1999; Federica *et al.*, 2009). To the best of our knowledge, the application of SPME for plywood is rarely found. In the present works, it will be correlated with DC-AA, small chamber (SC) and LLE methods, aiming to evidence its comparability meantime to boost the methodology developments for the wood and plywood industry.

Apart from the new sampling technique, more accurate analysis method is on demand. Although the chromatographic analysis has been introduced by Kim & Kim

(2005), majority are preferably carried out through the certified standards, using the spectrophotometric analysis, which is also the popular quality control method in the wood industry (Park *et al.*, 2011; Risholm-Sundman *et al.*, 2007; Que & Furuno, 2007; Que *et al.*, 2007a; Wiglusz *et al.*, 2000; Myers, 1984). Within current studies, gas chromatography (GC) coupled with different detectors are vigorously pursued. The combination of GC with flame ionization detector (FID), electron capture detector (ECD) and mass spectrometry (MS) are compared with the ultraviolet-visible (UV-VIS) spectrophotometry analysis.

2.4 Minimisation of Formaldehyde Emission

Plenty of methods were attempted to reduce the emission of formaldehyde. The earliest approach was the reduction of the formaldehyde to urea molar ratio (F/U). By changing of molar ratio from 1.6 to 1.12, the formaldehyde emission could be reduced as much as four-fold (Myers, 1984). The reduction has brought up to the 70% to 84% as molar ratio was lowered from 1.27 to 0.97 (Que *et al.*, 2007a). However, the resin cure time was elongated and causes substantially lower internal bond strength and yielding deterioration to the modulus of rupture of the boards. (Roffael *et al.*, 2010; Xu *et al.*, 2010; Hse, 2009; Que *et al.*, 2007b; Myers, 1984)

The clearly loss in the mechanical properties was improved through a modification in molar ratio with an addition of melamine, F/ (M+U). Melamine is a good string cross linkages agent in the cure resin structure that contributed to improve the bond performances. However, result obtained in previous study suggested that the reduction in formaldehyde emission by increasing the melamine content has limitation (Tohmura *et al.*, 2001). Moreover, the cost factor is a burden for melamine formaldehyde or melamine urea formaldehyde to substitute urea formaldehyde in overall.

Total replacement of urea formaldehyde with phenol formaldehyde, polyurethane or polyvinyl acetate could eliminate the formaldehyde emission issue as demonstrated in preliminary experiments. Presumably, the greater cost burden could be covered; there are still conspicuous problems with the substitution. It is well documented that the primary components making phenol formaldehyde and polyurethane resin, together with their toxic production waste has raised the occupational concerns, health risk and safety problems (Brown, 2012; IARC, 1999; IARC, 2004). Emerging evidence showed that the solvent benzene used to produce methylene diphenyl diisocyanate, is not only a volatile organic compound (VOC), but may also be linked to the leukaemia, multiple myeloma, prostate cancer and non-Hodgkins lymphoma (Clapp *et al.*, 2006). In addition, there are still no exact data to verify the sufficiency of remediation efforts that can be utilised to reduce the occupational exposure concerns in the workplace. The polyvinyl acetate or more familiar as rubbery synthetic polymer performed weak bond-ability if compared to urea formaldehyde resin, especially in the presence of moisture.

A substantial reduction in the indoor formaldehyde concentration can be achieved by using paintings or lamination with polymer films, metal films and impregnated papers (Myers, 1986). Apart from that, thicker surface veneer is used as solid barrier in the current research to reduce the emission of formaldehyde. It is used with the purpose to pertain originality and natural appearance of wood grains also considering the sealants themselves may release other VOC for a period of time exposure.

A lot of formaldehyde scavenger substances have been discussed in the efforts to solve the indoor formaldehyde emission problem. The direct additions of urea changes glue mix formula and provide a path for further co-polymerisation of formaldehyde exists with

amine functional group and thus lower the emission (Ayrilmis & Winandy, 2009). Other chemicals such as ammonium sulphite and sulphur compounds of sodium have been used (Wang *et al.*, 2008; Kunaver *et al.*, 2010; Que *et al.*, 2007b). Besides the inorganic chemical, green substrates like *karamatsu* bark and bark ingredients, recycled bamboo charcoal, coffee ground by products or cashew nut shell liquid were discussed to have formaldehyde reduction abilities (Takano *et al.*, 2008; Park *et al.*, 2004; Baek, 2010; Kim, 2010).

The changes in glue mix formula are not enough to ensure finished wood products achieve the limitation of several standard regulations. An idea to pre-treat veneers with scavenger has been suggested (Myers, 1985). This reduced the availability of the formaldehyde-reactive ingredient meanwhile it also retarded the cure interference as the segregation with resin was induced. Thereafter, several researchers switched to after manufacture coating or treatments. The urea again became the target of researchers and the others have been used were ammonium carbonate, ammonium bicarbonate, inorganic salts, and amine hydrochlorides (Luftman, 2005; Boyer *et al.*, 2008; Roffael, 1993; Kim *et al.*, 2006c; Park *et al.*, 2006; Park *et al.*, 2009).

This time, author has included melamine and urea in urea formaldehyde glue mix formula as an additional remedy to facilitate formaldehyde reduction together with the post formaldehyde scavenging treatments by considering their functional groups (amino) accept formaldehyde molecules easily (Kim & Kim, 2005). This is different from the previous efforts that always focus on either the glue formula revision or the scavengers treatments.