ABSTRACT

The effect of formaldehyde scavenger on the curing behavior, bonding strength, formaldehyde emission and chemical characteristics of urea-formaldehyde resin (UF) for the particleboard manufacturer were investigated. The formaldehyde scavenger was added to UF resin at 0, 6, 12, 18 and 24 % w/w. The cure behavior of UF resin on a wood substrate containing different formaldehyde scavenger content was evaluated by differential scanning calorimetry (DSC). The results indicated that the reaction enthalpy ($\Delta H$) and peak temperature ($T_{peak}$) decrease with the increase of formaldehyde scavenger content. Notable, the $\Delta H$ and $T_{peak}$ values decreased up to the formaldehyde scavenger content of 12 % w/w and then were rather constant with its further addition. To determine properties, the laboratory-made particleboards bonded with UF resin at various contents of formaldehyde scavenger were manufactured. The results showed that the addition of formaldehyde scavenger could improve bonding strength of the panels and greatly reduced their formaldehyde emission. The particleboard properties were relatively stable with the further addition of formaldehyde scavenger more than 12 % w/w. The Fourier Transform Infrared Spectrophotometer (FTIR) spectra of particleboards showed variations of methylene and methylene-ether bridges which were corresponded to the curing characteristic and board properties. The corrected area under absorbance of methylene bridge increased with the increasing of formaldehyde scavenger content.

KEYWORDS: Formaldehyde scavenger, urea formaldehyde resin, curing behavior, particleboard.

INTRODUCTION

Urea formaldehyde resin (UF) is a thermosetting resin made from urea and formaldehyde heated in an alkaline condition (Dunky 1998; Pizzi 1994). It is widely used for wood composite production particularly the interior grade products such as particleboard, medium density
fiberboard and plywood. It is also used as a laminating adhesive to bond furniture overlays to panels. The advantages of UF resin including low cost, curing at low temperature, water solubility and lack of color of the cured resin. On the other hand, it cannot resist to the moist and hot conditions which lead to break the bond and release of formaldehyde.

Formaldehyde is a natural gas that lacks color but which has a pungent odor. It is widely used and can be found in building materials, clothing, and cleaning supplies (Dunky 2003). For wood composite products, formaldehyde gas is emitted from formaldehyde-based resins used as binder in many types products, due to the release of unbound formaldehyde remaining after the pressing process and the ongoing hydrolysis of the cured resin. Since formaldehyde can cause cancer in humans, the formaldehyde emission level has become a concern issue. In developed countries such as USA, Japan, Australia, New Zealand and some countries in Europe, the preventive of the import and use of wood products containing formaldehyde has been done. Subsequently, the technology and manufacturing methods which can reduce the formaldehyde emission from wood composites bonded with UF resin have been investigated.

Nowadays, there are many methods for reducing the formaldehyde emission for wood composite products. The main ones are: (i) Modification of resin formula, usually be the reduction of formaldehyde-urea molar ratio (Dunky 1995; Markessini 1993; Quea et al. 2007) or mixing of UF resin with other resins (H'ng et al. 2011; Markessini 1993; Quea et al. 2007) (ii) addition of formaldehyde scavenger to the UF resin or wood furnish (Hematabadi and Behrooz 2012; Lorenz et al. 1999; Moubarki et al. 2013) (iii) changing the pressing parameters such as pressing time or pressing temperature increasing (Kronospan Technical Company Limited 2002; Petinarakis and Kavvouras 2006) (iv) treating of finish boards, generally posing with ammonium gas or surface processing with formaldehyde scavenger solution (Luftman 2005; Roffael 2011) and (v) changing to an entirely different adhesive system (Wanga et al. 2007). The most widely used method is the addition of formaldehyde scavenger. The substance can be used as the formaldehyde scavenger actually including: Urea, melamine, phenol, resorcinol, polyethelene-polyamidc, lignin-sulphonates, polyacrylamide, diphenylmethandiisocyanate, aniline and hydroxylamine. Notable, the scavengers widely used in the industry are composed of urea and ammonium salt. This substance can be used by adding into the liquid UF resin and directly spraying into wood furnish with the generally equipments. There are actually many practical advantages in using the scavenger system. One advantage to note is the flexibility it provides to the plant manager to vary its quantity, and subsequently, control the reduction of formaldehyde emission according to the conditions and production requirements. It provides a much more efficient system than that of a straight resin. However, the addition of formaldehyde scavenger can influence the cure properties of resin and product properties.

Differential scanning calorimetry (DSC) is a technique which is most widely used to study for resin curing behavior during cure in the hot press. Furthermore, it can be used to predict the optimization of process variables which improve production efficiency, also reducing the need of costly trial and error tests. Several research have been studied the effect of additive on curing behavior of UF resin by DSC techniques (Kim et al. 2006; Lee et al. 2006; Myers 2009; Popović et al. 2011; Sun et al. 2011). They reported that the additives can influence the overall cure properties of UF resin.

Fourier Transform Infrared Spectrophotometer (FTIR) spectroscopy is an analytical method to monitor and identify the presence of functional groups in material such as wood. It can be used to investigate a chemical finger-print of the main organic constituents in wood (Fengel and Wegener 2003). It is also used to analyze chemical bonding between wood, wood components and resin (Fabo 2004). In the literature, numerous studies characterized the cured UF resin by
FTIR method (Jada 1988; Siimer et al. 2006; Yasar et al. 2010; Zorba et al. 2008).

The main objective was to determine the effect of formaldehyde scavenger adding on the curing behavior of UF resin and properties of particleboard-bonded with UF resin. In this research, the DSC method was used to follow curing behavior of UF resin on a wood substrate related to the different content of formaldehyde scavenger. This study also reports the formaldehyde emission, physical and mechanical properties of particleboards made from rubberwood bonded with UF resin. Additionally, the chemical characteristic of laboratory-made particleboards was analyzed by FTIR technique.

**MATERIAL AND METHODS**

**Raw materials preparation**

Rubberwood particles used in this study were obtained from the local particleboard plants. All particles were separated into five fractions with a mesh size of 5.0, 3.15, 1.25 and 0.25 mm. Each fraction of particles with different dimensions were then dried to a moisture content of 2 % and then stored in plastic bags and further used.

UF resin E2 type (Model: UA-243) and formaldehyde scavenger (Model: TD CATCH) were used in this research was supplied by TOA Dovechem Co. Lt. The water solution with 40 % of Ammonium sulfate [(NH₄)₂SO₄] was used as catalyst and mixed with the resin before spraying into wood particles. The working properties of UF resin and formaldehyde scavenger were determined according to standard analysis method. The general characteristics of UF resin and formaldehyde scavenger are presented in Tab. 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Urea formaldehyde resin</th>
<th>Formaldehyde scavenger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Pale liquid</td>
<td>Muddy-yellow liquid</td>
</tr>
<tr>
<td>Viscosity at 20°C (cps)</td>
<td>245</td>
<td>3.75</td>
</tr>
<tr>
<td>Solid content (%)</td>
<td>64.24</td>
<td>46.41</td>
</tr>
<tr>
<td>Density at 20°C (g.cm⁻³)</td>
<td>1.29</td>
<td>1.14</td>
</tr>
<tr>
<td>pH value at 20°C</td>
<td>8.46</td>
<td>7.54</td>
</tr>
<tr>
<td>Buffer capacity (Milliequivalent)</td>
<td>0.99</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Determination of resin curing behavior**

Rubberwood-fine powders of 0.25 mm size with moisture content of 2 % were used to investigate the wood-resinated curing behavior by DSC analysis. The represented proportion of UF resin, wood, catalyst and formaldehyde scavenger was subjected to a blending process in particleboard manufacturing. About 10 parts of liquid UF resin per 100 parts of wood powders were mixed with 1 % w/w based on resin solid content of catalyst. Additionally, the effect of formaldehyde scavenger content on the resin curing was obtained with the following content of formaldehyde scavenger: 0, 6, 12, 18 and 24 % w/w. All components were combined in the glass plates and blended together at room temperature. Subsequently, the mixtures were placed in a circulating air oven at 60±1°C until most of the solvent was evaporated.

Differential scanning calorimeter (DSC METTER Model: TOLEDO DSC822e) was used to investigate the curing reactions of UF resin. Small amounts of sample, which was described above, were weighed accurately and placed in the aluminum pans with a crimpable seal. An empty pan served as a reference. All samples were tested run with a heating rate 5°C.min⁻¹
and a temperature range of 25-250°C. The analysis was performed under nitrogen atmosphere. The DSC thermograms display the heat flow as a function of temperature and the area of the endothermic peaks presenting the reaction enthalpy. The instrument software was used to determine the position of the peak temperature.

**Laboratory particleboard manufacture and its properties testing**

Three-layer particleboards with target density of 0.65 g.cm⁻³ were manufactured using laboratory equipment based on five levels of formaldehyde scavenger content. The surface layer of board consisted of particles with the size of 1.25 mm while the core layer was composed of particles with the size of 3.15 mm. The wood particles were weighted and placed in an inhouse-made paddle type blender. The aqueous solution of resin and additive mixture with six level of formaldehyde scavenger (0, 6, 12, 18 and 24 % w/w) was applied by an air-atomizing nozzle. To ensure uniform glue distribution, the optimal conditions of rotation rate, retention time in the blender and the amount of furnish for one-glue application were determined by pretests. After blending, the furnish was then hand felted into 40 × 40 cm box to form the mat. After forming, mats were transferred to a single-opening hydraulic lab hot press (WABASH MPI Model 200H-24-X) and pressed into boards at a nominal thickness of 10 mm. In this study, 25 boards were produced by employing a manufacturing parameter following the suggestion of glue supplier, as presented in Tab. 2.

**Tab. 2: Manufacturing parameters used for the particleboard production.**

<table>
<thead>
<tr>
<th>Manufacturing parameters</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface : Core ratio</td>
<td>-</td>
<td>45:55</td>
</tr>
<tr>
<td>Resin content</td>
<td>% w/w</td>
<td>Surface layer = 10, Core layer = 7</td>
</tr>
<tr>
<td>Catalyst content</td>
<td>% w/w</td>
<td>Surface layer = 1, Core layer = 5</td>
</tr>
<tr>
<td>Mat moisture content</td>
<td>%</td>
<td>Surface layer = 9, Core layer = 7</td>
</tr>
<tr>
<td>Pressing temperature</td>
<td>°C</td>
<td>180</td>
</tr>
<tr>
<td>Pressing time</td>
<td>Second/millimeter</td>
<td>10</td>
</tr>
<tr>
<td>Pressure</td>
<td>N.mm⁻²</td>
<td>25</td>
</tr>
</tbody>
</table>

All boards were machined into test specimens and placed in a conditioning room maintained at 65 % RH and 20°C for 4 weeks until constant weight was attained. The properties of specimens were determined as follow: Density (D), Moisture content (MC), thickness swelling (TS), modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding strength (IB) and formaldehyde emission (FE) were performed in accordance with JIS A 5908-2003. Effects of formaldehyde scavenger content on the properties of the boards were evaluated by analysis of variance at the 0.01 level of significance. The Duncan’s Range tests were conducted to determine significant differences between mean values.

**FTIR spectroscopy analysis**

The infrared spectrum analysis was performed on the manufactured particleboards using a Perkin Elmer FTIR Spectrometer (Model: Spectrum one) in the absorbance mode. The board samples manufactured with the different level of formaldehyde scavenger were grounded into small particles having a size of 250 μm. 1 part of the each sample (on oven dry basis) was dispersed in a matrix of 1.000 parts of KBr, followed by compression to form KBr-IR pellet. The spectra were obtained in the spectral area 4000-400 cm⁻¹, with a resolution of 4 cm⁻¹ and 32 scans at room temperature. Typically, this procedure yielded spectral data that could be reproducibly obtained with < 2 % deviations in relative peak ratios.
RESULTS AND DISCUSSION

Resin curing behavior

To investigate the effect of scavenger on the cure characteristic of UF resin, samples of wood powders blended with UF resin and five different amounts of formaldehyde scavenger were investigated. The DSC thermograms display the relative characteristic shifting, onset temperature and peak positions of endotherm, as the amounts of scavenger in samples increase (Fig. 1). This shifting indicates different enthalpy levels of curing reaction occurred in each sample during heated in the DSC furnace. To clarify this result, the information from DSC showed in Fig. 1 is illustrated in terms of reaction enthalpy and peak temperature as a function of formaldehyde scavenger contents (Fig. 2). Obviously, reaction enthalpy rapidly decreases as the amounts of scavenger increased from 0 to 12 % w/w and then it gradually decays until the amount of scavenger reaches 24 % w/w. The reduction in reaction entropy observed here is accounted for lower energy needed for UF curing in samples with greater amounts of formaldehyde scavenger. Additionally, the position of peak temperature tends to appear earlier and shorter UF curing time is also observed when the amounts of scavenger increase. These evidences indicate that curing of UF become more active when higher amounts of formaldehyde scavenger are introduced in samples. In other words, higher degrees of UF curing would be achieved when the sample consisting of greater scavenger amount is cured under the same condition.

![Fig. 1: DSC thermograms of wood powders blended with UF resin and various contents of formaldehyde scavenger obtained from DSC at the heating rate of 5°C.min⁻¹.](image1)

![Fig. 2: The effect of formaldehyde scavenger on the reaction enthalpy and peak temperature of wood powders blended with UF resin.](image2)

This phenomenon can be explained by the effect of ammonium chloride added in the composition of scavenger on the decreasing of resin pH value resulting in the increased adhesive reactivity. It is known that UF resin is an acid-catalyzed curing resin and, thus, the curing rate increases when pH value of UF resin decreases. Interestingly, UF curing rate stated above is significantly affected at lower contents of formaldehyde scavenger (6-12 % w/w), the values of reaction enthalpy and peak temperature decrease very rapidly, and the addition of formaldehyde scavenger at the levels above 12 % w/w is not as much effective. The possible mechanism might explain that most of reactive groups in UF resin were activated when the formaldehyde scavenger was added. With further addition of formaldehyde scavenger, there is slightly effect on resin curing rate.
Performance of UF-bonded particleboards

Average physical and mechanical properties and the formaldehyde emission form particleboards bonded with UF resin and added five level contents of formaldehyde scavenger are summarized in Tab. 3. In accordance with Duncan’s multiple range tests also presented in Tab. 3, there is a significant difference in thickness swelling, modulus of rupture, modulus of elasticity, internal bonding strength and formaldehyde emission as function of formaldehyde scavenger content. These properties improve with increasing of formaldehyde scavenger content. It is interesting to note that particleboard added with 24 % w/w formaldehyde scavenger results in the best overall board properties. The results suggest that the board property results are consistent with DSC results. Particleboards made with higher formaldehyde scavenger content show better properties. It could be also noticed the addition of formaldehyde scavenger at the levels above 12 % is not as much effective because the board properties are constant.

Tab. 3: The average property values of UF-bonded particleboard with various contents of formaldehyde scavenger.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Formaldehyde scavenger content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 (n=5) 6 (n=5) 12 (n=5) 18 (n=5) 24 (n=5)</td>
</tr>
<tr>
<td>Density (g.cm⁻³)</td>
<td>0.65 A,₂ (0.03) 0.65 A (0.03) 0.64 A (0.03) 0.65 A (0.02) 0.65 A (0.02)</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>9.66 A (0.20) 9.56 AB (0.08) 9.41 B (0.31) 9.38 B (0.08) 9.50 AB (0.11)</td>
</tr>
<tr>
<td>Thickness swelling (%)</td>
<td>17.46 A (1.38) 16.20 AB (1.64) 14.58 BC (1.17) 14.21 BC (1.84) 14.00 C (1.99)</td>
</tr>
<tr>
<td>Modulus of rupture (MPa)</td>
<td>8.19 B (1.48) 8.27 B (1.40) 10.27 A (1.53) 10.62 A (1.22) 10.67 A (1.53)</td>
</tr>
<tr>
<td>Modulus of elasticity (MPa)</td>
<td>1.522.5 A (204) 1.634.6 A (264) 1.626.3 A (94) 1.716.4 A (192) 1.764.9 A (40)</td>
</tr>
<tr>
<td>Internal bonding strength (MPa)</td>
<td>0.32 B (0.07) 0.35 AB (0.05) 0.39 AB (0.08) 0.45 A (0.18) 0.47 A (0.07)</td>
</tr>
<tr>
<td>Formaldehyde emission (mg/L)</td>
<td>13.65 A (0.17) 6.91 B (0.30) 4.93 C (0.18) 3.57 D (0.10) 1.67 E (0.01)</td>
</tr>
</tbody>
</table>

Note: ¹ n is the number of replications per treatment.
² The average values with the same letter are not significantly different.
³ Numbers in parentheses are standard deviations from the sample mean.

Chemical structure of UF-bonded particleboards

Tab. 4 summarizes the major bands and corrected area values according to previous study (Jada 1988). Jada identified that the board band at around 3.000 – 4.000 cm⁻¹ is the characteristic of hydroxyl (-OH) stretchings of the methylol group. The small bands at 1.443 – 1.487 cm⁻¹ and 1.097 – 1.145 cm⁻¹ can be assigned to methylene (-CH₂-) bridge and methylene-ether (-CH₂OCH₂-) bridge, respectively.

The results revealed that the corrected area of methylene bridge increased with the increasing of formaldehyde scavenger content while the corrected area of hydroxyl group and methylene ether bridge decreased. It is interpreted these changes could be related to the formation cross-linking structure between urea and formaldehyde. It has been demonstrated that methylene-ether bridges can rearrange themselves to methylene bridges with the formaldehyde release (Garnier 2002). UF resin cure is catalyzed by acid. This commercial formaldehyde scavenger contains ammonium...
chloride which release acid and decrease the pH of resin. This occurrence can accelerate curing process which influence change of methylene-ether bridges (low cohesive strength, low resistance to hydrolytic degradation and less dimensional stability) to the methylene bridges (high cohesive strength, high resistance to hydrolytic degradation, and best dimensional stability). The high content of methylene bridges can improve board strength and stability. In consequence, the decreasing of methylene-ether bridges causes the reduction of formaldehyde emission. Moreover, it is expected that urea react with free formaldehyde and form a rigid cross-linked polymer of urea formaldehyde. Therefore, changes in the composition between methylene and methylene-ether bridges in samples containing five levels of formaldehyde scavenger found here also reflect the different reaction enthalpy took place inside the samples and are consistent to the results of DSC mentioned previously. The results of FTIR testing also correlate very well with the thickness swelling, internal bonding strength and formaldehyde emission studies.

Increasing the formaldehyde scavenger content of particleboard can increase product properties. However, the product properties distinctly increase when the formaldehyde scavenger content increases to 12%. With further increasing in formaldehyde scavenger content (>12%), the particleboard properties are slightly constant. Therefore, it appears that the optimum content of formaldehyde scavenger is around 12% based on the solid content in the resin.

**CONCLUSIONS**

In this study, we demonstrated the effect of formaldehyde scavenger on the curing behavior, bonding strength, formaldehyde emission and chemical characteristics of UF resin for particleboard manufacturer. The following conclusions can be drawn at this stage:

1. The reaction enthalpy and peak temperature during curing of wood powders blended with UF resin decrease with the increase of formaldehyde scavenger content. All values decreased up to the formaldehyde scavenger content of 12% w/w and then were rather constant with its further addition.

2. The addition of formaldehyde scavenger could improve bonding strength of the panels and greatly reduced their formaldehyde emission.
(3) The FTIR spectra of lab-made particleboards showed variations of methylene and methylene-ether bridges which were corresponded to the curing characteristic and board properties. the corrected area under absorbance of methylene bridge increased with the increasing of formaldehyde scavenger content.

(4) With regard to the most optimum properties and production cost of particleboard, the best results were obtained by using 12 % formaldehyde scavenger content.

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REFERENCES


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