Urea-formaldehyde resins: production, application, and testing

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Urea-formaldehyde resins: production, application, and testing

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Abstract. Urea-formaldehyde (UF) resin, one of the most important formaldehyde resin adhesives, is a polymeric condensation product of formaldehyde with urea, and being widely used for the manufacture of wood-based composite panels, such as plywood, particleboard, and fiberboard. In spite of its benefits such as fast curing, good performance in the panels (colorless), and low cost, formaldehyde emission (FE) originated from either UF resin itself or composite products bonded by UF resins is considered a critical drawback as it affects human health, particularly in indoor environment. In order to reduce the FE, lowering the formaldehyde urea (F/U) mole ratio in the synthesis of the UF resin was done. In this study, synthesis of UF resins was carried out following the conventional alkaline-acid two-step reaction with a second addition of urea, resulting in F/U mole ratio around 1.0, namely 0.95, 1.05, and 1.15. The UF resins produced were used as binder for particleboard making. The board was manufactured in the laboratory using shaving type particle of Gmelina wood, 8% UF resin based on oven dry particle, and 1% NH₄Cl (20%wt) as hardener for the resin. The target of the thickness was 10 mm and the dimension was 25 cm x 25 cm. The resulted particleboard then was evaluated the physical and the mechanical properties by Japanese Industrial Standard (JIS) A 5908 (2003). Further, the resulted particleboard also was used for the mice cage’s wall in order to mimic the real living environment. After four weeks exposure in the cages, the mice then were evaluated their mucous organs as well as their blood. The experiment results were as follows: 1) It was possible to synthesis UF resins with low F/U mole ratio. 2) However, the particleboard bonded UF resins with low F/U mole ratio showed poor properties, particularly on the thickness swelling and modulus of elasticity. 3) There was no significant differences among the mucous organs of the mice after a month exposure FE originated from cages wall using histopathology assessment.

1. Introduction

Urea-formaldehyde (UF) resin, one of the most important formaldehyde resin adhesives, is a polymeric condensation product of formaldehyde with urea. Traditionally, UF resins were used as a wood adhesive. Initially, wood working industry used this resin, and in the development, wood based panels industry has been mainly used this resin up to date [1] for manufacturing wood-based composite panels, such as plywood, particleboard, and fiberboard. In other words, the wood panel industry is a major consumer of UF resin adhesive [2].

In spite of its benefits such as good appearance (due to colorless when it is applied in wood), good performance (the strength properties fulfill the required standards), fast curing (as thermosetting polymer, we can apply heat for making faster curing), and economical (the raw material is quite inexpensive and distribute elsewhere, thus large scale production can be applied), formaldehyde emission (FE) originated from either UF resin itself or panel products bonded by UF resins is
considered a critical drawback as it affects human health particularly in indoor environments [3-6]. Many countries applied stringent policies on FE regulation. For instance, the United Kingdom, China, and Japan followed a recommendation of the World Health Organization (WHO) which adopted a limit of 0.1 mg/m³ or about 0.08 ppm, while Canada, Germany, and Singapore had a slightly higher limit of 0.123 mg/m³ or about 0.1 ppm [7]. Either manufacturers of UF adhesive or researchers responded to produce ideal resin to satisfy both the regulations as well as public awareness in health regarding the FE using various methods, for instance modifying UF resins itself [8-14] or modified UF resin bonded wood products [5, 15-23].

It is believed that producing resins which fulfilled these requirements could be done by decreasing the formaldehyde/urea (F/U) mole ratio [3]. Extensive works have been reported that the properties of UF resins are significantly influenced by the mole ratio of F/U, and it is often done by the incorporation of excess urea during the condensation step [24]. This procedure can remove most of the free formaldehyde species and hemiformals when hot pressing stage. Further, Bizzi et al., (1994) [25] strengthened that theoretically, low mole ratio of UF resin can deal with the physical and mechanical properties on the wood panels bonded by UF resins.

Yet, despite aforementioned studies in low mole UF resins, there is still an information gap on the comprehensive report on UF resins. Therefore, this study prepared synthesis of low F/U mole ratio liquid UF resins, their application on particleboard, and then rendered them to expose into mice in order to imitate the real condition of FE in building. The objective of this study is to evaluate the synthesis of low F/U mole of UF resins, the application to panel products particularly particleboard, and the effect of formaldehyde release originated from particleboard bonded low F/U mole of UF resin into mice.

2. Materials and Methods

In this study, synthesis of UF resins was carried out following the conventional alkaline-acid two-step reaction (the pH of addition and condensation reaction was 7.8 and 4.6, respectively) with an addition of second urea, resulting in F/U mole ratio around 1.0, namely 0.95; 1.05, and 1.15. For higher mole, UF resin with F/U mole of 2.0 was also prepared.

Then, UF resins produced were used as binder for particleboard making. The board was manufactured in the laboratory using shaving type particle of Gmelina wood, 8% UF resin based on oven dry particle, and 1% NH₄Cl (20%wt) as hardener for the resin. The target of the thickness was 10 mm and the dimension was 25 cm x 25 cm. The resulted particleboard then was evaluated the physical and the mechanical properties by Japanese Industrial Standard (JIS) A 5908 (2003) [26], including their class emissions.
Further, the resulted particleboard was used for the mice cage’s wall and floor in order to imitate the real living environment. The mice were acclimatized prior to enter the cages for a week. During four weeks exposure in the cages, the mice were examined their behavior (movement and feeding manners) including the body weight. Observation on tissue organs changes was evaluated by histopathology anatomy for evaluation the effect of FE releasing from the particleboard. Additional analysis has been studied on the hematology of the mice.

3. Results and Discussions

3.1. Synthesis of Low F/U mole of UF Resins

UF resins are synthesized by the reaction of formaldehyde and urea. Usually, technical grade urea granules (99%) and formalin (37%) are used for the raw materials and aqueous solutions of both formic acid (20%wt) and sodium hydroxide (20%wt) are used to adjust the pH level during and the final of reaction.

The reaction is influenced by several parameters. It requires precise control of purity, amount and sequence of addition of the raw materials, alkaline and acid catalysts. The preparation conditions are adjusted and monitored with respect to temperatures, pH, and concentration of the reactants. Initially, the resin was reacted with an alkaline catalyst to initiate the addition reaction, and at the appropriate reaction time the resin solution was converted to the acid side to promote the condensation reaction [27]. Even though there were three possible procedures according to reaction pH conditions for synthesis, namely alkaline, weak acid, and strong acid [28-29], however, synthesis of UF resin in alkaline condition resulted in the best internal bond strength on particleboard [29].

Synthesis of UF resins in the laboratory was described elsewhere [29-37]. It is usually based on conventional two step reactions, consisted of methylation or addition reaction and condensation reaction. Briefly, the formalin is placed in the glass cooking reactor with the mantle heater and the condition is adjusted into pH 7.8–8.0. Then, the 1st urea is placed into the reactor, yielding a molar ratio F/U of 2.0. The mixture is heated to 90°C for one hour to allow the methylation reaction. The temperature is then adjusted to 80°C and the condensation reaction is carried out in the pH 4.6 up to target viscosity. When the condition is reached, the 2nd urea is added in order to consume excess of formaldehyde and determine the F/U mole ratio of final UF resins. After all of the urea dissolve, the UF resins are cooled to room temperature, and the pH is subsequently adjusted to 8.0 for terminating the reaction. Figure 1 showed the synthesis of UF resin and its result.
In this work, it was not possible to synthesis UF resins with low F/U mole ratio, i.e., 0.90. Even though Pizzi et al., (1994) [25] stated that theoretically F/U mole ratio of 0.70 can give adequate balance between strength and emission, but practically only F/U mole ratio in between 0.90 and 1.0 was effective for industrial application. Therefore, in this study, synthesis on UF resins was carried out to the final F/U mole ratio of 0.95, 1.05, and 1.15. For comparison, high F/U mole of 2.0 was also made.

Table 1 showed the characteristics of UF resins synthesized in this work. Reducing the F/U mole ratio resulted in increasing of solid content of the resin due to the addition of the second urea used in raw materials. Moreover there was a tendency of the density; the lower F/U mole ratio of UF resin the higher of the density. UF resin with the lowest F/U mole ratio gave the highest density probably because of the sol fraction containing in the resin. Previous work on film UF resin exhibited abundant sol fraction in low F/U mole UF resin compare to in high F/U mole UF resin [38].

In this work, the viscosity performed fluctuate but the trend showed the highest F/U mole ratio of UF resin has had the most viscous, indicating that the reactivity of high F/U mole ratio UF resin adhesive was greater compared to that of the low F/U mole ratio. A lower viscosity indicated a low molecular weight of UF resin adhesives because the viscosity of liquid UF resin adhesives is proportional to their molecular weight [39]. Related to gel time measurements, indeed UF resin with high F/U mole ratio was more reactive contrasted by low F/U mole ratio. The milky white color of the resin is due to ageing or further advancement of the resin by condensation reaction [40-42].
Table 1. Characteristics of UF Resins Synthesized in this Study

<table>
<thead>
<tr>
<th>No</th>
<th>F/U mole ratio</th>
<th>Solid Content (%)</th>
<th>Density (g/cm³)</th>
<th>Viscosity (MPa.s)</th>
<th>Gel time (minutes)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.95</td>
<td>52.65 ± 0.38</td>
<td>1.54</td>
<td>215</td>
<td>13.13</td>
<td>Dispersed, milky white</td>
</tr>
<tr>
<td>2</td>
<td>1.05</td>
<td>48.64 ± 0.08</td>
<td>1.48</td>
<td>144</td>
<td>11.41</td>
<td>Opaque, milky white</td>
</tr>
<tr>
<td>3</td>
<td>1.15</td>
<td>46.99 ± 0.07</td>
<td>1.47</td>
<td>131</td>
<td>9.45</td>
<td>Milky white</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>37.17 ± 0.38</td>
<td>1.46</td>
<td>444</td>
<td>4.41</td>
<td>Dispersed, milky white</td>
</tr>
</tbody>
</table>

3.2 Properties of Particleboard Bonded by low F/U mole of UF Resin

Comparison among the properties was made not only using particleboard bonded by low F/U mole ratio UF resins data but also using particleboard bonded by higher mole UF resin, commercial and JIS standard as well. Figure 2 showed the performance of particleboard bonded by either UF resin synthesized in this work or commercial one.

![Figure 2. Performance of Particleboard Bonded by UF Resins in this Study](image)

Generally, the performance among the particleboard was similar. Because of the excess of thickness (more than 10 mm) in consequence of spring back effect [43], the density of the particleboard was obviously below the target of 0.75 kg/cm³ as shown in Table 2. Fortunately, the average values of the density have been fulfilled the JIS standard. This means in this case the UF resin adhesives with low F/U mole were able to compete with higher F/U mole (2.0) and commercial one to reach the density target. Thus the particleboard can be used as raw material of mice cage.
Table 2. The Properties of Particleboard Bonded by UF Resin with Various F/U mole ratio

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>0.95</th>
<th>1.05</th>
<th>1.15</th>
<th>2.0</th>
<th>Commercial</th>
<th>JIS A 5908 (2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>0.54 (0.05)</td>
<td>0.50 (0.02)</td>
<td>0.51 (0.02)</td>
<td>0.57 (0.03)</td>
<td>0.54 (0.04)</td>
<td>0.40-0.90</td>
</tr>
<tr>
<td>Internal Bonding</td>
<td>kgf/cm²</td>
<td>1.06 (0.84)</td>
<td>0.31 (0.09)</td>
<td>0.45 (0.40)</td>
<td>2.76 (0.53)</td>
<td>3.07 (1.23)</td>
<td>&gt; 1.5</td>
</tr>
<tr>
<td>Modulus of Elasticity (MOE)</td>
<td>kgf/cm²</td>
<td>296 (77)</td>
<td>359 (176)</td>
<td>246 (211)</td>
<td>99 (25)</td>
<td>154 (36)</td>
<td>&gt; 20000</td>
</tr>
<tr>
<td>Modulus of Rupture (MOR)</td>
<td>kgf/cm²</td>
<td>45 (26)</td>
<td>36 (13)</td>
<td>49 (25)</td>
<td>145 (35)</td>
<td>134 (19)</td>
<td>80</td>
</tr>
</tbody>
</table>

Remarks: The data were mean values based on three replications from three different particleboard and data in the parentheses were the standard deviation.

The mechanical properties the particleboard bonded UF resins with low F/U mole ratio comprising of internal bonding, MOE, and MOR, were not satisfactory (Table 2). Even though the physical property i.e. density, has met the JIS standard, combination these two resulted in dimensional instability, viz. greater thickness swelling and water absorption. The similar phenomenon has been occurred in many previous works [43-46].

By contrast, both higher mole F/U of 2.0 UF resin and commercial one exhibited reasonable mechanical properties particularly for internal bonding and MOR. However, values of MOE were far away from the target. This condition was prevalent in particleboard products particularly which was made in laboratory scale. Therefore, there are many ways to improve these circumstances such as making oriented particleboard [47] or covering the particleboard using veneer [48]. In this study, the particleboards were used as cage mice’s wall which did not need structural requirements. Therefore, the lower values of MOE were not a barrier for this necessity.

According to the JIS standard, the formaldehyde release originated from all the observed particleboard showed range values between 0.1032 and 0.3741 mg/L except commercial one. These values were categorized as class emission of F**** or very low concentration. We did not include the commercial one because we cannot determine the initial formalin used in this type of adhesive. From this point, we can assume that the particleboard used in this experiment have very low emission of formaldehyde even though many factors affected this situation, namely relative humidity, temperature, ventilation, periods of storage, type of adhesive, type of the wood used, and condition of production [10].

3.3 Effect of FE Release from Particleboard bonded by low F/U mole of UF Resin on Mice

Figure 3 shows mice in the cage with particleboard wall except the control. During
observation for a month, there were no mortality rate and no differences on the behavior between treated mice and the control. The behavior including normal movement, normal feeding behavior, and no weight body loss which indicated the mice were not stress.

![Figure 3](image-url)

*Figure 3.* Typical mice in their cage with particleboard wall when four weeks exposed (a) control; (b) using particleboard wall bonded by UF resin of 0.95 (c) using particleboard wall bonded by UF resin of 1.05 (d) using particleboard wall bonded by UF resin of 1.15, and (e) using particleboard wall bonded by UF resin of 2.0

Table 3 showed the body weight of mice before, after and the changes during observation. There was addition of mice’s body weight around 18-36% which indicated the mice did not suffer and their nutrition was appropriate.

<table>
<thead>
<tr>
<th>UF resin adhesive used on particleboard wall</th>
<th>Body weight</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (without)</td>
<td>Initial (g)</td>
<td>28.6</td>
</tr>
<tr>
<td>Mole F/U of 0.95</td>
<td>27.6</td>
<td>35.4</td>
</tr>
<tr>
<td>Mole F/U of 1.05</td>
<td>27.2</td>
<td>32.2</td>
</tr>
<tr>
<td>Mole F/U of 1.15</td>
<td>25.6</td>
<td>34.4</td>
</tr>
<tr>
<td>Mole F/U of 2.0</td>
<td>24.2</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Related to the influence of formaldehyde release originated from particleboard bonded of UF resins, investigation on organ’s tissue alteration such as lung and liver by histopathology anatomy examination have to be carried out.

According to the aforementioned mice’s behavior, presumably there were no differences on histopathology mucous membrane (trachea) among the examined mice because it needs longer time periods [49]. Therefore, in this experiment the first investigation on histopathology mucous membrane was carried out on the trachea. Trachea is the first area that contact with the air. Figure 4 showed the
example of the photomicrograph of mice’s trachea tissue which exposed to formaldehyde emission, with the magnification of 40x and 400x, respectively.

\[ \text{Figure 4. Photomicrograph of observed mice’s trachea tissue which exposed to formaldehyde emission from particleboard a) on mol of formalin 0.95 with magnification of 40x b) on mol of formalin 2.0 with magnification of 400x.} \]

As demonstrated in Figure 4, there was no specific lesion between control (without exposure on formaldehyde emission) and treatment (on mol of formalin 2.0, the highest exposure). In other words, the histological examination of the trachea revealed normal condition. Therefore, additional testing, such as blood analysis [50] has been also recommended in order to investigate further. The blood was examined and then was analyzed on the differences of hemoglobin, white blood cell (WBC), red blood cell (RBC), and platelets as shown in Table 4.

\[ \text{Table 4. Results of hematology parameters of control mice and those exposed to particleboard bonding of UF resin on various mol of formalin} \]

<table>
<thead>
<tr>
<th>No</th>
<th>Sample code</th>
<th>Hemoglobin (g/dL)</th>
<th>WBC (10^9/L)</th>
<th>RBC (10^12/L)</th>
<th>Platelets (10^9/L)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>0.95 I</td>
<td>15.7</td>
<td>2.6</td>
<td>7.23</td>
<td>212</td>
</tr>
<tr>
<td>2</td>
<td>0.95 II</td>
<td>12.4</td>
<td>3.9</td>
<td>6.29</td>
<td>378</td>
</tr>
<tr>
<td>3</td>
<td>1.05</td>
<td>16.5</td>
<td>2.9</td>
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<td>4</td>
<td>1.15 I</td>
<td>14.1</td>
<td>4.5</td>
<td>6.39</td>
<td>174</td>
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<tr>
<td>5</td>
<td>1.15 II</td>
<td>14.1</td>
<td>3.7</td>
<td>7.17</td>
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<td>6</td>
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<td>5.2</td>
<td>4.28</td>
<td>196</td>
</tr>
<tr>
<td>7</td>
<td>2.0 II</td>
<td>16.9</td>
<td>8.1</td>
<td>6.23</td>
<td>392</td>
</tr>
<tr>
<td>8</td>
<td>control</td>
<td>15.5</td>
<td>3.5</td>
<td>6.93</td>
<td>158</td>
</tr>
</tbody>
</table>

The observed increase in WBC as the increasing of mol of formalin in exposed mice in this study may be attributed to the primarily function of the WBC in body defense against foreign bodies including emissions of formaldehyde [50].
4. Conclusion

In this work, it was not possible to synthesis UF resins with low F/U mole ratio i.e. 0.90. Therefore, in this study, synthesis on UF resins was successfully carried out to the final F/U mole ratio of 0.95, 1.05, 1.15 (for low mole) and 2.0 (for high mole).

All the UF resins produced can be applied as adhesive for making particleboard. Even though the quality of particleboard was poor, particularly in MOE, in this study the particleboards were only used as cage mice’s wall which did not need structural requirements. Therefore, at least the particleboard can be utilized for this purpose.

According to the mice behavior, presumably there were no significant alterations among the mucous membrane of the mice because it is not adequate time in exposing mice into particleboard bonded by UF resins.

Acknowledgments

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<td>Publication</td>
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