Development of melamine modified urea formaldehyde resins based on strong acidic pH catalyzed urea formaldehyde polymer

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Abstract

To upgrade the performance of urea-formaldehyde (UF) resin bonded particleboards, melamine modified urea-formaldehyde (MUF) resins based on strong acidic pH catalyzed UF polymers were investigated. The study was conducted in a series of two experiments: 1) formulation of MUF resins based on a UF polymer catalyzed with strong acidic pH and 2) determination of the effects of increased melamine content and melamine reaction pH on performance of MUF resins. Formaldehyde emission, internal bond (IB) strength, and thickness swell (TS) of the panels made with the formulated MUF resins were evaluated. UF polymer as backbone structure prepared by strong acidic pH had a significant effect on the overall performance of the MUF resin system. Strong acidic pH was the single most important factor effecting the formaldehyde emission of the panels. Melamine content and melamine reaction pH were evaluated in the final 24 MUF resins prepared in the study. The effects of increased melamine content were significant only for IB strength, but changes in melamine reaction pH in resin preparation resulted in a resin system that had a significant effect on the overall performance of the panels. IB strength increased, formaldehyde emission decreased, and TS decreased as melamine reaction pH decreased from 6.0 to 4.5. These results indicated that the changes in molecular species and resin structure in resin preparation as effected by melamine reaction pH were the most important factors in upgrading the performance of MUF resins. A low melamine content MUF resin was fabricated with formaldehyde (F)/urea (U)/melamine (M) molar ratios of 1.38F/1U/0.055M (melamine content of 6.4%) and reacted under melamine reaction pH of 4.5. This resin produced panels that satisfied the required performance standards of both formaldehyde emission (National Particleboard Association 2-h-desicator test) and IB strength (American National Standard Institute’s IB strength for industrial boards).

Exterior-grade melamine-urea-formaldehyde (MUF) resin adhesives are considered too costly to replace urea-formaldehyde (UF) resins for interior applications. Melamine-modified UF resins with reduced melamine content levels have been developed to improve durability and moisture resistance properties. These low-melamine content UF resins have been relatively popular in Europe (Dunky 1995) and in the Asia-Pacific region (Maylor 1995, Parker and Crew 1999) for many years. More recently, melamine-modified UF resins were also shown to yield particleboards with significantly lower formaldehyde emissions than the control UF resins (Graves 1993, Rammon 1997).

It is generally recognized that formulation of low formaldehyde emission UF resins are accomplished primarily by decreasing the formaldehyde/urea (F/U) ratio (i.e., down to 1.2 or even 1.1 ratio). But, it was shown that lower F/U ratio, while yielding substantially lower formaldehyde emission, also resulted in longer resin cure time and lower internal bond (IB) strength (Hse et al. 1994). A method most commonly used to cope with this formaldehyde problem is to react formaldehyde with urea initially at a much higher F/U ratio and strong acidic condition to form the backbone of the resin system; then, after attaining a desired degree of condensation, additional urea is added to adjust the F/U ratio to meet the desired low F/U ratio in final resin products. Similar methods of reacting urea and formaldehyde at strong acidic pH and adjusting F/U ratio to attain the desired low formaldehyde emission were applied in formulating MUF resin adhesives.

Although the low-melamine content MUF resins have not been widely accepted in North America, interest in the development of cost effective resin systems for upgrading particleboard and medium density fiberboard (MDF) remains high because of increasing exports of particleboards to Japanese and Asian markets. This paper is one of a series to describe the development of melamine modified UF resins.
efforts to develop a low melamine content MUF resin system to improve gluebond durability and formaldehyde emissions of particleboard. The study involved two experiments: 1) formulation of MUF resins based on a UF polymer catalyzed with strong acidic pH and 2) determination of the effects of increased melamine content and melamine reaction pH on the performance of MUF resins.

**Experiment 1 – Formulation of MUF resin based on UF polymer catalyzed with a strong acidic pH**

The two guidelines for this experiment were 1) to react formaldehyde and urea at strong acidic pH of 1.0 to form a UF polymer as a backbone structure and then coreact with melamine to form the MUF resin and 2) to set the maximum melamine contents in the system not to exceed 0.035 mol (i.e., 4.39% weight basis) per each mole of urea in a UF polymer at U/F ratio of 1.2. This was for economic considerations because the MUF resin developed was intended to upgrade UF resin for interior applications.

**Experimental procedure**

Resin preparation. — All of the resins were fabricated in the laboratory by reacting formaldehyde (3 mol) and urea (1 mol) at pH 1.0 for 30 minutes at 70°C. Then the pH was adjusted to either 4.5 or 6.5 and melamine (either 0.0625 or 0.0875 mol) was added to react for 30 minutes at 80°C. Thereafter, 1.5 mol of urea was added in three equal parts at 30-minute intervals at 80°C, and finally reaction was terminated by cooling to room temperature within 10 minutes. The final molar ratios of F/U/M were 1.2F/1U/0.025M and 1.2F/1U/0.035M. Furthermore, with two levels of melamine reaction pH (4.5 and 6.5) and three resin replications for each condition, a total of 12 resins (two F/U/M ratios × two melamine reaction pH × three resin replications) were fabricated.

Particleboard manufacture. — All of the panels were prepared in the laboratory with wood particles obtained from a local particleboard plant. The particles were classified in the plant as core materials with a mean moisture content (MC) of 3 percent. The particles were stored in polyethylene bags directly from the dry-end of the mill dryer and were used in the laboratory without further treatment.

To prepare each panel, the wood furnishes were weighed (target board density was 48 pcf [0.769 g/cm³]) and placed in a rotating drum-type blender. The resin, 4.5 percent based on oven-dry weight of wood, was then weighed and applied by an air-atomizing nozzle with air line pressure maintained at 40 psi. Wax and a catalyst were not used in the study. After blending, the wood furnishes were carefully felted into a 19- by 20-in. (48.3- by 50.8-cm) box to form the mat. The mat was transferred immediately to a 40- by 40-in. (101.6- by 101.6-cm) single-opening hot-press with the platen temperature regulated at 375°F (190.6°C). Sufficient pressure (about 550 psi [3,792 kPa]) was applied so that the platen closed to 1/2-in.(1.27-cm)-thickness stops in approximately 45 seconds. Press times were 4 minutes. Board manufacture replication was two boards per condition.

**Particleboard testing.** — All of the boards were conditioned in a chamber at 50 percent relative humidity (RH) and 80°F (26.7°C) before testing, ending with a MC that averaged 5.5 percent. After conditioning, each board was cut to yield ten 2- by 2-inch (5.08- by 5.08-cm) specimens for tensile strength perpendicular to the face, eight 2.75- by 5-inch (6.99- by 12.7-cm) desicator samples for formaldehyde release testing, and four 6- by 6-inch (15.24- by 15.24-cm) dimensional stability specimens (thickness swell [TS]). The internal bond (IB) strength test was performed in accordance with the ASTM standard for evaluating the properties of wood-based fiber and particle panel materials (D 1037-93). For TS evaluation, a 24-hour water soak was employed. The TS values measured changes in thickness after the specimens were submerged in water at room temperature for 24 hours.

**Free formaldehyde and formaldehyde emission measurement.** — Free formaldehyde in the MUF resin was determined by a slightly modified sodium sulfate method as described in a previous study (Hse et al. 1994). For the formaldehyde emission measurement, the test was performed in accordance with the National Particleboard Association (NPA) 2-hour-desicator test.

**Results of Experiment 1**

Table 1 summarizes the properties of MUF resins and bond performances (i.e., IB and formaldehyde emission) of the particleboards. Variance analysis indicated that the changes in melamine reaction pH and F/U/M molar ratio significantly affected the formaldehyde emission but not IB strength. As shown in Duncan’s multiple range tests, higher melamine content and lower melamine reaction pH resulted in lower formaldehyde emissions (Table 2).

It is important to note, however, that:

1. the MUF resin contains a fairly large amount of unreacted formaldehyde (free formaldehyde), even though melamine is known to be highly reactive with formaldehyde,
2. average values of gluebond strength were very low considering the well recognized functional fortification of melamine to UF resin, and

**Table 1. — Properties of MUF resins and IB strength and formaldehyde emission of particleboards.**

<table>
<thead>
<tr>
<th>Melamine reaction pH</th>
<th>Molar ratio of F/U/M*</th>
<th>Resin pH</th>
<th>Resin solid content (%)</th>
<th>Free formaldehyde content (g/mL)</th>
<th>IB strength (psi)</th>
<th>Formaldehyde emission (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>1.2/1/0.025</td>
<td>6.38</td>
<td>48.7</td>
<td>2.13</td>
<td>49.5</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>1.2/1/0.035</td>
<td>6.60</td>
<td>51.8</td>
<td>2.51</td>
<td>56.6</td>
<td>2.08</td>
</tr>
<tr>
<td>6.5</td>
<td>1.2/1/0.025</td>
<td>6.87</td>
<td>52.3</td>
<td>3.45</td>
<td>47.4</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>1.2/1/0.035</td>
<td>6.52</td>
<td>52.9</td>
<td>4.28</td>
<td>54.2</td>
<td>2.38</td>
</tr>
</tbody>
</table>

* F = formaldehyde; U = urea; and M = melamine.
Molar ratio of F/U/M resin system, the formaldehyde per functionality for melamine is six. Therefore, for a molar ratio of 1.2, the formaldehyde per functionality is calculated to be 0.30 (i.e., 1.2/4). The resin system had four functional groups, at a F/U ratio of 1.2, the formaldehyde emission UF resins are primarily formulated at an extremely low F/U ratio of 1.2 or lower. Since urea has four functional groups, at a F/U ratio of 1.2, the formaldehyde per functionality is calculated to be 0.30 (i.e., 1.2/4). On the other hand, in the MUF resin system, the functional group for melamine is six. Therefore, for a molar ratio of 1.2F/1U/0.025 M resin system, the formaldehyde per functionality is calculated to be 0.285 \( \frac{1.2}{(1 \times 4) + (0.035 \times 6)} \). The computation did not take into consideration that melamine is more reactive toward formaldehyde than urea and the reaction of MUF was inadequate and there is some possibility of insoluble gel formation was also greatly increased, which implies a favorable reaction system was increased, which implies a favorable condensation reaction was attained as a result of formaldehyde adjustment.

Duncan's multiple range tests (Table 4) indicated that an increase in melamine content resulted in significantly higher IB and lower formaldehyde emission. The effects of strong acidic pH on formaldehyde emission and IB strength, however, were conflicted. Lower pH yielded lower formaldehyde emission but also resulted in lower IB strength. Furthermore, the effects of acidic pH on IB strength was significant only when comparing between pH of 1.2 and 1.4 or the pH of 1.6 and 1.4; it is possible that an optimum acidic pH for the formulation of MUF resin can be obtained in a narrow range of reaction pH between 1.2 and 1.6 to attain a satisfactory trade off between formaldehyde emission and IB strength requirements.

The American National Standard Institute’s (ANSI) IB strength standard for industrial boards (3/4-in. basis) is 80 to 100 psi, while the Composite Panel Association’s (CPA) formaldehyde emission standard for particleboard is 0.2 ppm by the large scale chamber emission test method. For quality control purposes in the laboratory, a 2-hour-desicator method was often used, and the formaldehyde emission level was set at 1 μg/mL.
Based on above standard and guidelines, two resins (1.38F/1U/0.035M with pH 1.4 and 1.38F/1U/0.035M with pH 1.6) show IB strength met the ANSI standard, but the formaldehyde emission standards were not met. Similarly, only one resin (1.38F/1U/0.035M with pH 1.2) met the formaldehyde emission goal, but not the IB strength. Since all of these resins were fabricated with higher melamine content (0.035M), it was concluded that overall melamine content needed to be increased in order to fabricate a resin to meet both IB strength and formaldehyde emission standards.

**Experiment 2 – Effect of increased melamine content and melamine reaction pH on the performance of MUF resins**

With the reaction pH and F/U ratio for the formation of a desirable UF polymer as a backbone for MUF resin evaluated and optimized in experiment 1, the adjustment of the melamine content and pH control for the melamine reaction were next in-line for further improvements regarding the performance of MUF resins.

**Experimental procedure**

Based on the results from the previous experiment, the formulation variables considered in the experiment were:

- Reaction pH for UF polymer formation: 1.25 and 1.55
- Melamine content: 1.38F/1U/0.055M and 1.38F/1U/0.074M
- pH control for melamine reaction: 4.5 and 6.0

All of the resins were fabricated in the laboratory by reacting formaldehyde (1.38 mol) and urea (0.46 mol) at pH 1.25 or 1.55 for 30 minutes at 70°C. Then, the pH was adjusted to 4.5 or 6.0 and melamine (0.055 mol or 0.074 mol) was added and reacted for 90 minutes at 80°C. Thereafter, 0.54 mol of urea was added in three equal parts at 30-minute intervals at 80°C, and finally the reaction was terminated by cooling to room temperature. The final molar ratios of F/U/M resins were 1.38F/1U/0.055M and 1.38F/1U/0.074M. Resin preparations were replicated three times and two panels were made for each resin. Performances of the resins were evaluated by IB strength, formaldehyde emission, and TS. TS was determined by the differences in panel thickness before and after 24-hour water soak and expressed as a percentage of the original panel thickness. A commercial UF resin was also included in the experiment as a control sample.

**Results of Experiment 2**

Average IB, formaldehyde emission, and TS are summarized in Table 5. ANOVA indicated that the effects of acidic pH were significant on formaldehyde emission, but not on IB strength and TS; the effects of melamine content were significant on IB strength, but not on formaldehyde emission and TS. The effects of melamine reaction pH were significant on all of the properties evaluated.

The most significant results in the experiment were the overall increase in IB strength as melamine content increased. All of the resins yield IB higher than the ANSI standard and two resins yielded formaldehyde emission less than the 1 ppm level which was set as a quality control standard in the laboratory by the 2-hour-desicator method. Furthermore, the MUF resins were also highly comparable with that of the commercial UF resin as a control. It is noted that all of the resins yielded lower TS than that of the UF resin control. In fact, four resins resulted in higher IB and four other resins yielded less formaldehyde emission than that of the commercial UF resin.

Analysis of IB strength, formaldehyde emission, and TS by Duncan’s multiple range tests is presented in Table 6. IB strength was significantly improved by higher melamine content. Formaldehyde emission was significantly improved by lowering acidic pH. All of the properties of the particleboard (i.e., IB, formaldehyde emission, and TS) were significantly improved by the changes of melamine reaction pH from 6.0 to 4.5.

**Discussion**

The type of resins fabricated in this study were sequential MUF resins in which the UF polymer was prepared first under strong acidic pH conditions and then melamine was coreacted after the UF polymer had been formed and adjusted to be weakly acidic pH. Then, a small amount of urea was added to adjust the F/U/M ratio to meet the desired low F/(U+M) ratio. The major consideration was to use the methylene linkage and cyclic uron formation of a strong acidic pH catalyzed UF polymer as a backbone to coreact with the melamine to
form a MUF polymer to control formaldehyde emission. The results confirmed that a strong acidic pH at the initial reaction of formaldehyde with urea had a significant effect on the overall performance of the MUF resin adhesives. The panels prepared with the MUF resins resulted in substantially lower formaldehyde emission, but also yielded lower IB strength. These two sets of divergent effects of strong acidic catalyst indicated that, in general, a low formaldehyde emission MUF formulation must be a compromise between strength and emission requirements.

To upgrade the performance of the UF resin with melamine fortification, the maximum quantity of melamine that can be used to improve performance is limited because of the cost of melamine is more than twice that of urea. The final molar ratios of MUF in the study ranged from 1.38F/1U/0.055M to 1.38F/1U/0.074M, and the calculated melamine contents were 6.4 percent and 8.4 percent on mass basis, respectively. The study showed that a MUF resin fabricated with 1.38F/1U/0.055M reacted under melamine pH of 4.5 satisfied the required performance standards of both formaldehyde emission and IB strength. Furthermore, it should be mentioned that this MUF resin also yielded 10 percent less formaldehyde emission and 7.9 percent less TS as compared to that of commercial UF resin used in the study as a control. Based on current costs of melamine ($0.79/lb), urea ($0.34/lb), and formaldehyde ($0.16/lb on 53% solution or $0.30/lb on a solid base), with 6.4 percent melamine content, a MUF resin system as developed in this study could result in increasing resin costs of 8.6 percent as compared to a conventional 1.15/1 ratio (F/U) UF resin system for bonding particleboard. For most particleboard plants, resin cost is estimated to be 30 to 35 percent of production raw material costs. Thus, the 8.6 percent increase in resin cost represents 2.58 to 3.01 percent of production raw material costs. This slight increase in resin cost in effect produces a “different type” of composite board. This low melamine content MUF resin definitely will improve the environmental and durability aspects of North American-made particleboard.

It has been well recognized that reaction conditions, such as temperature, time, chemical ratio, pH, and catalyst, are the factors that largely control co-condensation reactions between urea and melamine with formaldehyde as well as the final chemical structure of MUF resins. With melamine as such a minor component in the system, optimizing the distribution of melamine in MUF polymer chains and maximizing its effect on resin reactivity are considered the most important guidelines in upgrading gluebond performance and control of formaldehyde emission for the UF resins. In the study, melamine content and melamine reaction pH were investigated. It was shown, at the final MUF formulation, the effects of increased melamine content was significant only for IB strength, but changes in melamine reaction pH in resin preparation resulted in a resin system that had significant effects on the overall performance of the panels (Table 6). Furthermore, it is interesting to note that melamine reaction pH was the only factor significantly effecting TS. These results indicated that significant differences in molecular species and resin structure might exist between MUF resins prepared at a melamine reaction pH of 4.5 and 6.0. An attempt was made to use carbon-13 nuclear magnetic resonance (NMR) spectroscopy to evaluate the reaction mechanism of co-condensation of urea and melamine through carbon-13 enriched formaldehyde (Tomita and Hse 1995a, 1995b). Precise analyses among three resins (i.e., melamine formaldehyde, UF, and MUF) by C-13 NMR, however, are still not fully attainable at the present time.

Since cyclic uron formation is one of the characteristic molecular structures of a strong acidic catalyzed UF resin used as a backbone for the MUF resin system in this study, the possible effects of uron on upgrading performance of MUF system should be discussed. Previous studies (Hse et al. 1994; Gu et al. 1996a, 1996b) showed that in resin with a F/U molar ratio of 3:1, formation of the uron ring amounted to 25 percent of the total urea. It was also shown that the uron structure did not just exist as a separate structure from the resin, but it was copolymerized with the UF resin; furthermore, the uron structure was in equilibrium with the open dimethylolurea form and the open dimethylolurea form increased as the pH increased from very acidic to pH = 6.0. An attempt was made to use carbon-13 nuclear magnetic resonance (NMR) spectroscopy to evaluate the reaction mechanism of co-condensation of urea and melamine through carbon-13 enriched formaldehyde (Tomita and Hse 1995a, 1995b). Precise analyses among three resins (i.e., melamine formaldehyde, UF, and MUF) by C-13 NMR, however, are still not fully attainable at the present time.

Utilizing a UF polymer as a backbone structure to coreact with melamine provides an option for upgrading the performance of particleboard. MUF resins based on a strongly

### Table 6. — Analysis of IB strength, formaldehyde emission, and TS of particleboard made with MUF resin formulated with two F/U/M ratios, two acidic pH levels, and two melamine reaction pH levels.

<table>
<thead>
<tr>
<th>F/U/M molar ratio*</th>
<th>IB (psi) Duncan grouping</th>
<th>Mean</th>
<th>Formaldehyde emission (µg/mL) Duncan grouping</th>
<th>Mean</th>
<th>TS (%) Duncan grouping</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38/1.0/0.055</td>
<td>B</td>
<td>112.0</td>
<td>A</td>
<td>1.214</td>
<td>A</td>
<td>30.5</td>
</tr>
<tr>
<td>1.38/1.0/0.074</td>
<td>A</td>
<td>121.3</td>
<td>A</td>
<td>1.172</td>
<td>A</td>
<td>30.1</td>
</tr>
<tr>
<td>Acidity pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>A</td>
<td>115.8</td>
<td>A</td>
<td>0.986</td>
<td>A</td>
<td>30.0</td>
</tr>
<tr>
<td>1.55</td>
<td>A</td>
<td>117.7</td>
<td>B</td>
<td>1.400</td>
<td>A</td>
<td>30.6</td>
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<tr>
<td>Melamine reaction pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>A</td>
<td>122.4</td>
<td>A</td>
<td>1.127</td>
<td>A</td>
<td>28.2</td>
</tr>
<tr>
<td>6.0</td>
<td>B</td>
<td>110.9</td>
<td>B</td>
<td>1.259</td>
<td>B</td>
<td>32.3</td>
</tr>
</tbody>
</table>

* F = formaldehyde; U = urea; M = melamine.
B A indicates the best property among 24 resins adhesives. The same letter in the column indicates no significant difference at the 5% level.
acidic catalyzed UF polymer coreacting with melamine resulted in an overall substantial performance improvement as compared to the MUF resins fabricated with a weakly acidic catalyzed UF polymer from a previous study by Hse et al. (2008). It should be noted, however, that the variation in sensitivity of performance improvement occurred in the narrow strongly acidic pH ranges of 1.25 to 1.55. Precise pH control in the laboratory size resin reactor was not a concern, but that may not be the case for industrial applications. Further research regarding the safety window of pH adjustment is needed to achieve optimal industrial application of this technology.

Conclusions

A melamine modified UF resin system has been developed for upgrading the performance of UF-bonded particleboards. The UF polymer, with a backbone structure prepared by strong acidic pH, had a significant effect on the overall performance of the MUF resin system. Strong acidic pH was the single most important factor effecting the formaldehyde emission from the panels. With melamine as a minor component (i.e., a maximum melamine content limit of 6.4%), the changes in molecular species and resin structure effected by melamine reaction pH were the most important factors in upgrading the performance of MUF. IB strength increased, formaldehyde emission decreased, and TS decreased as melamine reaction pH decreased from 6.0 to 4.5. A low melamine content MUF resin fabricated with 1.39F/1U/0.055M reacted under melamine reaction pH of 4.5 produced panels that satisfied the required performance standards of both formaldehyde emission (NPA’s 2-h desicator test) and IB strength (ANSI). This MUF resin yielded 10 percent less formaldehyde emission and 7.9 percent less TS as compared to that of commercial UF resin used in study as a control, but also resulted in a 2.58 to 3.01 percent increase in production raw material costs.

Literature cited


