

# Low Mole Ratio Urea–Melamine–Formaldehyde Resins Entailing Increased Methylene–Ether Group Contents and Their Formaldehyde Emission Potentials of Wood Composite Boards

An Mao,<sup>a,b</sup> El Barbary Hassan,<sup>b</sup> and Moon G. Kim<sup>b,\*</sup>

A previous study of synthesizing low mole ratio urea–formaldehyde (UF) and urea–melamine–formaldehyde (UMF) resins, which included an acidic reaction step at the beginning of the typical resin synthesis procedure to obtain higher uron-type methylene–ether group contents, was repeated with the acidic reaction step extended to a higher viscosity. Compared to previous resins, the synthesized resins showed additional increases in the uron-type and linear-type methylene–ether groups, resulting in longer storage times, longer pot lives, longer gel times, and comparable internal bond strengths and water absorption values of particleboards; however, the formaldehyde contents (FC) of boards increased. It was concluded that the extended acidic reaction resulted in increased formaldehyde emission potential of boards because of additional methylene–ether groups formed. The results led to the hypothesis that the FC values of current UF resin-bonded boards are mainly due to the methylene–ether-type groups present in significant levels in UF and UMF resins.

*Keywords:* UF resins; UMF resins; Wood composite boards; Formaldehyde emission

*Contact information:* a: College of Forestry, Shandong Agriculture University, 271018, Taian, China; b: Department of Forest Products, Mississippi State University, Mississippi State, MS 39762-9820, USA;

\*Corresponding author: [mkim@cfr.msstate.edu](mailto:mkim@cfr.msstate.edu)

## INTRODUCTION

This paper is the third in a series of publications (Mao *et al.* 2013a, b) on various urea–formaldehyde (UF) resins and urea–melamine–formaldehyde (UMF) resins synthesized with low levels of melamine as particleboard binders, conducted with an emphasis on lowering the formaldehyde emission potential of boards. UF resins have been widely used as binders for interior-grade wood composite boards, such as particleboard, medium density fiberboard, and interior-grade hardwood plywood with the advantages of low cost, high dry bond strength, fast curing, low curing temperature, and light color (Marra 1992; Pizzi 1994). However, the formaldehyde emission from these wood composite boards due to the resin binders has been an important public issue, since formaldehyde is a human carcinogen (IARC 2004) and indoor formaldehyde levels have been linked to various health problems (Cruz 2007; Athavaley 2009; EPA 2009). This public pressure recently came to a head in the United States, leading to the new formaldehyde emission laws that mandate drastically lower formaldehyde emission levels for all UF resin-bonded wood composite boards (CARB 2008; US Senate 2011).

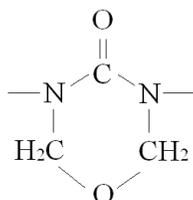
The new formaldehyde emission laws have been forcing the board manufacturing industries to use UF resins made with lower formaldehyde/urea (F/U) mole ratios of

about 1.05 or lower, which is significantly lower than the recent past values of about 1.15 to 1.25. The low mole ratio resins, however, necessitate longer hot pressing times, which result in lower board strength values and still do not achieve the new formaldehyde emissions law levels without other secondary measures, such as airing the boards or further lowering the mole ratio (Pavia *et al.* 2012). Thus, modifying UF resins with low levels of melamine (M), *i.e.*, urea–melamine–formaldehyde (UMF) resins, and also using low F/(U+M) mole ratios in resin synthesis, have been reported to maintain board strength values while achieving lower formaldehyde emission values, although the hot pressing times may still have to be extended significantly (Lukkaronien and Dunky 2006; Sigvartsen and Dunky 2006; Pavia *et al.* 2012); however, these reports did not show some practicable aspects of details. UF resins have performed adequately until recently by meeting key process parameters: high resin solids content, adequate resin storage life, adequate pot life of catalyzed resins, fast curing rates of catalyzed resins, and adequate board strength and water-soak test performance. In synthesizing UMF resins, these various resin parameters need to be considered in addition to ways of achieving the maximum efficiency of added melamine, since melamine is significantly more expensive than urea. The level of melamine, base UF resin synthesis procedure, melamine addition points during resin synthesis, and hot pressing time and temperature are the parameters that were selected for study in the previous and current reports (Mao *et al.* 2013a, b).

Although the formaldehyde emission problems of UF resin-bonded wood composite boards have been known for many years, the causes with respect to the resins' chemical/polymer structures have not been adequately addressed, except that FC values of boards principally depend on binder resins' formaldehyde/urea (F/U) mole ratios used in resin manufacturing (Myers 1984; Myers and Koutsky 1990; Go 1991; Dunky 1998; No and Kim 2004, 2005, 2007). The authors of this work considered the methylene–ether group contents of resins to be another key parameter of the formaldehyde emission potential of UF and UMF resins. In a previous paper (Mao *et al.* 2013a), UF resins and UMF resins synthesized with 2.5% and 5.0% melamine using the typical three-step resin procedure were investigated. The addition point of melamine was selected to be in the third alkaline step, to minimize polymerization and resultant precipitation of melamine components that can shorten the resin's storage life (Wirpsza and Brezezinsky 1973). The F/(U+M) mole ratio was chosen to be 1.05 in order to reach the E1 class of European standards ( $\leq 8$  mg/100g dry board) in regards to formaldehyde contents (Lukkaronien and Dunky 2006; Sigvartsen and Dunky 2006). The synthesized resins showed methylene–ether group contents of 18% to 20% based on the formaldehyde used in resin synthesis. Additionally, some selected combinations of UF and UMF resins in the face and core layers of boards, as well as different catalysts and catalyst levels, were investigated for the slower curing rates of UMF resins expected from melamine addition. The UMF resins resulted in FC values of the E1 class of European standards but did not reach the E0 class. Also, the FC values did not decrease significantly due to any combination of various catalyst effects. The UMF resins showed longer curing times and shorter resin storage lives.

In the second of this series of works (Mao *et al.* 2013b), the base UF resin synthesis procedure was altered to include a strongly acidic reaction step (pH 3.5) at the beginning of the resin synthesis procedure with an F/U mole ratio of 2.70 in order to engender uron-type methylene–ether groups in the resins (Fig. 1) (Gu *et al.* 1995; Soulard *et al.* 1999; Tohmura *et al.* 2001; Zanetti and Pizzi 2003; Park *et al.* 2006; Park *et al.* 2009; Sun *et al.* 2011). As expected, the acidic reaction step resulted in resins having

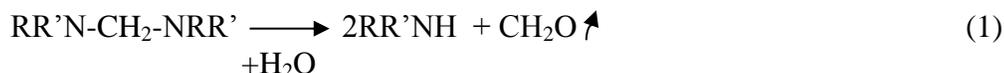
some uron-type methylene–ether groups (Mao *et al.* 2013a). These UF and UMF resins showed increased board strength values, but the boards' formaldehyde contents (FC) were also higher. The question of whether higher uron-type methylene–ether group contents cause higher formaldehyde emissions seems to have significant implications.



Uron Structure

**Fig. 1.** Uron-type methylene–ether group

The causes of formaldehyde content or emission potential of UF resin-bonded boards have been considered in various ways. First of all, the methylene groups in cured resins were considered to be a source of free formaldehyde in boards (Eq. 1), but such decomposition would occur only in extreme conditions such as long hot pressing times (Myers 1984; Myers and Koutsky 1990). Furthermore, the free formaldehyde present in resins (Eq. 2) and the hydroxymethyl groups of resins, which produce free formaldehyde by the reversibility of the reaction in Eq. 3 (De Jong and De Jonge 1952a, b), have been considered to be the main causes.



The linear and uron-type methylene–ether groups in resins can break into two hydroxymethyl groups during curing in the presence of water at elevated temperatures (Eq. 4b) (Wirpsza and Brezezinsky 1973). In the case of linear-type methylene-ether groups, the breakup can also form one methylene group and one formaldehyde molecule during resin curing in the absence of water at high temperatures (Eq. 4a). Thus, the methylene–ether groups could be a direct source of free formaldehyde, although not much attention has been given to reducing the levels in resins until now. These various formaldehyde-emitting routes would occur at different rates in different stages of resin curing, and the formaldehyde present or formed in the early stages of resin curing (Eq. 2 and 3) is likely to be incorporated back into the resin matrix because of the low mole ratios used in current resins. The issue in this study is when the methylene–ether groups break up during curing (Eq. 4), because if it occurs in a later stage of curing, the free

formaldehyde is more likely to escape from the resin matrix due to the high viscosity. The experimental results of higher board strength values and higher FC values of the previous study (Mao *et al.* 2013b) were thus explained by the fact that the decomposition reaction of uron-type methylene–ether groups occurred in a later stage of curing. This deduction is in accordance with the higher board strength values, because such bond breakup would extend the resin’s ‘flow’ during curing, due to lowering of the overall molecular weight, resulting in more complete curing. This preliminary result of uron-type methylene–ether groups’ role in formaldehyde emission potential needs to be confirmed.

The results also offer an interesting new direction for research, because the linear-type methylene–ether groups in UF or UMF resins present at 18%-20% levels based on charged formaldehyde are expected to behave similarly and therefore account for much of the FC of current UF resin-bonded boards. In this work, since there is currently no known method of reducing the methylene–ether group contents in UF resins, the strongly acidic reaction step was pushed further to reach a higher viscosity than in the previous study (Mao *et al.* 2013b) to obtain higher methylene-ether group contents in resins. A necessary variation was to lower the F/U mole ratio of resin to 2.60 from the previous value of 2.70, because the viscosity of resin would not advance further with the latter mole ratio within the pH range of 3.0 to 3.5 (Kim and Amos 1990; Kim 1999). The purpose was to find out whether the resins would give particleboards with proportionately higher FC values. All other procedures were exactly repeated and the resins were analyzed, tested for general properties and curing rates, and evaluated as binders of particleboards in the same way. The results of this work were compared with the previous results.

## EXPERIMENTAL

### Materials

A formaldehyde solution of 50.0% concentration was obtained from Georgia-Pacific Corp. (Taylorsville, MS, USA), and reagent-grade urea (98.0%) and melamine (99.0%) were used for resin synthesis. All pH adjustments were done using 8.0% sodium hydroxide solution and 4.0% sodium hydroxide solution. Mixed pine wood particles (face layer and core layer) and a wax emulsion with a 50.0% solids content were obtained from the Roseburg Forest Products Corp. (Taylorsville, MS, USA). Catalyst A (25% ammonium sulfate solution in water) and catalyst B (25% ammonium sulfate and 5.0% sulfuric acid solution in water) were made in the laboratory. Catalyst A was used in UF resins and catalyst B was used mostly in UMF resins. Both were used as curing catalysts in various tests and board manufacturing.

### Resin Synthesis

Urea–formaldehyde condensate (UFC) was made first. A 50% formaldehyde solution (1229.3 g) was added to a 2 L reactor equipped with a condenser and stirring and heating devices. The pH was adjusted to 8.0 with sodium hydroxide solution, and the reaction mixture was heated to 70 °C. Urea (278.8 g) was then added over a period of 30 min (F/U = 4.50), followed by heating to and maintaining at 90 °C for 30 min at pH 8.0. The reaction mixture was then cooled and stored at room temperature until use.

Control UF resins with higher viscosity in the strongly acidic reaction step were synthesized as follows. In the first step, 1508.1 g of UFC was added to a 2 L reaction

flask equipped with a condenser and heating, stirring, and cooling devices. The pH of the solution was adjusted to 8.0 and heated to 70 °C, followed by slowly adding 185.8 g of urea ( $U_1$ ) to reach to an initial F/ $U_1$  mole ratio of 2.60. After the urea was completely dissolved, the temperature was raised to 90 °C and maintained for 30 min while maintaining the pH at 8.0. In the second step, the pH of the reaction mixture was lowered to 3.50 by using a 8.0%  $H_2SO_4$  solution and the reaction was continued at 90 °C while the viscosity was checked every 10 min until it reached the target viscosity of H-I on the Gardner-Holdt (G-H) scale, in about 40 min. In the third step, the pH was adjusted to 8.0 and 162.7 g of urea ( $U_2$ ) was added, reaching the target F/( $U_1+U_2$ ) mole ratio of 2.00, followed by reacting at 90 °C for 20 min. In the fourth step, the pH was adjusted to 4.75 and the viscosity was checked every 5 min, reaching the target viscosity of P-Q on the G-H scale in 20 min. In the fifth step, the pH was adjusted to 8.0 and the reaction mixture was cooled to 60 °C, and 567.4 g of urea ( $U_3$ ) was added, reaching the target F/( $U_1+U_2+U_3$ ) mole ratio of 1.05, followed by stirring and cooling to room temperature, resulting in resin UF1.05ee. Control UF resins that had mole ratios of 1.15 and 1.25 were synthesized in the same way through the fourth step. In the fifth step, 463.6 and 376.2 g of urea ( $U_3$ ) were respectively added to reach the target F/U mole ratio of 1.05, resulting in resin UF1.15ee and resin UF1.25ee. All resins were stored in a refrigerator at 4 °C until use.

The UMF resin with 2.5% melamine content was synthesized using the same formulation and procedure as the control resin UF1.05ee as described above in the first, second, third, and fourth steps. In the fifth step, after the pH was adjusted to 8.0, 61.4 g of melamine (M) was added, and the reaction temperature was kept at 90 °C for 60 min while maintaining the pH at 8.0. Next, the reaction mixture was cooled to 60 °C and 537.9 g of urea ( $U_3$ ) was added, reaching the target F/( $U_1+U_2+U_3+M$ ) mole ratio of 1.05. The finished resin was then stirred and allowed to cool to room temperature, resulting in resin 2.5%UMF1.05ee. The UMF resin with 5.0% melamine content was similarly synthesized, except that the amounts of melamine and  $U_3$  were 124.5 and 507.7 g, respectively, resulting in resin 5.0%UMF1.05ee. All resins were stored in a refrigerator at 4 °C until use.

### Resin Physical Property Measurements

Non-volatile solids contents (in triplicates) and specific gravity values of the synthesized resins were measured using laboratory standard procedures. The storage stability of synthesized resins was measured by placing the Gardner-Holdt (G-H) resin viscosity measurement samples in a convection oven at 30 °C and checking the viscosity changes daily for 50 days.

### Chemical Structure Determinations

$^{13}C$  nuclear magnetic resonance (NMR) spectra of selected resins were obtained on a Techmag 400-2 NMR instrument from Spectral Data Services (Champaign, IL, USA). The resin samples were prepared by mixing 2.0 g of resin with 1.0 g of deuterium oxide. A 12  $\mu$ s pulse-width and 10 s pulse-delay were used for quantitative results, with 400 scans accumulated for each resin sample. Spectral values of urea carbonyls, melamine triazine carbonyls, and methylenic carbons were integrated and quantified as percentages. Urea carbonyls were converted to their percentage values according to their substitution patterns: free urea, mono-substituted urea, di-/tri-substituted urea, and cyclic uron-type urea.

### Pot Lives and Gel Times of Catalyzed Resins

Pot lives of catalyzed resins were measured in triplicates by placing catalyzed resin samples in a convection oven at 30 °C and checking the viscosity every 15 min for 12 h. Gel times of catalyzed resins at 100 °C were measured in duplicates by stirring and heating a catalyzed resin sample in a glass tube placed in boiling water. Catalyst A and catalyst B were tested at 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% based on the weight of the liquid resin.

### Gel Time and Curing Time by Rheometry

Gel times and curing times of catalyzed resins were carried out in duplicates using an oscillatory Rheometer (AR1500ex, TA Instruments Corp, New Castle, DE, USA) with an 8 mm diameter probe at test temperatures of 90 °C, 120 °C, 135 °C, and 145 °C. The resin sample was allowed to balance at 20 °C for 10 s, heated to the target temperatures in 50 s, and time sweeps were performed at a frequency of 1.0 Hz and strain of 1.0%. Gel times and cure times were obtained from the storage and tan delta curves as in the previous report (Mao *et al.* 2013a).

### Particleboard Manufacturing

Particleboards were manufactured in the laboratory using the typical three-layer formatting method with the same materials charge target values as those used in previous studies (Mao *et al.* 2013a, b). Fifteen resin/catalyst parameter combinations were made in duplicates to result in 30 boards, as shown in Table 1.

**Table 1.** Particleboard Preparation Parameters \*

| Board number | Face layer    |            |          |           | Core layer    |            |          |           |
|--------------|---------------|------------|----------|-----------|---------------|------------|----------|-----------|
|              | Resin         |            | Catalyst |           | Resin         |            | Catalyst |           |
|              | Type          | Mole ratio | Type     | Level (%) | Type          | Mole ratio | Type     | Level (%) |
| 1            | UF (ee)       | 1.05       | A        | 0.5       | UF (ee)       | 1.05       | A        | 0.5       |
| 2            |               |            |          |           |               | 1.15       |          |           |
| 3            |               |            |          |           |               | 1.25       |          |           |
| 4            | UF (ee)       | 1.05       | A        | 0.5       | 2.5% UMF (ee) | 1.05       | B        | 0.5       |
| 5            |               |            |          |           |               |            |          | 1.0       |
| 6            |               |            |          |           |               |            |          | 1.5       |
| 7            |               |            |          |           |               |            |          | 2.0       |
| 8            | UF (ee)       | 1.05       | A        | 0.5       | 5.0% UMF (ee) | 1.05       | B        | 0.5       |
| 9            |               |            |          |           |               |            |          | 1.0       |
| 10           |               |            |          |           |               |            |          | 1.5       |
| 11           |               |            |          |           |               |            |          | 2.0       |
| 12           | 2.5% UMF (ee) | 1.05       | B        | 0.5       | 5.0% UMF (ee) | 1.05       | B        | 1.0       |
| 13           |               |            |          | 1.0       |               |            |          |           |
| 14           | 5.0% UMF (ee) | 1.05       | B        | 0.5       | 5.0% UMF (ee) | 1.05       | B        | 1.0       |
| 15           |               |            |          | 1.0       |               |            |          |           |

\*(ee) denotes high "ether" content of the resins synthesized in this study in comparison with other resins reported in previous studies (Mao *et al.* 2013a, b); resin solids and wax solids loading were 9.0% and 1.0%, respectively.

Wood particles were first dried to a moisture content of 5.0% and put in a rotary blender. Wax and catalyzed resin were then successively sprayed on the tumbling particles using an air-atomizing nozzle for 15 min. Face particles and core particles were blended separately. Blended particles were weighed and hand-laid on a steel plate in a wooden box of 24 in × 22 in dimensions to obtain three-layer mats of a 1:2:1 weight ratio for top, core, and bottom layers. After removing the box, another steel plate was put on the mat and hot pressing was carried out in a Dieffenbacher hot press at 350 °F. Two boards were made for each resin formulation using press times of 3.0 and 3.5 min. The press closing rate was 0.5 in/s to a mat thickness of 1.0 in and then 0.03 in/s to reach to the target board thickness of 0.5 in. The boards were allowed to cool to room temperature on a bench for one day and then cut into test samples using the same cutting pattern used in the previous work (Mao *et al.* 2013a).

### Physical and Mechanical Testing of Particleboards

Internal bond (IB) strength (8 samples from each board), modulus of rupture (MOR), and modulus of elasticity (MOE) (3 samples from each board) were measured on an Instron machine (Norwood, MA), and water-soak thickness swelling (TS) and water absorption (WA) values (2 samples from each board) were measured in a water bath at 20 °C according to ASTM D 1037-06a. The data reported represent the averages of multiple measurements.

### Formaldehyde Content Measurements

The formaldehyde contents (FC) of the boards were measured in duplicates about three months after board manufacturing due to an instrument breakdown. FC test samples were cut to dimensions of 6 in × 6 in after one day of airing the boards and, because of this unexpected waiting period, each board sample was sealed on the edges with duct tape, wrapped in saran film, put in a sealed plastic bag, and kept in a refrigerator at 4 °C until testing. Formaldehyde content decreases in the boards from the storage period were considered to be small. The FC tests were carried out using the European standard perforator method (EN 120 2001).

## RESULTS AND DISCUSSION

### Resin Physical Properties

The synthesized resins had a pH of 8.0, specific gravity of 1.258 to 1.272, viscosity of G-H to I-J on the G-H scale, and solids content of 62.3 to 63.5%. These obtained values were generally as expected from the synthesis procedures used and were also within the range of industrial values, as in the previous studies (Mao *et al.* 2013a, b). The small property differences are considered to make little differences in comparing the resins' bonding or formaldehyde emission potential values determined, because the resin solids content values are accounted for in the material calculation steps.

### Resin Chemical Structures

The chemical structures of resin UF1.05ee and resin 5.0%UMF1.05ee obtained from <sup>13</sup>C NMR are summarized in Table 2, along with the differences in functional group contents compared with the corresponding values of the uron-type resins from the previous study. Spectra of the resins are shown in Figs. 2a and 2b. Chemical shift values

were assigned and carbon groups were quantified by the same methods used in previous studies (Mao *et al.* 2013a, b). The observed group values were, in general, very similar to those of previous studies, but the difference values that resulted from the strongly acidic reaction step carried out to reach the viscosity H-I on the G-H scale at a slightly lower F/U mole ratio of 2.60 were as follows: (a) total hydroxymethyl group contents, especially type I hydroxymethyl groups, increased in resin UF1.05ee, but the increases were minimal in resin 5.0%UMF1.05ee, (b) total methylene–ether group contents, especially type I methylene–ether groups, increased in both resins, as intended, (c) cyclic urea contents of uron-type methylene–ether groups decreased to a small extent, and (d) total methylene group contents decreased to the extent of the combined increases of hydroxymethyl and methylene–ether group contents in (a) and (b) above.

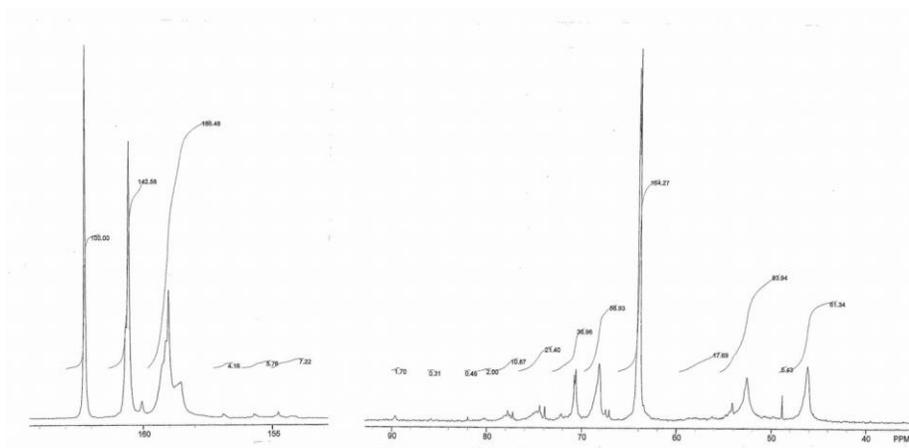


Fig. 2a.  $^{13}\text{C}$  NMR spectra of resin UF1.05ee in water

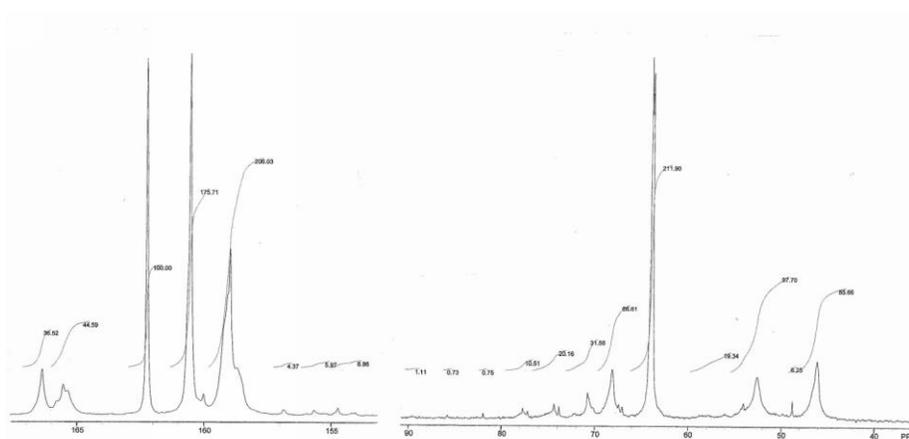


Fig. 2b.  $^{13}\text{C}$  NMR spectra of resin 5.0%UMF1.05ee in water

The fact that the uron-type methylene–ether group contents decreased slightly indicates that the increased methylene–ether group contents observed are linear groups in the polymer backbone structure. Linear methylene–ether groups generally exist at contents of about 17% to 20% in UF resins. In the past, the strongly acidic reaction step

included in resin synthesis for uron structure formation has been often carried out with F/U mole ratios of 2.70 and higher (Zanetti and Pizzi 2003; Park *et al.* 2006). Thus, the use of a lower F/U mole of 2.60 and extension of the reaction to a higher viscosity point carried out in this study resulted in increasing the linear methylene–ether group contents in addition to the uron-type methylene–ether groups, although the content of the latter groups were slightly lower than in the previous study.

**Table 2.** Percentage Integration Values for Various Methylenic and Carbonyl Carbons of Resin Samples Determined From  $^{13}\text{C}$  NMR Spectra

| Carbon groups                      | Resin UF1.05ee |                 | Resin 5.0%UMF1.05ee |                 |
|------------------------------------|----------------|-----------------|---------------------|-----------------|
|                                    | Groups (%)     | Difference* (%) | Groups (%)          | Difference* (%) |
| Free urea                          | 22.41          | -0.19           | 21.10               | 0.08            |
| Monosubstituted urea               | 31.95          | -0.05           | 35.10               | 0.19            |
| Di, tri-substituted urea           | 41.79          | 0.52            | 39.64               | -0.06           |
| Cyclic urea                        | 3.84           | -0.29           | 4.16                | -0.20           |
| <b>Total urea</b>                  | <b>100.0</b>   |                 | <b>100.0</b>        |                 |
| Free melamine                      | NA             |                 | 47.4                | 0.57            |
| Mono, di-substituted melamine      | NA             |                 | 52.6                | -0.57           |
| <b>Total melamine</b>              | <b>NA</b>      |                 | <b>100.0</b>        |                 |
| Free formaldehyde                  | 0.54           | -0.43           | 0.52                | 0.10            |
| <b>Total hydroxymethyl</b>         | <b>43.95</b>   | <b>2.09</b>     | <b>43.77</b>        | <b>-0.07</b>    |
| Type I                             | 35.88          | 2.16            | 38.41               | 0.13            |
| Type II                            | 8.07           | -0.07           | 5.36                | -0.20           |
| <b>Total methylene–ether</b>       | <b>20.0</b>    | <b>0.50</b>     | <b>20.2</b>         | <b>1.60</b>     |
| Type I                             | 12.43          | 1.39            | 12.92               | 1.21            |
| Type II                            | 4.67           | -0.27           | 4.03                | 0.13            |
| Type III                           | 2.81           | -0.50           | 3.23                | 0.19            |
| <b>Total methylene</b>             | <b>35.59</b>   | <b>-2.08</b>    | <b>35.53</b>        | <b>-1.57</b>    |
| Type I                             | 13.4           | -0.80           | 14.32               | -0.78           |
| Type II                            | 18.33          | -1.00           | 17.38               | -0.65           |
| Type III                           | 3.86           | -0.47           | 3.83                | -0.14           |
| <b>Total CH<sub>2</sub></b>        | <b>100.0</b>   |                 | <b>100.0</b>        |                 |
| <b>CH<sub>2</sub>/CO**</b>         |                | <b>1.026</b>    |                     | <b>1.025</b>    |
| <b>Degree of polymerization***</b> |                | 1.878           |                     | 1.879           |

\* Difference indicates the increases and decreases of integration values compared with the data of corresponding resins made by typical synthesis procedures, reported in the previous study (Mao *et al.* 2013b)

\*\* CH<sub>2</sub>/CO refers to methylenic carbons/carbonyl ratios calculated from the integration values

\*\*\* Degree of polymerization was calculated using:  $DP = 1 / [1 - (\text{methylene} + 0.5 \times \text{methylene-ether})/\text{urea}]$

For chemical structures and names of functional groups, refer to Kim's work (1999, 2000, 2001)

### Resin Storage Stabilities

The storage stabilities of synthesized resins are presented in Fig. 3 as viscosity increases measured over a period of 50 days. The general trends and ranges with respect to the effects of melamine addition levels and mole ratios are very similar to those of the resins synthesized by the uron-type synthesis procedures of the previous study (Mao *et al.* 2013b); however, all resins in the present work showed storage lives about 4 to 8 days longer, for example, to reach to the viscosity K on the G-H scale than the corresponding uron-type resins. Thus, the methylene–ether group content increases observed in  $^{13}\text{C}$  NMR results appear to increase the resin storage lives more than similar effects observed in the previous study (Mao *et al.* 2013b). Current industrial UF resins stored at a weakly

alkaline pH of about 8.0 show viscosity increases at room temperature due to acid-catalyzed methylene bond-forming reactions (Kim *et al.* 2001). Thus, methylene-ether groups appear to counteract the acid-catalyzed, viscosity-increasing reactions, either by slowing down the reaction rate of the acid catalyst or by decomposing to two hydroxymethyl groups to result in a breakage of polymer chains that lowers the molecular weight and viscosity.

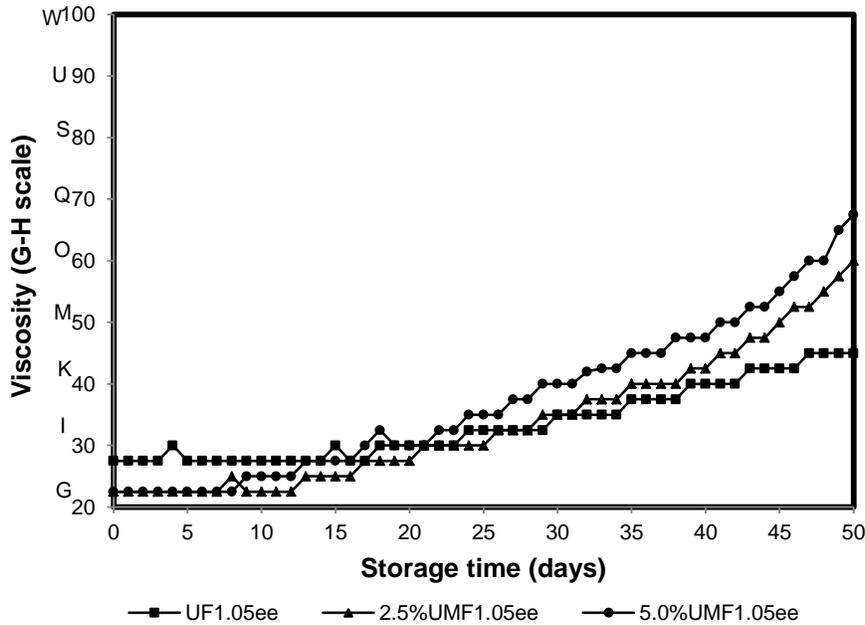


Fig. 3. Viscosity increases of resin UF1.05ee and resins 2.5% and 5.0% UMF1.05ee measured over 50 days of storage at 30 °C

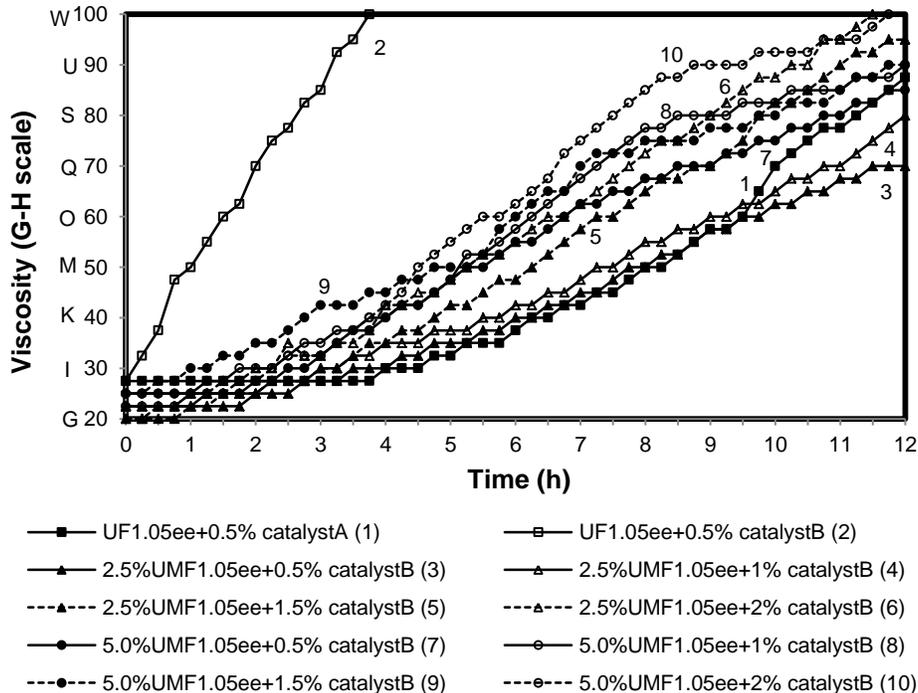


Fig. 4. Pot lives of catalyzed UF and UMF resins with different catalysts and levels

### Pot Lives of Catalyzed Resins

The pot lives of acid-catalyzed resins measured at 30 °C observed as viscosity increases for 12 h are presented in Fig. 4. The general trends of pot lives and effects of different catalysts and levels, melamine levels, and mole ratios are similar to those of the corresponding resins in previous studies (Mao *et al.* 2013a, b), but all of the present resins' pot lives were longer by about 30 min, a trend similar to the resin storage lives discussed above. Longer pot lives are generally a desirable characteristic of resins, but slower curing rates are implied.

### Gel Times of Catalyzed Resins Measured at 100 °C

The gel times of acid-catalyzed resins measured at 100 °C are reported in Table 3 with the gel time differences calculated in comparison with the corresponding data of the uron-type resins in the previous study (Mao *et al.* 2013b). The relatively large gel time increases that were observed can be ascribed to the increased contents of polymer backbone methylene–ether groups in line with the longer storage lives and longer pot lives discussed above. Gel time measurements, as with the storage life and pot life measurements, were carried out with resins containing about 40% constituent water; therefore, the conclusion that longer gel times arose from the hydrolysis of the polymer backbone methylene–ether groups by acidic curing catalysts to form low molecular weight polymers appears more plausible. Longer gel times of resins give greater process flexibility in wood composite manufacturing plants, but slower resin curing rates are implied.

**Table 3.** Gel Times (s) of Resins with Catalysts A and B at Various Levels Measured at 100 °C

| Catalyst level | 0.5% |     | 1%  |     | 1.5% |     | 2%  |     | 2.5% |     | 3%  |     |
|----------------|------|-----|-----|-----|------|-----|-----|-----|------|-----|-----|-----|
|                | A    | B   | A   | B   | A    | B   | A   | B   | A    | B   | A   | B   |
| Catalyst kind  |      |     |     |     |      |     |     |     |      |     |     |     |
| UF1.05ee       | 319  | 167 | 287 | 142 | 256  | 112 | 229 | 101 | 197  | 89  | 171 | 87  |
| Diff.*         | 56   | 42  | 65  | 47  | 55   | 26  | 50  | 23  | 60   | 24  | 40  | 24  |
| 2.5%UMF 1.05ee | 598  | 424 | 520 | 368 | 475  | 331 | 378 | 287 | 319  | 233 | 287 | 208 |
| Diff.*         | 111  | 89  | 112 | 93  | 143  | 94  | 89  | 88  | 64   | 55  | 60  | 44  |
| 5.0%UMF 1.05ee | 607  | 418 | 531 | 374 | 465  | 319 | 397 | 256 | 309  | 247 | 278 | 199 |
| Diff.*         | 125  | 81  | 112 | 109 | 114  | 85  | 104 | 58  | 41   | 66  | 49  | 21  |

\*Difference indicates the increased times(s) compared with corresponding resins made by the typical synthesis procedures reported in the previous study (Mao *et al.* 2013b)

### Gel and Cure Times of Catalyzed Resins Measured on the Rheometer

The rheometric measurement results of gel and cure times of acid-catalyzed resins are presented in Table 4, and selected gel and cure time differences were also calculated in comparison with the uron-type resins in the previous study. The difference values were relatively small and varied in this test. For example, resin UF1.05ee and resins 2.5% and 5.0%UMF1.05ee showed longer gel and cure times at a lower temperature (90 °C), in agreement with pot lives and gel times discussed above. At higher temperatures (120 °C, 135 °C, and 145 °C), however, the differences were negligible, indicating that the acidic catalysts were strong enough at these temperatures to break up the uron-type or other methylene–ether groups ahead of the rate-determining curing step of resin. The curing

process in this test progressed under anhydrous conditions because of the higher temperatures and, therefore, the acid catalyst can become more efficient and factors other than the acid-catalyzed hydrolysis reaction of methylene-ether groups appear to become the rate-determining factors of resin curing.

### Particleboards Test Results

Particleboard test results are shown in Table 5, arranged according to the resin pairs in the face and core layers and the catalyst kinds and levels in the same way as in the previous studies (Mao *et al.* 2013a, b). Additionally, the differences of formaldehyde contents, internal bond (IB) strengths, and water absorption values calculated in comparison with the previous results (Mao *et al.* 2013b) are reported in Table 6.

**Table 4.** Gel Times and Cure Times Obtained Under Isothermal Conditions at Different Catalyst Levels from the Rheometric Method

| Resin type     | Catalyst type | Catalyst level (%) | Gel time (s) |        |        |        | Cure time (s) |        |        |        |
|----------------|---------------|--------------------|--------------|--------|--------|--------|---------------|--------|--------|--------|
|                |               |                    | 90 °C        | 120 °C | 135 °C | 145 °C | 90 °C         | 120 °C | 135 °C | 145 °C |
| UF1.05ee       | A             | 0.5                | 197          | 116    | 107    | 101    | 378           | 158    | 147    | 135    |
|                |               | Difference*        | -2           | 0      | 5      | -1     | -67           | -37    | -13    | -12    |
| 2.5%UMF 1.05ee | B             | 0.5                | 86           | 67     | 67     | —      | 211           | 119    | —      | —      |
|                |               | 1.0                | 269          | 136    | 126    | 106    | 540           | 215    | 220    | 145    |
|                |               | Difference*        | 205          | 111    | 114    | 86     | 490           | 195    | 188    | 115    |
|                |               | 1.5                | 89           | 9      | 12     | -9     | 155           | 14     | 18     | -31    |
|                |               | Difference*        | 180          | 121    | 96     | 101    | 490           | 196    | 155    | 155    |
| 5.0%UMF 1.05ee | B             | 2.0                | 85           | 19     | 8      | 13     | 238           | 3      | -20    | -13    |
|                |               | 0.5                | 175          | 96     | 86     | 81     | 488           | 164    | 132    | 120    |
|                |               | 1.0                | 209          | 136    | 106    | 101    | 600           | 210    | 208    | 180    |
|                |               | Difference*        | 199          | 145    | 96     | 86     | 490           | 230    | 190    | 115    |
|                |               | 1.5                | 83           | 50     | 1      | -9     | 74            | 37     | 4      | -45    |
| 5.0%UMF 1.05ee | B             | Difference*        | 121          | 130    | 111    | 91     | 358           | 240    | 180    | 135    |
|                |               | 2.0                | 19           | 42     | 23     | 10     | 91            | 52     | 0      | 0      |
|                |               | Difference*        | 111          | 106    | 101    | 86     | 317           | 186    | 168    | 118    |

\* Difference indicates the increases and decreases of values compared with the data of corresponding resins made by the typical synthesis procedures, reported in the previous study (Mao *et al.* 2013b)

Particleboards made with resin UF1.05ee in the face layer and resins UF1.05ee, UF1.15ee, and UF1.25ee in the core layers with catalyst A (boards 1-3) represent the range of UF resin mole ratios used in the industry. Using the high F/U mole ratio of 1.25 in the core layer had been common in the board manufacturing industry, but it results in high formaldehyde content (FC) values, 17.9 mg/100 g dry board, far higher than E1 class European standards of less than 8.0 mg/dry board (EN 13986). The general trends of FC contents and board physical properties on mole ratios are similar to those of resins in the previous studies (Mao *et al.* 2013a, b). However, the differences calculated in comparison with boards made with uron-type resins (Table 6) indicate that the resins in the current work showed increased FC values and slightly poorer IB and water absorption values, ascribable to the increased methylene-ether group contents in the <sup>13</sup>C NMR results (discussed above).

Particleboards made with resin UF1.05ee in the face layer and resin 2.5%UMF1.05ee in the core layer using various levels of catalyst B (boards 4-7) showed the best IB values with 1.0% catalyst as shown in Table 5.

**Table 5.** Formaldehyde Content and Physical Property Test Results of Particleboard

| Board number* | Formaldehyde content (mg/100g dry Bd) |         | Physical properties of particleboards average for 3.0 and 3.5 min press times |          |           |            |                             |                           |
|---------------|---------------------------------------|---------|-------------------------------------------------------------------------------|----------|-----------|------------|-----------------------------|---------------------------|
|               | Hot press time                        |         | Dens. (lb/ft <sup>3</sup> )                                                   | IB (psi) | MOR (psi) | MOE (kpsi) | 24 h thickness swelling (%) | 24 h water absorption (%) |
|               | 3.0 min                               | 3.5 min |                                                                               |          |           |            |                             |                           |
| 1             | 10.2                                  | 10.4    | 49.8                                                                          | 83.0     | 1250      | 164        | 24.4                        | 58.7                      |
| 2             | 16.0                                  | 15.1    | 50.2                                                                          | 101.3    | 1299      | 177        | 21.4                        | 58.1                      |
| 3             | 17.9                                  | 17.2    | 50.4                                                                          | 111.9    | 1416      | 197        | 18.4                        | 54.6                      |
| 4             | 9.7                                   | 9.0     | 50.2                                                                          | 118.4    | 1479      | 198        | 22.9                        | 55.5                      |
| 5             | 8.8                                   | 7.2     | 50.4                                                                          | 126.6    | 1554      | 202        | 22.2                        | 53.2                      |
| 6             | 8.0                                   | 6.8     | 50.5                                                                          | 108.8    | 1476      | 231        | 23.6                        | 54.0                      |
| 7             | 6.7                                   | 5.9     | 50.7                                                                          | 102.3    | 1476      | 214        | 24.4                        | 57.5                      |
| 8             | 9.3                                   | 7.2     | 50.4                                                                          | 126.8    | 1715      | 235        | 22.1                        | 52.5                      |
| 9             | 7.4                                   | 6.2     | 50.6                                                                          | 123.5    | 1744      | 246        | 21.7                        | 52.0                      |
| 10            | 6.0                                   | 5.5     | 50.8                                                                          | 118.5    | 1691      | 227        | 22.8                        | 55.4                      |
| 11            | 5.7                                   | 5.2     | 50.8                                                                          | 107.0    | 1572      | 216        | 23.7                        | 58.1                      |
| 12            | 7.7                                   | 6.9     | 51.2                                                                          | 125.6    | 1886      | 264        | 17.8                        | 46.5                      |
| 13            | 7.0                                   | 6.3     | 51.0                                                                          | 124.4    | 1799      | 270        | 17.3                        | 48.4                      |
| 14            | 6.8                                   | 6.1     | 51.4                                                                          | 133.3    | 2117      | 279        | 16.2                        | 43.4                      |
| 15            | 6.3                                   | 5.9     | 51.8                                                                          | 131.0    | 2093      | 278        | 16.4                        | 47.6                      |

\*Board number refers to the numbers in Table 1

**Table 6.** Differences in Formaldehyde Content and Physical Properties of Particleboards Compared with the Previous Study (Mao *et al.* 2013b)

| Board number* | Formaldehyde content (mg/100g dry Bd) |         | IB (psi) | 24 h water absorption (%) |
|---------------|---------------------------------------|---------|----------|---------------------------|
|               | Hot press time                        |         |          |                           |
|               | 3.0 min                               | 3.5 min |          |                           |
| 1             | 0.7                                   | 0.0     | 5.1      | 0.6                       |
| 2             | 0.6                                   | 0.2     | -5.6     | 2.8                       |
| 3             | -0.1                                  | 0.1     | -8.5     | 6.0                       |
| 4             | 1.3                                   | 0.6     | 16.7     | -0.4                      |
| 5             | 1.2                                   | 0.4     | 7.2      | -0.2                      |
| 6             | 1.3                                   | 0.5     | -5.2     | 2.1                       |
| 7             | 0.8                                   | 0.3     | 3.1      | 1.3                       |
| 8             | 2.1                                   | 0.7     | 16.1     | -1.4                      |
| 9             | 0.9                                   | 0.3     | -24.4    | 0.3                       |
| 10            | 0.3                                   | 0.1     | -10.6    | 1.5                       |
| 11            | 0.3                                   | 0.2     | -6.3     | 4.5                       |
| 12            | 0.9                                   | 1.2     | -12.8    | 1.6                       |
| 13            | 0.4                                   | 0.5     | -23.8    | 6.4                       |
| 14            | 0.8                                   | 0.3     | -10.2    | 4.7                       |
| 15            | 0.5                                   | 0.1     | -27.9    | 9.0                       |

\* Board number refers to the numbers in Table 5

The increasing trends of physical properties and lowered FC contents of boards caused by the addition of melamine to the resin are similar to the typically synthesized or uron-type resins of previous studies (Mao *et al.* 2013a, b). The differences obtained in comparison with boards made with uron-type resins (Table 6), however, indicated slightly increased FC values and minor variations in IB and water absorption values. The increased FC values of boards are similarly ascribable to the increased levels of methylene–ether bonds observed in the  $^{13}\text{C}$  NMR data discussed above.

Thus, the extended acid-catalyzed reaction used in the present resin synthesis procedure of UMF resins with 2.5% melamine did not provide any advantage over the shorter reaction procedure of the previous study. Overall, the FC values of boards were still in the range of 5.9 to 9.7 mg/100 g boards, corresponding to E1 and E2 classes of European standards (EN 120 2001).

Particleboards made with resin UF1.05ee in the face layer and 5.0%UMF1.05ee with various levels of catalyst B (boards 8-11) also showed the best IB values with 0.5%~1.0% catalyst levels. The increasing trends of board performance properties and decreasing trends of FC contents of boards with respect to the melamine content in the resin were similar to those of the previous studies (Mao *et al.* 2013a, b). Further, the differences in IB and water-soak test values (Table 6) were relatively small, but the FC values showed increases as with the resin 2.5% UMF1.05ee used as core layer resin (discussed above). The effects of the increased methylene–ether group contents are thus apparent. Overall, the FC values of boards were still in the range of 5.2 to 9.3 mg/100 g boards, corresponding to E1 and E2 classes of European standards (EN 120 2001).

Particleboards made with resin 2.5%UMF1.05ee with 0.5% and 1.0% catalyst in the face layer and 5.0%UMF1.05ee in the core layers with 1.0% catalyst B (boards 12-13) showed that the face layer catalyst levels of 0.5% and 1.0% made little difference in IB and water-soak test values. The FC values decreased slightly with 1.0% catalyst in the face layer. Further, the IB and water-soak test values (Table 5) indicated improvements over the boards made with resin UF1.05ee in the face layer, but the FC values were similar. Further, the difference values (Table 6) indicate increases in FC values and decreases in IB values. Water-soak test values also decreased. Thus, the effect of the increased methylene–ether group contents apparently resulted in increased FC contents of boards. Overall, the FC values of boards were still in the range of 6.3 to 7.7 mg/100 g boards, corresponding to E1 class European standards (EN 120 2001).

Boards made with resin 5%UMF1.05ee with 0.5% and 1.0% catalyst contents in the face layer and the same resin with 1.0% catalyst in the core layer (boards 14-15) showed FC values of 5.9 to 6.8 mg/100 gram boards with relatively good internal bond (IB), bending strength, and water-soak test values (Table 5). However, the difference values (Table 6) similarly indicated higher FC values due to the increased methylene–ether group contents, as well as some negative effects on IB and water-soak test values. Overall, the FC values of boards were still in the range of 5.9 to 6.8 mg/100 g boards, corresponding to E1 class European standards (EN 120 2001).

Industrial boards made with multi-opening presses using the same resin and same hot pressing temperature and time would show lower IB strengths and higher FC values than boards made in a laboratory because of the larger sizes of boards manufactured in the industry. Overall, this research proposes a hypothesis that the uron-type and linear-type methylene–ether group contents in UF resin binders are a major determinant of the FC values of particleboards, as opposed to the widely held conception that the existing free formaldehyde in resin (Eq. 2) and the reversibility of hydroxymethyl groups (Eq. 3)

play the major role. Although the uron-type methylene–ether groups in UF resins can be increased in resins, there is no known synthesis procedure for decreasing the linear methylene–ether group contents that commonly range between 17% and 20%. Thus, the proposed hypothesis could be a guide for new research in addressing the decades-long formaldehyde emission problem of wood composite boards, towards finding ways to decrease the linear methylene–ether group content in resins.

## CONCLUSIONS

1. The extended acidic reaction included in the UF and UMF synthesis procedures at an F/U mole ratio of 2.60 resulted in an increased content of linear methylene–ether groups. The uron-type methylene–ether groups formed at slightly lower levels in comparison with the previous study, in which the acidic reaction was done at an F/U mole ratio of 2.70.
2. The resulting UF and UMF resins showed longer storage times, longer pot lives, and longer gel times in comparison with the corresponding resins made in the previous study.
3. The particleboards bonded with the resultant resins showed minor variations in physical properties, but the formaldehyde contents increased significantly. This is explained by the fact that the linear and uron-type methylene–ether groups decomposed during hot pressing in such a way that the majority of the formaldehyde generated remained as free formaldehyde.
4. The resultant UMF resins showed free formaldehyde contents in boards that meet the E1 class of European standards, in contrast to the E2 class achieved by the resultant UF resins, which is ascribed to the higher functionality of melamine as well as stronger bond strength between melamine and the methylene group.
5. The overall results led to a new hypothesis that the high linear methylene–ether group contents in UF and UMF resins might be the major cause of the high free formaldehyde contents in particleboards.

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