Low Mole Ratio UF and UMF Resins Entailing Uron-Type Methylene-Ether Groups and their Low Formaldehyde Emission Potentials

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The previous study on low mole ratio urea-formaldehyde (UF) and urea-melamine–formaldehyde (UMF) resins synthesized in the typical way as particleboard binders was repeated with the inclusion of a strong acidic reaction step at a mole ratio of 2.7 in the beginning of the resin synthesis procedure. The resulting UF and UMF resins showed longer storage- and pot-lives, longer gel times, and the particleboards gave higher internal bond and lower water-soak absorption values. However, the free formaldehyde contents of boards were increased with UF resins and decreased with UMF resins, indicating that the uron-type methylene-ether groups formed from the strong acidic step resulted in enhancement of the bonding, but they give off some extra formaldehyde, which is captured more effectively in UMF resins because of the higher reaction capacity of melamine. The extra acidic reaction step could be useful in UMF resin syntheses. The generation of extra formaldehyde by uron-type methylene-ether bonds is documented.

Keywords: UF resins; UMF resins; Uron groups in UF resins, Wood composite boards; Formaldehyde emission

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INTRODUCTION

This paper is the sequel to a previous publication (Mao *et al.* 2013) concerning various urea–formaldehyde (UF) and urea–melamine–formaldehyde (UMF) resins as particleboard binders. The goal of this work was to factor out some key resin synthesis parameters for lowering the formaldehyde emission potentials of particleboard. UF resins have been used as binders for interior-grade wood composite boards, such as particleboard (PB), medium-density fiberboard (MDF), and interior-grade hardwood plywood with the advantages of low cost, high dry bond strength, fast curing, and light color (Marra 1992; Pizzi 1994). However, the formaldehyde emission problem of wood composite boards due to UF resin binders has been an important public issue (Cruz 2007; Athavaley 2009; EPA 2009), because formaldehyde has been classified as a human carcinogen (IARC 2004), and indoor formaldehyde gas derived from wood composite boards has been pointed out to be the cause of various immediate health problems (Cruz 2007; Athavaley 2009; EPA 2009). New formaldehyde emission laws have been enacted with drastically lowered formaldehyde emission levels for UF resin-bonded wood composite boards (California 2008; U. S. Senate 2011).

The new formaldehyde emission laws have been forcing the wood composite board and resin manufacturing industries to lower the formaldehyde/urea (F/U) mole ratio of UF resins to about 1.05 or even lower. However, it has been reported that the low mole ratio resins would result in longer hot-pressing times and lower board strength values (Lukkaronien and Dunky 2006; Sigvartsen and Dunky 2006). Further, 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, have been reported to be able to partly counter the low board strength values as well as to achieve lower formaldehyde emission values, although the hot-pressing times of boards may have to be extended significantly (Lukkaronien and Dunky 2006; Sigvartsen and Dunky 2006). UF resins have served well until recently as binders of wood composite boards, meeting the key process requirements of board manufacturing plants.

Formaldehyde emission levels of wood composite boards, normally measured as the amounts present in the surrounding air space in ppm, are generally proportional to the boards' free formaldehyde contents (FC) or potentials of boards, although various other boards' internal structures such as porosity also come into play. The free FC of particleboards, normally measured by extracting into boiling toluene, are generally proportional to the F/U or F/(U+M) mole ratios of resin binders (Go 1991; Dunky 1998; No and Kim 2004; No and Kim 2005; No and Kim 2007). The hot-pressing times and temperatures would also affect the FC values of boards as secondary factors (Christiansen and Anderson 1989; Go 1991). In UMF resins the key is to obtain the maximum efficiency of melamine *vs*. the increased materials cost. Melamine levels, base UF resin synthesis procedure, melamine addition points in resin syntheses, and hot-pressing times and temperatures are the parameters partly addressed in our previous and present studies.

The previous paper (Mao *et al.* 2013) was focused on the UMF resin synthesis procedure with 2.5% and 5.0% levels of melamine. The base UF resin synthesis procedure was the typical three-step procedure, and the addition point of melamine was in the third alkaline step. Also, the F/(U+M) mole ratio was chosen to be 1.05 to reach to the E1 class of formaldehyde content values by European standards (Lukkaronien and Dunky 2006; Sigvartsen and Dunky 2006), which approximately corresponds to new U.S. formaldehyde emission law levels. Further, different UF and UMF resins for the face-layer and core-layer of boards were experimented with to see if the overall resin costs could be reduced. Overall, the UMF resins in the previous study resulted in FC values that can meet the E1 class level requirement of European standards, but the possibility of longer hot-pressing times and some shortening of resin storage lives were indicated. However, the FC values of UMF resins are still significantly higher than for the E0 class and, therefore, further improvements are desirable.

The causes of formaldehyde emission from UF resins during curing or hot-pressing of boards have not been fully understood or discussed in the literature in terms of the underlying chemical reactions. Two major routes for formaldehyde generation during board processing can be considered, as shown in Eq. 1 and Eq. 2:

$$\mathrm{RR'N\text{-}\underline{CH_2OH}} \longrightarrow \mathrm{RR'N\text{-}H} + \mathrm{CH_2O}\uparrow \tag{1}$$

$$\mathrm{RR'N\text{-}\underline{CH_2\text{-}O\text{-}CH_2\text{-}}NRR'} \longrightarrow \mathrm{RR'N\text{-}CH_2\text{-}NRR'} + \mathrm{CH_2O}\uparrow \tag{2a}$$

$$\xrightarrow[(+\mathrm{H_2O})]{} \mathrm{2RR'N\text{-}CH_2\text{-}OH} \longrightarrow \mathrm{2RR'NH} + \mathrm{2CH_2O}\uparrow \tag{2b}$$

The route in Eq. 1 represents the reversibility of hydroxymethyl groups, which is an inherent property of the basic resin-forming reaction between urea and formaldehyde (De Jong and De Jonge 1952a). Although the equilibrium constant is relatively small at room temperature, it increases with increasing temperatures (De Jong and De Jonge 1952b) such as in curing during hot-pressing of boards, and therefore it has been tacitly assumed to be the main underlying cause of formaldehyde emission in wood composite boards. On the other hand, the present authors have been curious about the methylene-ether groups present in UF resins (Eq. 2), present up to about 18% to 20% of charged formaldehyde (Kim and Amos 1990). In the past, the methylene–ether groups were suggested to be breaking down during curing, generating free formaldehyde as shown in Eq. 2a and Eq. 2b (Wirpsza and Brezezinski 1973). It thus appears that methylene-ether groups present in UF resins could affect the formaldehyde emission levels. Various UF and UMF resin synthesis procedures have been reported in the past (Tohmura *et al.* 2001; Zanetti and Pizzi 2003; Park *et al.* 2006, 2009; Sun *et al.* 2011), but there is no report on reducing or eliminating the methylene–ether group contents. On the other hand, the uron-type methylene-ether groups (Fig. 1) are a special case of methylene-ether groups and are known to be formed in UF resins by including a strongly acidic reaction segment in the common UF resin synthesis procedure (Gu *et al.* 1995; Soulard *et al.* 1999). Further, some industrial UF resins have been known to harbor uron-type methylene–ether groups, but their effects on the formaldehyde emission potentials or other performance properties have not been clearly understood or reported.

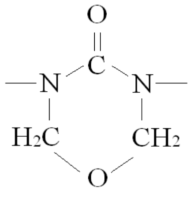

Fig. 1. Uron structure

Therefore, an investigation on new syntheses of UF and UMF resins aimed at lowering the formaldehyde emission potential of wood composite boards was considered to be worthwhile with inclusion of the uron-type methylene–ether group procedure. By comparing the results with those of the typical UF and UMF resin synthesis procedure studies (Mao *et al.* 2013), the advantages or disadvantages could be shown and an inference can be made as to whether the curing processes of Eq. 2a and Eq. 2b occur in a way that the liberated formaldehyde would remain in boards or be assimilated back into resin phase to leave little extra formaldehyde in boards. It can be theorized that the uron-type ether groups' breakup reaction, if occurring during curing at a high resin viscosity, can extend the resins' 'flow'. A longer 'flow' in thermosetting wood composite resins often results in increasing the bond strength of boards, although this may also indicate a slower curing rate of resins and a remainder of liberated formaldehyde (Eq. 2) in cured resins.

In this study, UF and UMF resins having the same overall component formulations with those prepared in the previous study (Mao *et al.* 2013) were synthesized with inclusion of a reaction step at an F/U mole ratio of 2.7 and pH 3.5 in the beginning, followed by the typical three-step resin synthesis procedure. The objectives were to find out whether there were any ways to improve the efficiency of UMF resins by incorporating the uron-type methylene–ether bonds as well as to understand and gauge the uron groups' curing and formaldehyde emission behaviors. It was also hoped that some insight on the curing behavior of the chemically similar linear methylene–ether groups present up to 18% to 20% of charged formaldehyde in UF and UMF resins would be gained. The resultant UF and UMF resins were subjected to the very same wet chemical, storage stability, and curing rate tests. Characterization by ^{13}C NMR spectroscopy and evaluation as particleboard binders were also carried out with the same methods and procedures to allow direct comparison of the results to derive the effects of the strong acidic step included in the resin synthesis procedures.

EXPERIMENTAL

Materials

A formaldehyde solution of 50.0% concentration was obtained from Georgia-Pacific (Taylorsville, MS), and reagent-grade urea (98.0%) and melamine (99.0%) were used for resin syntheses. All pH adjustments were made by using 4.0% and 25% sodium hydroxide solution and 4.0% sulfuric acid solution. Pine wood particles (face-layer and core-layer) and a wax emulsion with a 50.0% solid content was obtained from Roseburg Forest Products (Taylorsville, MS). 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 and used as catalysts.

Resins Syntheses

Urea–formaldehyde condensate (UFC) was made first. Formaldehyde solution (1229.3 g, 50.0%) was added to a 2-L reactor equipped with a condenser and stirring and heating device, and the pH was adjusted to 8.0 with sodium hydroxide solution. The reaction mixture was heated to 70 ^{o}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 ^{o}C for 30 min at pH 8.0. The reaction mixture was then cooled and stored at room temperature until use.

Control UF resins having uron-type methylene–ether groups were synthesized by including a strong acidic reaction step as in the following: In the first step, 1508.1 g 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 ^{o}C, followed by adding 185.8 g first urea (U_1) slowly to reach to an initial F/U_1 mole ratio of 2.70. After the urea was completely dissolved, the temperature was raised to 90 ^{o}C and maintained for 30 min while maintaining the pH at 8.0. In the second step, the pH of reaction mixture was adjusted to 3.5 by using 8.0% sulfuric acid solution to start the uron-type methylene–ether bond formation, and the viscosity was checked every 10 min until it reached the target viscosity of EF by the Gardener-Holdt (G-H) scale, in about 1 h. In the third step, the pH was adjusted to 8.0 and 162.7 g second urea (U_2) was added, reaching to the target $F/(U_1+U_2)$ mole ratio of 2.0, followed by reacting at 90 ^{o}C for 20 min. In the fourth step, the pH was adjusted to 4.75 and the viscosity was checked every 5 min, reaching to the target viscosity of PQ by G-H scale in 20 min. In the fifth step, the system pH was adjusted to 8.0, cooled to 60 ^{o}C, and 567.4 g third urea (U_3) was added reaching to 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 UF1.05e. Control UF resins having mole ratios of

1.15 and 1.25 were synthesized in the same way until the fourth step, but in the fifth step, 463.6 and 376.2 g of urea (U_3) were, respectively, added to reach to the target F/U mole ratios, resulting in Resin UF1.15e and Resin UF 1.25e. All resins were stored in a refrigerator at 4 °C until use.

UMF resins were synthesized according to the same formulations and procedures of the control UF resin with an F/U mole ratio of 1.05, 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. Then, the reaction mixture was cooled to 60 °C and 537.9 g of urea (U_3) was added, reaching to 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%UMF1.05e. The UMF resin with 5% melamine content was similarly synthesized except that the amounts of melamine and U_3 were 124.5 g and 507.7 g, respectively, resulting in Resin 5.0%UMF1.05e. 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 synthesized resins were measured using standard procedures. Storage stabilities of synthesized resins were measured by placing the 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). The resin samples were prepared by mixing 2.0 g of resin with 1.0 g of deuterium oxide. A 12-us 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 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 duplicates by placing catalyzed resin samples in a convection oven at 30 °C and checking the viscosities every 15 min for 12 h. Gel times of catalyzed resins at 100 °C were measured in triplicates by stirring and heating a catalyzed resin sample in a glass tube in boiling water, catalyzed with Catalyst A and Catalyst B at 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% levels based on the weight of liquid resin.

Gel Times and Curing Times

Gel times and curing times of catalyzed resins were carried out in duplicates on an oscillatory Rheometer (AR1500ex, TA Instruments, New Castle, DE) 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%.

Particleboard Manufacturing

Particleboard manufacturing was carried out in the laboratory with the blending parameters shown in Table 1, similar to those used in the previous study (Mao *et al.* 2013). Wood particles were first dried to a moisture content of 5.0% and put in a rotating blender, and then wax and catalyzed resin were successively sprayed on the rotating particles using an air-atomizing nozzle within a blending time of approximately 15 min. Face particles and core particles were blended separately. Blended particles were weighted and hand-laid on a steel plate in a box for a three-layer mat with a 1:2:1 weight ratio of top: core: bottom layers. Two mats were made and one was pressed for 3.0 min and the other was pressed for 3.5 min. The press-closing rate was initially 0.5 in/s to a mat thickness of 1.0 in and then 0.03 in/s to reach the target board thickness of 0.5 in. The boards were cooled to room temperature for one day. Other board-preparation parameters were as follows: resin content of 9.0%, wax content of 1.0%, mat moist content of 8.0% based on the oven-dried wood weight; board dimensions of 24 in × 22 in × 0.5 in; board density of 50.0 pcf; and press temperature of 350 ^{o}F.

Table 1. Particleboard Preparation Parameters

Board Number	Particleboard Preparation Parameters							
	Face layer				Core layer			
	Resin		Catalyst		Resin		Catalyst	
	Type	Mole Ratio	Type	Level (%)	Type	Mole Ratio	Type	Level (%)
1	UF (e)	1.05	A	0.5	UF (e)	1.05	A	0.5
2						1.15		
3						1.25		
4	UF (e)	1.05	A	0.5	2.5% UMF (e)	1.05	B	0.5
5								1.0
6								1.5
7								2.0
8	UF (e)	1.05	A	0.5	5.0% UMF (e)	1.05	B	0.5
9								1.0
10								1.5
11								2.0
12	2.5% UMF (e)	1.05	B	0.5	5.0% UMF (e)	1.05	B	1.0
13				1.0				
14	5.0% UMF (e)	1.05	B	0.5	5.0% UMF (e)	1.05	B	1.0
15				1.0				

(e) denotes high "ether" content of the resins synthesized in this study in comparison with the typical resins reported in Part I (Mao *et al.* 2013).

Physical and Mechanical Testing of Particleboards

Each board was cut and tested for internal bond (IB) strength (8 test pieces) and bending strengths (MOR and MOE) (4 test pieces) on an Instron machine (Norwood, MA), and water-soak thickness swell (TS) and water absorption (WA) values (2 test pieces) were measured in a 20 ^{o}C water bath according to ASTM D 1037-06a.

Formaldehyde Content Measurements

Formaldehyde content (FC) values were measured after about three months of hot-pressing due to an instrument breakdown. One FC test sample was cut from each board with dimensions of 6 in × 6 in after one-day airing of boards after hot-pressing and, because of this unexpected waiting period, each test sample was sealed on the edges with duct tape, wrapped in saran film, and put in a sealed plastic bag, and all samples were kept in the refrigerator at 4 ^{o}C until testing. The formaldehyde content decreases in the boards from the long storage period appeared minimal, and tests were carried out according to the European standard method (EN120 2001).

RESULTS AND DISCUSSION

For resin physical properties, the synthesized resins showed pH values of 8.0; specific gravity values of 1.259 to 1.272; viscosity values of GH to IJ by the G-H scale; and solid content values of 62.15 to 63.68%. The test values were generally what was expected from the synthesis procedures used and also within the ranges of industrial values similarly as in the previous study (Mao *et al.* 2013). The small property differences would make little difference in comparing the resins' bonding or formaldehyde emission performances.

Chemical structures of Resin UF1.05e and Resin 5.0%UMF1.05e from ^{13}C NMR are summarized in Table 2 along with the differences in group values calculated by subtracting the values of current study from those corresponding spectral data obtained in the previous study (Mao *et al.* 2013). The spectra are shown in Fig. 2a and Fig. 2b.

Chemical shift values were assigned and carbon groups were quantified by using similar methods as those in our previous study (Kim 1999, 2000, 2001). The observed group distributions are in general very similar to those of the previous study, but the differences that occurred due to the strong acidic reaction step used in the resin synthesis were clearly shown, summarized as: (a) lower total hydroxylmethyl group contents; (b) higher total methylene–ether group contents, especially Type III methylene–ether contents; (c) similar total methylene group contents, but higher Type III methylene contents; and (d) higher cyclic urea contents to indicate the uron-type structures for some of the methylene–ether groups (Gu *et al.* 1995; Soulard *et al.* 1999).

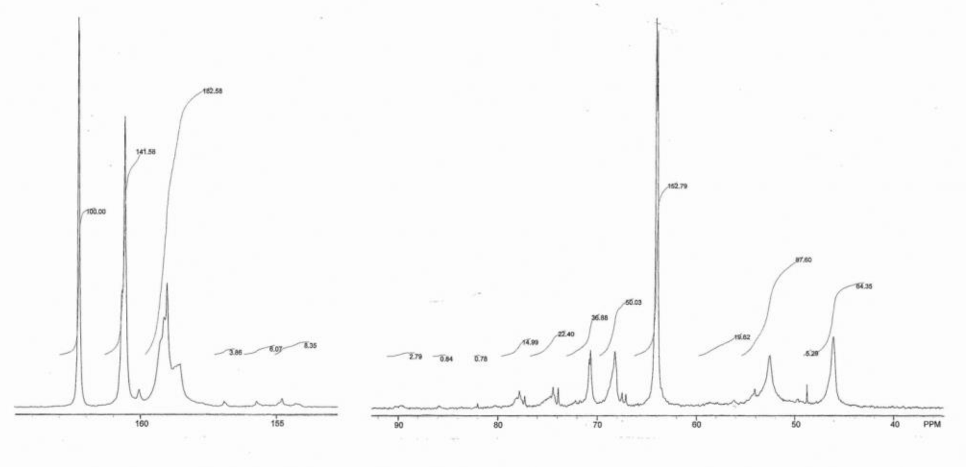

Fig. 2a. ^{13}C NMR spectra of Resin UF1.05e in water

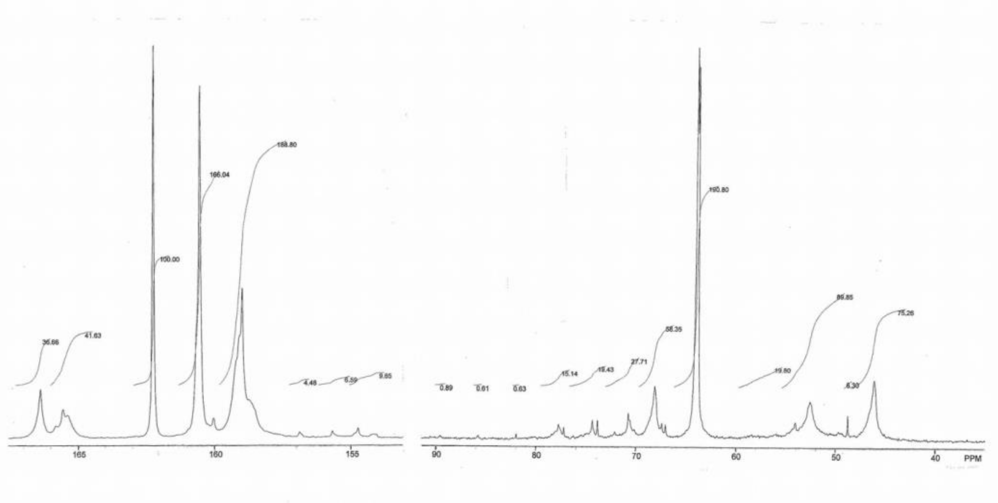

Fig. 2b. ^{13}C NMR spectra of Resin 5.0%UMF1.05e in water

Table 2. Percentage Integration Values for Various Methylenic and Carbonyl Carbons of Resins Determined from ^{13}C NMR Spectra

Carbon Groups	**Resin UF1.05e**		**Resin 5.0% UMF1.05e**	
	Groups (%)	**Difference * (%)**	**Groups (%)**	**Difference * (%)**
Free urea	22.60	1.22	21.03	0.99
Monosubstituted urea	32.00	0.04	34.91	−0.31
Di, tri-substituted urea	41.27	−2.42	39.70	−1.59
Cyclic urea	4.13	1.39	4.36	0.91
Total urea	**100.0**		**100.0**	
Free melamine			46.83	1.83
Mono, di-substituted melamine			53.17	−1.83
Total melamine			**100.0**	
Free formaldehyde	0.97	0.37	0.42	−0.05
Total hydroxylmethyl	**41.86**	**−1.44**	**43.84**	**−0.75**
Type I	33.72	−0.74	38.28	−0.53
Type II	8.14	−0.70	5.56	−0.22
Total methylene–ether	**19.5**	**1.58**	**18.60**	**0.78**
Type I	11.04	−0.67	11.71	−0.49
Type II	4.94	0.35	3.90	0.22
Type III	3.31	1.69	3.04	1.12
Total methylene	**37.67**	**−0.51**	**37.10**	**−0.02**
Type I	14.20	−0.75	15.10	−0.59
Type II	19.33	−0.63	18.03	0.14
Type III	4.33	1.05	3.97	0.43
Total CH_2	**100.0**		**100.0**	
CH_2/CO**	**1.024**		**1.00**	
Degree of polymerization***	1.948		1.856	

***** Difference indicates the increases and decreases of integration values compared with the data of corresponding resins made by the typical synthesis procedures, reported in Part I (Mao *et al.* 2013).
****** CH_2/CO refers to methylenic carbons/carbonyl ratios calculated from the integration values.
******* Degree of polymerization was calculated using: DP = 1 / [1 − (methylene + 0.5 x methylene–ether)].
For chemical structures and names of functional groups, refer to Kim (1999; 2000; 2001).

The differences were generally greater for Resin UF1.05e than for Resin UMF1.05e, indicating that the melamine added in the last step of resin synthesis appears to have reacted in a way to partly open up the uron-type structures. Overall, the uron-type methylene–ether group contents are certainly higher in current resins, and this would be ascribed to the strong acidic reaction step included in the resin synthesis procedure.

Storage stabilities of synthesized resins are presented in Fig. 3 as viscosity increases observed for 50 days.

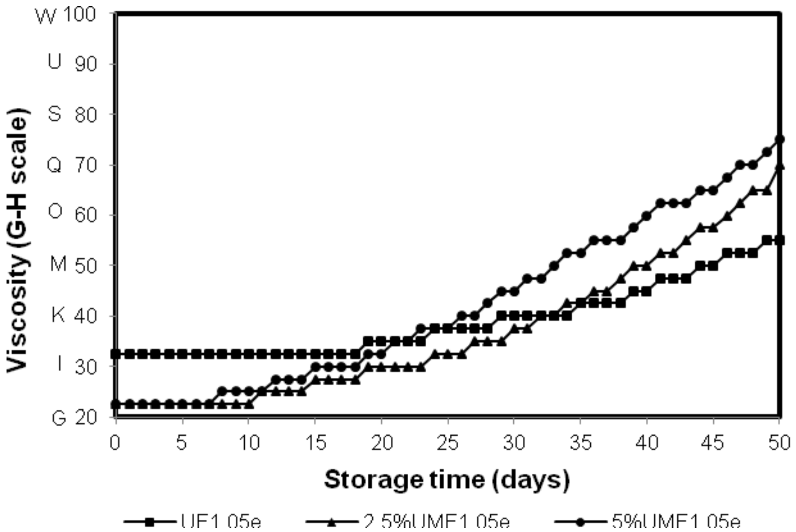

Fig. 3. Viscosity increases of Resin UF1.05e and Resins 2.5% and 5.0%UMF1.05e measured during 50-day storage at 30 °C

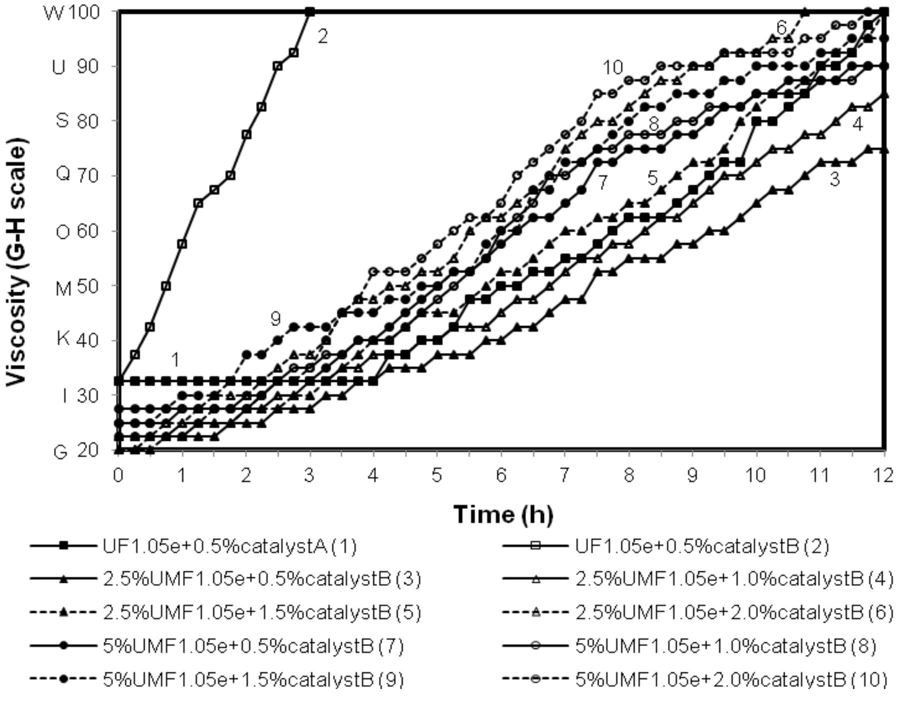

Fig. 4. Pot-lives of catalyzed UF and UMF resins with different catalysts and levels

The general trends and ranges with respect to melamine addition and mole ratios were very similar to those of the resins synthesized by the typical procedures in the previous study, but all present resins took about four (4) days longer to reach viscosity S by the G-H scale than the corresponding resins synthesized by the typical resin synthesis procedure of the previous study (Mao *et al.* 2013).

Pot-lives of catalyzed resins measured at 30 ^{o}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 and of melamine levels and mole ratios were similar to those in the previous study (Mao *et al.* 2013), but the present resins showed longer pot-lives: for example, 3 to 4 h longer for 2.0% catalyst level uses for Resin 2.5%UMF1.05e. These results are similar in trends to the storage lives discussed above. Longer pot-lives are generally a desirable characteristic, giving more flexibility in the manufacturing operations in industry, but they can be an indication of slower curing rates.

Gel times of catalyzed resins measured at 100 ^{o}C are reported in Table 3, along with the gel time differences calculated by subtracting the values of present resins from those of corresponding resins of the previous study (Mao *et al.* 2013). The gel time differences are significantly large, similar to the storage lives and pot-lives discussed above. These results indicate that the acidic catalysts, used for resin curing in the hot-pressing, are slower to activate the uron-type methylene–ether groups in comparison with hydroxymethyl groups, at room or 100 ^{o}C, in the presence of water in the resin. Longer gel times by themselves can give better flexibility in the hot-pressing operation in the wood composite manufacturing process, but also may imply resins' slower curing rates in the hot-pressing of boards. Overall, the longer storage stabilities, pot-lives, and 100 ^{o}C gel times of present resins all agree with the higher contents of uron-type groups as observed in ^{13}C NMR spectra. Overall, it appears that the slowing down of these curing processes indicates that the breakup of uron-type methylene–ether groups by acid catalysts is not instant, but time-dependent at the prevailing temperatures.

Table 3. Gel Times (s) of Resins with Catalysts A and B at Various Levels Measured at 100 ^{o}C

Catalyst Level	0.5%		1.0%		1.5%		2%		2.5%		3.0%	
Catalyst Kind	A	B	A	B	A	B	A	B	A	B	A	B
UF1.05e	263	125	222	95	201	86	179	78	137	65	131	63
Difference *	132	20	119	15	116	21	93	14	—	—	—	—
2.5%UMF1.05e	487	335	408	275	335	237	289	199	255	178	227	164
Difference *	268	148	207	103	156	75	120	53	88	40	—	25
5.0%UMF1.05e	482	337	419	265	351	234	293	198	268	181	229	178
Difference *	259	133	222	86	167	66	124	36	99	24	—	20

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

Rheometric measurement results of gel and cure times of catalyzed resins are presented in Table 4, obtained by the same methods and procedures used in our previous study. The general trends of the gel and cure times of UF and UMF resins in this study are similar with those of the previous study (Mao *et al.* 2013), but the gel and cure time differences between the present and previous studies are varied. Resin UF1.05e showed longer gel and cure times at lower temperature (90 ^{o}C), in line with the storage lives, pot-lives, and 100 ^{o}C gel times discussed above, but at higher temperatures (120 ^{o}C, 135 ^{o}C, and 145 ^{o}C) the resins showed shorter gel and cure times, possibly to indicate that uron-type methylene–ether groups break up more easily and then participate as hydroxymethyl groups in the curing process because of the ‘anhydrous’ curing condition prevailing in the rheometric tests. For Resins 2.5% and 5.0% UMF1.05e, the gel times are generally shorter than those of typically synthesized UMF resins in the previous study, but for cure times the differences are small, which appears to indicate that Catalyst B, which contains free sulfuric acid, is strong enough to break up uron-type methylene–ether groups ahead of the rate-determining resin-curing step.

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
UF1.05e	A	0.5	199	116	102	102	445	195	160	147
		Difference *	13	−36	−26	−7	45	−70	−20	—
	B	0.5	74	74	67	—	200	146	—	—
2.5%UMF 1.05e	B	0.5	164	145	102	109	467	270	190	158
		1.0	116	102	102	95	335	181	170	146
		Difference *	−7	−14	15	8	2	−4	37	6
		1.5	95	102	88	88	252	193	175	142
		Difference *	−27	−14	1	7	81	10	23	2
		2.0	81	95	81	81	254	175	142	122
5.0%UMF 1.05e	B	0.5	151	130	95	95	416	234	208	200
		1.0	116	95	95	95	325	193	186	160
		Difference *	−7	−24	0	−7	0	−34	−1	3
		1.5	102	88	88	81	267	188	180	135
		Difference *	−13	−24	−8	−7	−58	5	−27	15
		2.0	88	81	88	88	275	146	150	126

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

Particleboard test results are shown in Table 5, arranged similarly as in Table 1 and as in the previous study (Mao *et al.* 2013). Also, the differences of formaldehyde contents, internal bond (IB) strengths, and water absorption values calculated by subtracting the data of the present study from those obtained in the previous study are tabulated in Table 6. The results are discussed below.

Control particleboards made with Resin UF1.05e in the face-layer and Resins UF1.05e, UF1.15e, and UF1.25e in the core-layers (Boards 1-3) represent the range of UF resin uses in the industry. Using Resin UF1.25e in the core-layer has been more common due to shorter hot-pressing times and adequate board physical properties needed in the industry, although the high mole ratio led to high formaldehyde content (FC) values that correspond to the E2 class of European standards (EN 120 2001). The trends of board physical properties are similar to those of typically synthesized UF resins in the previous study (Part I), but the different values for these boards in Table 6 are significant: internal bond strength values were higher by 16 to 30 psi, water absorption values were somewhat lower, and the formaldehyde content (FC) value increased by small but significant extents (0.8 to 2.8 mg). Thus, the effects of uron-type methylene bonds on the bonding properties of boards were conflicting for UF resins, but some advantages might be found in industry practices, for example by lowering the F/U mole ratio of UF resins.

Further, the results appeared to indicate that the uron-type methylene–ether groups undergo the formaldehyde generating reaction of Eq. 2 in the later stage of the curing process, helping the resin cure to progress with an increased ‘flow', but inevitably formaldehyde was broken off and some remained as freed formaldehyde because of the limited mobility of resin molecules in the late curing stage.

Particleboards made with Resin UF1.05e in the face-layer and Resin 2.5%UMF1.05e in the core-layer (Boards 4-7) showed the best IB values at the 1.0% catalyst level. The increasing trends of physical properties and lower FC of boards by melamine addition in the core layer were similar to the typically synthesized UMF resins. Further, as shown in Table 6, the different IB values were significant, higher by 22.6 to 35.9 psi, the water-soak test values were also significantly better by 5.5% to 10.0%, and the FC value increases were somewhat smaller than for the UF resins used in the core-layer discussed above. It therefore appears that the uron-type methylene–ether groups in the resins had increased the physical properties of boards while the formaldehyde formed from the breakup of uron groups was partially assimilated back into the resin system especially with the core-layer UMF resin, possibly due to the melamine in the resin. Therefore, for UMF resins the uron-type synthesis procedure seemed to be positive overall. However, the FC values of boards were still in the range of 5.6 to 8.4 mg/100 g boards, corresponding to the E1 class of European standards (EN 120 2001). Thus, the present resin synthesis methods of UMF resins at 2.5% melamine levels might offer the similar advantage as with the uron-type UF resins discussed above, attainable through a lowering of the F/(U+M) mole ratio of resins because of the increased IB values of boards, possibly leading to a little bit lower FC values.

Table 5. Formaldehyde Emission and Physical Property Test Results of Particleboards

Board Number	Formaldehyde Content (mg/100g Bd)		Physical Properties of Particleboards Average (3.0 and 3.5 min press time)					
	Hot Press Time		Density (lbs/ft^3)	IB (psi)	MOR (psi)	MOE (kpsi)	24 h Thickness Swell (%)	24 h Water Absorption (%)
	3.0 Min	3.5 Min						
1	9.5	9.5	50.1	77.9	1160	170	28.3	58.1
2	15.4	14.9	50.3	106.9	1203	197	21.5	55.3
3	18.0	17.1	50.4	120.4	1268	197	17.7	48.6
4	8.4	8.4	50.4	101.7	1313	213	26.8	55.9
5	7.6	6.8	50.4	119.4	1470	211	25.0	53.4
6	6.7	6.3	50.5	114.0	1769	278	24.3	51.9
7	5.9	5.6	50.7	99.2	1302	232	25.0	55.7
8	7.2	6.5	50.7	110.7	1710	226	25.9	53.9
9	6.5	5.9	51.0	142.9	1879	244	22.7	51.7
10	5.7	5.4	50.9	129.1	1930	289	23.0	53.9
11	5.4	5.0	51.0	113.3	1623	227	23.4	53.6
12	6.8	5.7	51.0	138.4	1809	266	17.9	44.9
13	6.6	5.8	51.3	148.2	1901	287	15.9	42.0
14	6.0	6.0	51.5	143.5	2085	271	16.6	38.7
15	5.8	5.8	51.8	158.9	2141	294	15.7	38.6
Board Number refers to the numbers in Table 1.								

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

Board Number*	Formaldehyde Content (mg/100g Bd) Hot Press Time		IB (psi)	24-h Water Absorption (%)
	3.0 Min	3.5 Min		
1	1.6	1.5	19.9	−18.5
2	2.8	2.1	16.5	−3.2
3	1.4	1.2	30.0	−2.6
4	0.6	0.7	27.3	−5.5
5	0.9	0.8	22.6	−8.5
6	0.5	0.3	35.9	−10.0
7	0.2	0.2	27.4	−9.2
8	−0.8	−0.6	19.8	−14.7
9	−0.8	−0.1	18.6	−13.6
10	−0.5	−0.4	16.1	−20.8
11	−0.2	−0.2	10.1	−15.0
12	0.1	−0.4	22.1	−4.7
13	0.0	−0.1	31.9	−10.2
14	−1.4	−0.8	15.7	−2.6
15	−1.2	−0.1	24.6	−3.4

* Board number refers to the numbers in Table 5.

Particleboards made with Resin UF1.05e in the face-layer and with Resin 5.0%UMF1.05e in the core-layer (Boards 8-11) also showed the best IB value at the 1.0% catalyst level. The increasing trends of board performance properties and decreasing trends of FC of boards with respect to the melamine level in the core-layer were similar to boards made with typically synthesized resins in the previous study. Further, as shown in Table 6, the different IB values were significant, higher by 10.1 to 19.8 psi, and the water-soak test values were also significantly better by 13.6% to 20.8%. Further, the FC values were apparently decreased, indicating that the higher melamine level in the resin has led to a more effective capture of the off-gassing formaldehyde. Overall, the FC values of boards were still in the range of 5.0 to 7.2 mg/100 g boards, E1 class by European standards (EN 120 2001).

Particleboards made with Resin 2.5%UMF1.05e with 0.5% and 1.0% catalyst levels in the face-layer and Resin 5.0%UMF1.05e in the core-layers with 1.0% B catalyst level (Boards 12-13) showed that the face-layer catalyst level of 1.0% is better than 0.5% for IB and water-soak test values as shown in Table 5, indicating that the face-layer resin also has to be catalyzed with an adequate catalyst level due to the melamine it contains. The FC values were still in the range of 5.7 to 6.8 mg/100 g boards of the E1 class of European standards (EN 120 2001). Further, the differences between IB and the water-soak test values were significant but the FC value decreases were only slight as shown in Table 6, indicating that the 2.5% level melamine in the face-layer resin minimally reduced the FC values of boards.

Particleboards made with Resin 5.0%UMF1.05e with 0.5% and 1.0 catalyst levels in the face-layer and the same resins with 1.0% catalyst in the core layer (Boards 14-15) showed FC values of 5.8 to 6.0 mg/100 gram boards with relatively good internal bond (IB), bending strength, and water-soak test values, as shown in Table 5. These performance values are small improvements over the values of boards made by using Resin 2.5%UMF1.05e in the face-layer discussed above, ascribed to the increased melamine level in the face-layer resin. On the other hand, the differences of IB strength and water-soak values and FC values were all significant improvements over the values obtained in the previous study, shown in Table 6, indicating that the uron-type resin synthesis procedure were more effective with UMF resins with a 5.0% level of melamine than with 2.5% level melamine in reducing the FC of boards. However, the FC values of boards were still in the E1 class of European standards (EN 120 2001). Overall, the present UMF resin synthesis procedure of entailing the uron-type methylene–ether groups could be judged to be more effective than the typical three-step resin synthesis procedure of the previous study for lowering of formaldehyde emissions, especially if the melamine level is to be used at 5.0% or higher either as a core-layer or face-layer binder of particleboards.

It is noted here that the slower curing rates of UMF resins versus UF resins has required Catalyst B, which contains free sulfuric acid, and the curing rate data discussed above appear to require longer hot-pressing times for UMF resins, which cannot be addressed well in laboratory studies like the current efforts. The slower curing rates of resins could mean a limited flexibility in the running of board manufacturing plants and lowered productivity. Further, since the FC values of boards bonded with UMF resins at 5.0% melamine levels were still in the E1 class range of European standards, further research would be worthwhile toward lowering of FC values and increasing of curing rates.

The results of this study on the uron-type methylene group leaves two interesting questions. One is the extension of the strong acidic reaction segment, in order to bring up more uron-type methylene–ether groups in the resin. Some room appears to exist in the resin synthesis procedure, and this will be followed up in the next sequel paper.

The other question is regarding the linear methylene–ether groups (Eq. 2) present at 18% to 20% levels of the formaldehyde charged in the resin synthesis either for UF or UMF resins. As suggested in the literature (Wirpsza and Brezezinski 1973) and also observed in the present results of the breakdown of uron-type methylene–ether groups, the linear methylene–ether groups would similarly undergo breakdown during curing of the resin, generating free formaldehyde. However, the large methylene–ether group values of UF resins means a lot of free formaldehyde that would be forming and assimilating back into the resin system during curing, resulting in some un-assimilated formaldehyde in the end.

This scenario is interesting since the formaldehyde content (FC) value of 15.0 mg/100 g boards, common for commercial particleboards in the recent past, corresponds to about 0.37% of the formaldehyde used in the synthesis of resin used in the board. This means that only a small fraction of formaldehyde is left out in the board to cause the formaldehyde emission problem. This fact appears to be pointing to new research directions: Is there any way to control the curing process? This will also be discussed further in the sequel paper along with the results of extending the uron-type bond forming reaction in resin syntheses.

CONCLUSIONS

1. The modification of the UF and UMF resin synthesis procedure with the inclusion of a strong acidic reaction step in the beginning at the F/U mole ratio of 2.7 and pH of 3.5 has resulted in the formation of some uron-type methylene–ether groups in the resins and resulted in longer storage lives, longer gel times, and longer pot-lives.
2. The resultant UF and UMF resins tested by bonding laboratory particleboards, showed improved IB and water-soak test values, but the formaldehyde content values increased slightly for UF resins but decreased slightly for UMF resins, especially with 5.0% melamine addition levels.
3. The results indicated that the uron-type groups in resins break up in the hot-pressing of boards to participate in the curing process and enhance the bonding of boards, but the process also gives off some extra formaldehyde gas which is not effectively captured in the case of UF resins but is relatively well captured by melamine in UMF resins because of the increased reactive capacities of melamine.
4. From this reasoning, the 5.0% melamine level in UMF resin was concluded to be more effective than the 2.5% melamine level, and it is concluded that the strong acidic reaction step included in the beginning of synthesizing UMF resins would be useful in improving board physical properties as well as lowering the formaldehyde emission potential of particleboards, especially for UMF resins having a 5.0% melamine level or higher.
5. The curing rates of the UMF resins synthesized by the present procedure could be somewhat slower than UMF resins synthesized by the typical procedure. The results also point out new directions for research toward lowering of formaldehyde emission potentials of wood composite boards.

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