The Effects of Adding Melamine at Different Resin Synthesis Points of Low Mole Ratio Urea-Melamine-Formaldehyde (UMF) Resins

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Low mole ratio urea-melamine-formaldehyde (UMF) resins synthesized with 2.5% and 5.0% melamine levels added at the beginning, middle, and end points of the first alkaline step of the typical urea-formaldehyde (UF) resin synthesis procedure were compared with typical UMF resins synthesized with melamine additions made at the final alkaline step. Various resin analysis, particleboard preparation, physical performance, and formaldehyde emission level tests were carried out. UMF resins synthesized with melamine additions at the beginning of the first alkaline step showed adequate storage lives of 2 to 3 weeks, and their particleboard bonding tests showed small but significant improvements in water soak test values, while formaldehyde content values were slightly higher in comparison with typical UMF resins. The particleboards showed adequate board strength and the formaldehyde contents were relatively low to qualify for the E1 Class of European Standards. UMF resins synthesized with melamine addition made at the middle and end of the first alkaline step were highly turbid and showed chemical structure differences and very short storage lives and the resin synthesis procedures were concluded to be of little practical value.

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

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INTRODUCTION

Urea-formaldehyde (UF) resins have been used in the forest products industry for bonding particleboard, medium density fiberboard (MDF), and hardwood plywood. One current problem is the relatively high formaldehyde emission levels of boards arising from UF resin binders. A current approach for formaldehyde emission reduction has been modification of UF resins with low levels of melamine, *i.e.*, urea-melamine-formaldehyde (UMF) resins (Oh 1999; Tohmura *et al.* 2001; Sigvartsen and Dunky 2006; Young No and Kim 2007; Sun *et al.* 2011; Mao *et al.* 2013). Melamine has a higher functionality (≥ 3) than urea and UMF resins, indicating that its addition would make UMF resins have more functional sites available to react with formaldehyde. Under a mild alkaline condition, melamine reacts with formaldehyde in a similar manner to urea to form hydroxymethylmelamines with up to six hydroxymethyl groups. Dimers or trimers of hydroxymethylmelamines are also formed in slightly acidic pH that arises during resin manufacturing (Wirpsza and Brezezinski 1973; Devallencourt *et al.* 2000).

The key variables to consider in the synthesis and use of UMF resins are as follows: the base UF resin synthesis procedure; melamine level; point of melamine addition; final F/(U+M) mole ratio; and acid catalyst kind and level to use in curing (Young No and Kim 2005; Tohmura *et al.* 2001; Sigvartsen *et al.* 2006). In our previous reports (Mao *et al.* 2013), typical low mole ratio UMF resins synthesized with 2.5% and 5.0% melamine levels were investigated using the typical three-step UF resin synthesis procedure with the melamine addition carried out at the last alkaline step. Various kinds and levels of acid catalysts were also investigated. The question investigated in this article is the melamine addition point in resin synthesis. In the past, melamine was used at higher levels and the addition was often carried out at the beginning of resin synthesis, so that the melamine components were forced to go through the usual acidic second step (Oh 1999; Sun *et al.* 2011). It is known that dimeric or higher melamine-formaldehyde reaction products are quickly formed in the acidic reaction and precipitate out of the water phase (Wirpsza and Brezezinski 1973). This insoluble polymer-forming tendency would shorten the storage life of UMF resins, but this effect could be less severe at low melamine addition levels and has not been documented regarding the advantages or disadvantages.

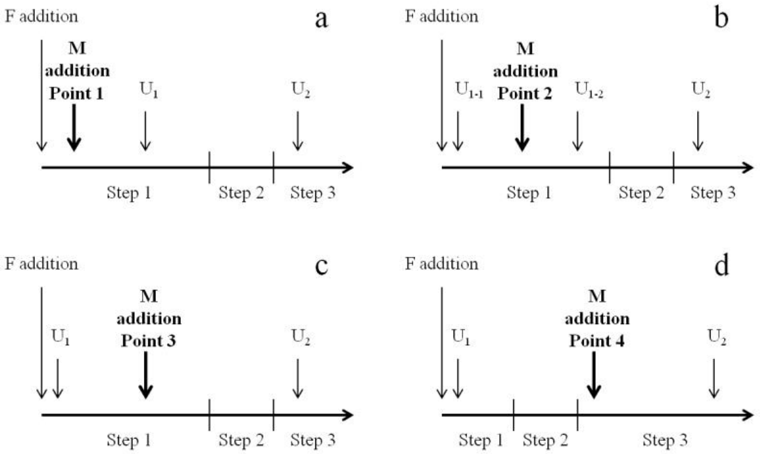

Fig. 1. Melamine addition points in a typical 3-step UF resin synthesis procedure. F: formaldehyde; M: melamine; U1: first urea; U1-1: first part of the first urea; U1-2: second part of the first urea; U2: second urea

The first step of the typical three-step UF resin synthesis begins with reacting 2.0 to 2.4 moles of formaldehyde with one mole of urea in a mild alkaline pH to form monomeric hydroxymethylureas. In the second step, the polymerization reaction of the monomeric UF components is carried out under a mild acidic pH of 4.5 to 5.0 to form methylene and methylene-ether groups between urea units. In the third step, the reaction mixture is adjusted to a mild alkaline pH and additional urea is added to reach the final mole ratio, followed by cooling to room temperature. In a previous study (Mao *et al.* 2013), the UF resin made with the typical 3-step procedure and UMF resin made with the melamine addition at the beginning of the third alkaline step (Fig. 1d) were investigated. In this study, melamine addition was carried out at three different points in the first alkaline reaction step: Point 1, before the addition of the first urea; Point 2, at the mid-point of the first urea addition; and Point 3, at the end of the first urea addition, as shown in Figs. 1a, 1b and 1c, respectively. Then, the acidic polymerization step at pH 5.25 was carried out, followed by the second urea addition step in alkaline pH. The resulting resins' chemical structures and particleboard bonding performances were investigated and compared with the previous report (Mao *et al.* 2013), where the melamine addition was performed at Point 4 shown in Fig 1d.

The melamine levels, curing catalyst kind and levels, resin property characterization methods, and particleboard manufacturing and testing methods were all kept the same as in the previous study. The objective was to determine whether the addition methods of melamine in the first alkaline step of UMF resin synthesis procedure would offer any advantages over the addition method in the last alkaline step in terms of the resultant resins' chemical structure, storage stability, catalyzed resin stability, curing rate, particleboard bonding, and formaldehyde emission potentials.

EXPERIMENTAL

Materials

A formaldehyde solution of 50% concentration obtained from Georgia-Pacific Corp. (Taylorsville, MS, USA) and reagent-grade urea (98.0%) and melamine (99.0%) were used. Sulfuric acid of 8% concentration and sodium hydroxide solution of 4% concentration were used as pH adjusters. Mixed pine wood particles (face layer and core layer) and a wax emulsion with 50% solids content used in industrial particleboard manufacturing 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 used as resin curing catalysts.

Resin Synthesis

First, the urea-formaldehyde condensate (UFC) was made using a 50% formaldehyde solution (1229.3 g) and urea (278.8 g) with an F/U mole ratio of 4.50 and used in the resin syntheses as described in a previous study (Mao *et al.* 2013).

UMF resins having 2.5% and 5.0% melamine levels added at point 1 with a final F/(U+M) mole ratio of 1.05 were synthesized: UFC (1508.1 g) was added to a 2-L reactor, the pH was adjusted to 8.0 with sodium hydroxide solution, and the reactor was heated to 70 °C. Melamine (61.4 g) was then added, and the temperature was raised to 90 °C and maintained for 30 min at pH 8.0. The first urea (319.2 g) was then slowly added, reaching an F/(U+M) mole ratio of 2.0, and the temperature was maintained at 90 °C for another 30 min at pH 8.0. In the second stage, the solution pH was adjusted to 5.25 with 8% sulfuric acid solution, the slightly higher pH value than the typical value being found necessary to slow down the reaction rate within a controllable range, and the viscosity of the reaction mixture was checked every 15 min until it reached the target viscosity of P-Q on the Gardner-Holdt (G-H) scale (1 h and 25 min). In the third stage, the pH was adjusted to 8.0 with sodium hydroxide solution and the third portion of urea (567.1 g) was added, reaching an F/(U+M) mole ratio of 1.05, giving resin 2.5%UMF-1. The resin was cooled to room temperature to have a final viscosity of G-H on the G-H scale. For the 5.0% melamine level, the same procedure was followed, using the first urea (289.1), melamine (124.5 g), and the second urea (566.9 g), resulting in resin 5.0%UMF-1 with a final viscosity of H-I on the G-H scale.

UMF resins having 2.5% and 5.0% melamine levels added at point 2 with a final mole ratio of 1.05 were synthesized: UFC (1508.1 g) was added to a 2-L reactor, the pH was adjusted to 8.0 with sodium hydroxide solution, and the reactor was heated to 70 °C.

The first half of the first urea (159.6 g) was slowly added, and the temperature was raised to 90 ^{o}C and maintained for 15 min; then, melamine (61.4 g) was added and the temperature was maintained at 90 ^{o}C for 30 min at pH 8.0. Next, the second half of the first urea portion (159.6 g) was slowly added until the F/(U+M) mole ratio reached 2.0, and the temperature was maintained at 90 ^{o}C for another 30 min at pH 8.0. In the second stage, the solution pH was adjusted to 5.25 with sulfuric acid solution, and the viscosity of the reaction mixture was checked every 15 min until it reached the desired viscosity of P-Q on the G-H scale (1 h and 25 min). In the third stage, the pH was adjusted to 8.0 and the third urea (567.1 g) was added, reaching an F/(U+M) mole ratio of 1.05, giving resin 2.5%UMF-2. The resin was cooled to room temperature with a final viscosity of H-I on the G-H scale. For the 5.0% melamine level, the same procedure was followed, using the first urea portion (144.6 g/144.6 g), melamine (124.5 g), and the second urea portion (566.9 g), resulting in resin 5.0%UMF-2 with a final viscosity of H-I on the G-H scale.

UMF resins having 2.5% and 5.0% melamine levels added at point 3 and a final mole ratio of 1.05 were synthesized: UFC (1508.1 g) was added to a 2-L reactor, the pH was adjusted to 8.0 with sodium hydroxide solution, and the reactor was heated to 70 ^{o}C. The first urea portion (319.2 g) was then slowly added, and the temperature was raised to 90 ^{o}C and maintained for 30 min at pH 8.0. Then, melamine (61.4 g) was added, reaching an F/(U+M) mole ratio of 2.0, followed by maintaining the temperature at 90 ^{o}C for 30 min at pH 8.0. In the second stage, the solution pH was lowered to 5.25 with sulfuric acid solution and the solution viscosity was checked every 15 min until it reached the target viscosity of P-Q on the G-H scale (1 h and 15 min). In the third stage, the pH was adjusted to 8.0 with sodium hydroxide solution, and the second urea portion (567.1 g) was added, reaching an F/(U+M) mole ratio of 1.05, giving resin 2.5%UMF-3. The resin was cooled to room temperature with a final viscosity of G-H on the G-H scale. For the 5.0% melamine level, the same procedure was followed, using the first urea (289.1 g), melamine (124.5 g), and the second urea portion (566.9.5 g), resulting in resin 5.0% UMF-3 with a final viscosity of H-I on the G-H scale.

Results for control UF resins having F/U mole ratios of 1.25, 1.15, and 1.05 and typical UMF resins (resins 2.5%UMF-4 and 5.0%UMF-4) made with melamine levels added at point 4 were taken from a previous study (Mao *et al.* 2013). The control UF resin with an F/U mole ratio of 1.05 was used as a face layer binder for selected boards.

Resin Physical Property and Storage Stability Measurements

The non-volatile solids content (in triplicate) and specific gravity of resins were measured using the common laboratory procedures. The storage stability of resins was measured by placing the Gardner-Holdt (G-H) resin viscosity measurement samples in a convection oven at 30 ^{o}C and checking the viscosity daily for 50 days.

Chemical Structure Determination of UMF Resins

^{13}C NMR chemical structure determinations of resins 5.0%UMF-1, -2, and -3 were carried out on a Techmag 400-2 NMR spectrometer (Spectral Data Services, Champaign, IL). For each test, 2.0 g of resin sample was mixed with 1.0 g of deuterium oxide. However, all three UMF resins synthesized were turbid, *i.e.*, containing solid resin particles; therefore, to help dissolve the resin particles, 1.0 g of DMSO-d_6 was added to each sample. The turbidity was still significant and in the absence of any suitable good solvent the tests were done with the turbid solutions. A 12-μs pulse-width and a 10-s pulse delay were used for quantitative results, and about 400 scans were accumulated.

Spectral peaks were integrated under the same scale factor, and the integration values were quantified as group percentages. Urea carbonyls were separately integrated with respect to free urea, mono-substituted urea, di-/tri-substituted urea, and cyclic urea. The ^{13}C NMR results showed the effects of the turbidity of resin samples; these results are discussed later. The spectra of resin 5.0%UMF-4 and a typical UF resin obtained in a previous study (Mao *et al.* 2013) were used for comparison.

Pot Life and Gel Time of Catalyzed Resins

The gel times of catalyzed resins were measured in duplicate with various levels of catalysts by heating in a glass tube at 100 ^{o}C until the samples set as solids. The pot-lives of catalyzed resins at various catalyst levels were determined in triplicate at 30 ^{o}C by checking the viscosity of resins in G-H viscosity sample tubes every 15 min until the sample reached viscosity S on the G-H scale.

Gel and Curing Times of Resins Measured on Oscillatory Rheometer

Gel and curing times of catalyzed resins were further investigated in duplicate using an oscillatory rheometer (AR1500ex, TA Instruments Corp., DE) with an 8-mm-diameter probe at test temperatures of 120 ^{o}C and 145 ^{o}C. The resin sample was allowed to balance at 20 ^{o}C for 10 s and heated to the target temperature in 50 s; time sweeps were performed at a frequency of 1.0 Hz and strain of 1.0%. Gel time and cure time values were obtained in duplicate from the storage and tan delta curves, as described in a previous report (Mao *et al.* 2013).

Particleboard Manufacturing

Particleboards were made using the various preparation parameters shown in Table 1 to find the optimum parameter ranges. Wood particles dried to 5.0% moisture content were put in a rotating blender, and wax and catalyzed resin were successively sprayed using an air-atomizing nozzle over approximately 15 min. Face and core particles were blended separately. Blended particles were weighed, and three-layer mats were formed with a 1:2:1 weight ratio for the top:core:bottom layers and pressed at 350 ^{o}F for 3.0 and 3.5 min. Two mats were formed from each blend. 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 thickness of 0.5 in. The boards were aired at room temperature for one day and cut into test samples. Other blending and mat parameters were as follows: resin solids loading level of 9.0%; wax loading level of 1.0%; target mat moisture content of 9.0% based on oven-dried wood weight; board dimensions of 24 in× 22 in × 0.5 in; and target board density of 50.0 pcf.

Physical and Mechanical Testing of Particleboards

Boards were cut and tested for internal bond (IB) strength (8 samples from each board) and bending strengths (MOR and MOE) (3 samples from each board) on an Instron machine (Instron Corp., MA) and the water-soak thickness swelling (TS) and water absorption (WA) values (2 samples from each board) were measured in a 20 ^{o}C water bath all according to ASTM D 1037-06a. The data presented are averages.

Formaldehyde Content Measurements

Formaldehyde contents were measured in duplicate using the European standard method (EN120 2001) after about one month of hot-pressing of boards due to a delay.

The samples were cut to dimensions of 6 in × 6 in after one-day of airing and, because of the expected delay, each cut 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 ^{o}C until the tests. Test board samples had moisture contents of about 3.0%, and the resultant FC data were not corrected, although the standard procedure is based on calculation at a moisture content of 6.5%.

Table 1. Particleboard Preparation Parameters

Board No.	Face Layer					Core Layer				
	Resin			Catalyst		Resin			Catalyst	
	Type	Mel. level (%)	Mole ratio	Type	Level (%)	Type	Mel. level (%)	Mole ratio	Type	Level (%)
1	UF	0	1.05	A	0.5	UF	0	1.05	A	0.5
2								1.15		
3								1.25		
4	UF	0	1.05	A	0.5	UMF -1(-4)	2.5	1.05	B	0.5
5										1.0
6										1.5
7										2.0
8	UF	0	1.05	A	0.5	UMF -1(-4)	5.0	1.05	B	0.5
9										1.0
10										1.5
11										2.0
12	UMF -1(-4)	2.5	1.05	B	0.5	UMF -1(-4)	5.0	1.05	B	1.0
13					1.0					
14	UMF -1(-4)	5.0	1.05	B	0.5	UMF -1(-4)	5.0	1.05	B	1.0
15					1.0					

RESULTS AND DISCUSSION

Resin Physical Properties

The synthesized UMF resins showed pH values of 8.0, specific gravity values from 1.262 to 1.281, viscosity values from G-H to I-J on the G-H scale, and solids content values from 62.3 to 64.0%. The obtained values were within the expected ranges from the synthesis methods and procedures used and also within the range of current industrial values. However, all six synthesized UMF resins in this work were turbid.

Resins' Chemical Structures from ^{13}C NMR Results

The turbidity of synthesized UMF resins resulted in a distortion of the ^{13}C NMR quantification results due to the liquid-state NMR method's inability to detect solid components in the sample. As shown in Table 2, the melamine/urea mole ratios calculated from the spectra were lower than theoretical values used in resin syntheses by about 30 to 38%, while the typical resin 5.0%UMF-4 showed only a minimal variation. Some formaldehyde reacted with the precipitated melamine components would also have precipitated out. These discrepancies need to be considered in the interpretation of the NMR data given in Table 2.

Table 2. ^{13}C NMR Quantification Values Showing Distortion Due to Partial Separation of Resin Molecules Compared with Theoretical Values

Resins	UMF-1	UMF-2	UMF-3	UMF-4	Theory
M/U mole ratio from spectra (a)	0.0368	0.0362	0.0329	0.0541	0.0527
Undetected melamine components (%) =100(1.00-(a)/0.0527)	30.18	31.31	37.58	-2.65	0.00

The chemical structure data from the ^{13}C-NMR spectra are summarized in Table 3, with the spectra shown in Fig. 2a through 2d. The spectra of the typical UF resin and resin 5.0% UMF-4 are reported in a previous paper (Mao *et al.* 2013). Chemical shift values were referenced to the free urea peak at 164.0 ppm, and the following signals were assigned to each carbon group type (Kim *et al.* 2001, 2003): 47.4, 53.9, and 60.1 ppm to methylene groups of types I, II, and III, respectively; 69.5, 75.7, and 79.1 ppm to methylene-ether groups of types I, II, and III, respectively; and 65.2 and 72.0 ppm to hydroxymethyl groups of types I and II, respectively. Types I, II, and III methylene and methylene-ether groups are defined by whether the two urea nitrogens bonded with them are substituted with 0, 1, or 2 other formaldehyde-derived groups, respectively. Similarly, Types I and II hydroxymethyl groups are defined by whether the urea nitrogen group bonded with them has 0 or 1 other formaldehyde-derived group, respectively. Signals at 83.1, 91.0, and 87.0 ppm belong to formaldehyde species of methanediol and methanediol's oligomers. Carbonyl peaks at 164.0, 162.2, and 160.7 were assigned to free urea, mono-substituted urea, and di- and tri-substituted urea carbonyls, respectively. Signals of melamine triazine carbons and mono- and di-substituted melamine triazine carbons occurred at 167.1 to 168.1 ppm. The small signal at 50.4 ppm is due to methanol. Methylenic groups of MF components overlap with those of UF resin components. Peak intensities were integrated, and percentage values based on total urea carbons or total formaldehyde-derived carbons were calculated. The calculated F/U mole ratio values (total $-CH_2-$ groups/total urea and melamine carbons) were slightly lower than the charged F/U mole ratio of 1.05. The degrees of polymerization were low, at about 1.56 to 1.93, partly reflecting the low final F/U mole ratio values used in the resin syntheses.

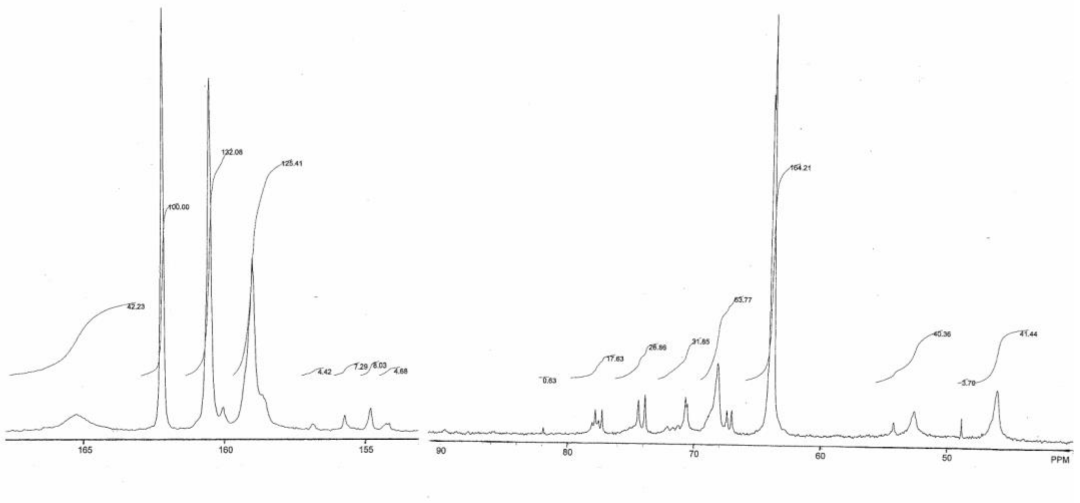

Fig. 2a. ^{13}C NMR spectra of resin 5.0%UMF-1 in water

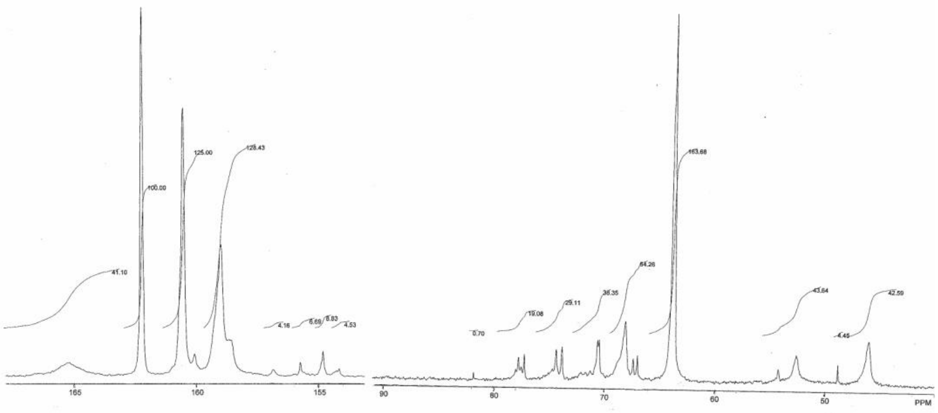

Fig. 2b. ^{13}C NMR spectra of resin 5.0%UMF-2 in water

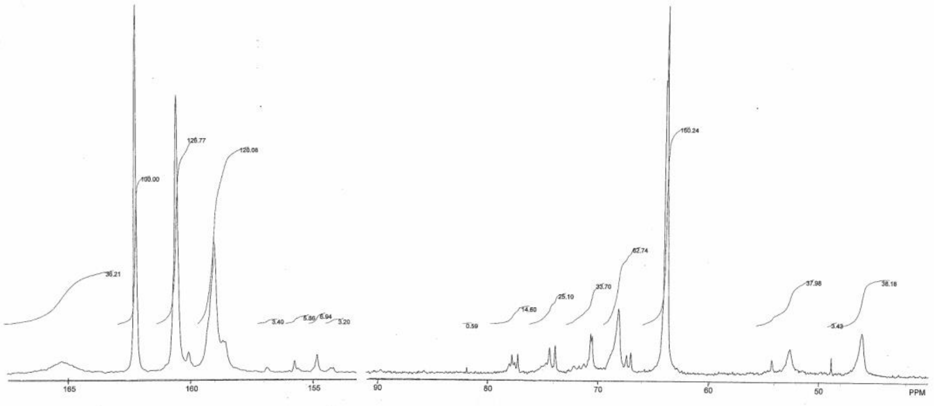

Fig. 2c. ^{13}C NMR spectra of resin 5.0%UMF-3 in water

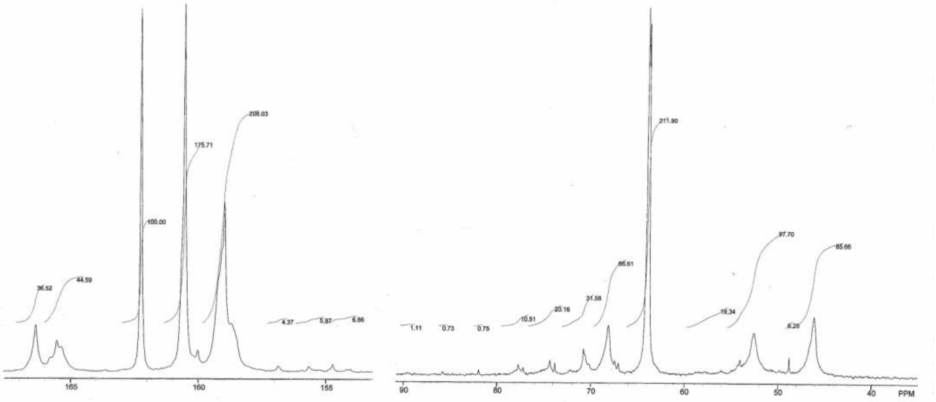

Fig. 2d. ^{13}C NMR spectra of resin 5.0%UMF-4 in water

Table 3. Percentage Integration Values for Various Methylenic and Carbonyl Carbons of Resin Samples Determined from ^{13}C NMR Spectra

Carbon Groups	**UF1.05 (%)**	**5.0%UMF-1 (%)**	**5.0%UMF-2 (%)**	**5.0%UMF-3 (%)**	**5.0%UMF-4 (%)**
Free urea	21.38	26.18	26.48	27.3	20.04
Mono-substituted Urea	31.96	34.58	33.10	34.61	35.22
Di- & tri-sub Urea	43.69	32.84	34.01	32.79	41.29
Cyclic urea	2.97	6.39	6.41	5.30	3.45
Total urea	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**
Free melamine	—	0	0	0	45.03
Mono- & di-sub melamine	—	100.0	100.0	100.0	54.97
Total melamine	—	**(100.0)**	**(100.0)**	**(100.0)**	**100.0**
Free form.	0.6	0.17	0.17	0.16	0.47
Total hydroxylmethyl	**43.3**	**51.54**	**50.33**	**51.98**	**44.59**
Type I	34.46	42.33	40.78	42.94	38.81
Type II	8.84	8.21	9.55	9.03	5.78
Total methylene-ether	**17.92**	**27.91**	**28.01**	**27.45**	**17.82**
Type I	11.71	16.44	16.01	16.81	12.2
Type II	4.59	6.92	7.25	6.73	3.68
Type III	1.62	4.54	4.75	3.91	1.92
Total methylene	**38.18**	**21.09**	**21.48**	**20.41**	**37.12**
Type I	14.95	10.68	10.61	10.23	15.69
Type II	19.96	10.40	10.87	10.18	17.89
Type III	3.28	0	0	0	3.54
Total CH_2	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**
CH_2/(CO+mel)	**1.023**	**0.980**	**1.026**	**0.986**	**1.038**
Degree of polymerization	1.931	1.553	1.606	1.533	1.915

Notes: CH_2/CO ratio refers to methylenic carbons/carbonyl ratios calculated from the integrated values. Degree of polymerization was calculated using DP=1/[1-(methylene+ 0.5 x methylene-ether)/urea]. For chemical structures and names of functional groups in the table, refer to the cited references (Kim 1999, 2000, 2001).

As shown in Table 3, all added melamine reacted with formaldehyde in resins 5.0%UMF-1, 5.0%UMF-2, and 5.0%UMF-3 due to high concentrations of formaldehyde being available at the addition points of melamine, while only 55.0% of melamine reacted in resin 5.0%UMF-4. Further, the total methylene-ether group contents of resins 5.0%UMF-1, 5.0%UMF-2, and 5.0%UMF-3 were increased, *i.e.*, dimers and trimers, *etc*., were formed, as the melamine-formaldehyde components have gone through the acidic reaction step. In the case of resin 5.0%UMF-4, the melamine components did not go through the acidic step, and its total methylene-ether group contents were lower and similar to those of the typical resin UF1.05. Thus, the resins' turbidity and the deviations of the NMR results discussed above for the synthesized UMF resins are in agreement with the increased methylene-ether group contents.

Another interesting result is that resins 5.0%UMF-1, 5.0%UMF-2, and 5.0%UMF-3 showed higher hydroxylmethyl group contents in comparison with resins UF1.05 or 5.0%UMF-4. Type I hydroxylmethyl groups increased from 34.46% to about

40.0%, and Type II hydroxylmethyl groups increased from 8.84% to about 12.0%. These increased hydroxymethyl group contents indicate that the UF components have not fully polymerized, which is likely a result of the milder acidic reaction procedure (pH 5.50) used in the resin syntheses than were used for resins UF1.05 and 5.0%UMF-4 (pH 4.75) due to the need to keep the reaction (viscosity advancement) under control. Thus, although all resins were synthesized to have similar end viscosity values of about GH on the G-H scale, a considerable part of the viscosity values attained appeared to have arisen from the polymerization of MF components at the expense of a lesser degree of polymerization of UF components. This result also agrees with the lower methylene group contents in the UMF resins.

Storage Stability and Pot Life of Synthesized Resins

The storage stability curves of un-catalyzed resins measured as viscosity increases occurred during a period of 50 days at 30 ^{o}C are shown in Fig. 3. Resins 2.5%UMF-1, 5.0%UMF-1, 2.5%UMF-2, 5.0%UMF-2, 2.5%UMF-3, and 5.0%UMF-3 were cloudy at room temperature from the beginning. Resins 2.5%UMF-4 and 5.0%UMF-4 remained clear for a few days and then turned cloudy, indicating the precipitation of solid particles of free melamine or melamine-formaldehyde reaction products, which can shorten the viscosity storage stability of resins. Resin UF1.05 showed the longest storage stability, and resins UMF-1 and UMF-4 showed only slightly shorter stabilities; however, resins UMF-2 and UMF-3, for both melamine levels, showed very short storage stabilities. Moreover, the storage stability of UMF resins decreased with increased levels of melamine. Further, if the viscosity K on the G-H scale is considered to be the maximum value allowed in particleboard manufacturing, then resin UF1.05 has a storage life of 31 days, resin 2.5%UMF-1 has a storage life of 22 days, resin 5.0%UMF-1 has a storage life of 17 days, resin 2.5%UMF-2 has a storage life of 9 days, resin 5.0%UMF-2 has a storage life of 7 days, resins 2.5%UMF-3 and 5.0%UMF-3 have storage lives of 3 days, resin 2.5%UMF-4 has a storage life of 24 days, and resin 5.0%UMF-4 has a storage life of 19 days. Currently, US particleboard manufacturing plants use resins within 14 to 21 days of delivery. Thus, resins UMF-2 and UMF-3 types were judged to be unacceptable on the basis of their storage lives and were excluded from the further testing. The short storage lives of resins UMF-2 and UMF-3 can be explained in that the oligomeric MF components formed in these cases have a higher tendency to separate out because they have less than full substitutions with hydroxymethyl groups due to the melamine addition points used, where the amounts of available formaldehyde are limited in comparison with resin UMF-1.

The pot lives of catalyzed resins are shown in Table 4, obtained at 30 ^{o}C by assuming that a viscosity of S on the G-H scale is the target value. As will be discussed later, UMF resins used as particleboard binders need to be cured with the stronger catalyst B; resin UF1.05 gelled in 15 min with 0.5% catalyst B at room temperature, indicating that catalyst B is too strong for use with UF resins. Further, it is apparent that different UMF resin types have different pot lives due to the melamine addition points used in resin synthesis. However, in particleboard manufacturing plants, resin is catalyzed, sprayed onto wood particles, and hot-pressed in about 30 min; it therefore appears that all UMF resins catalyzed at catalyst B concentrations of 0.5% and 1.0% would have adequate pot lives, as would resin UF1.05 catalyzed at a catalyst A concentration of 0.5%.

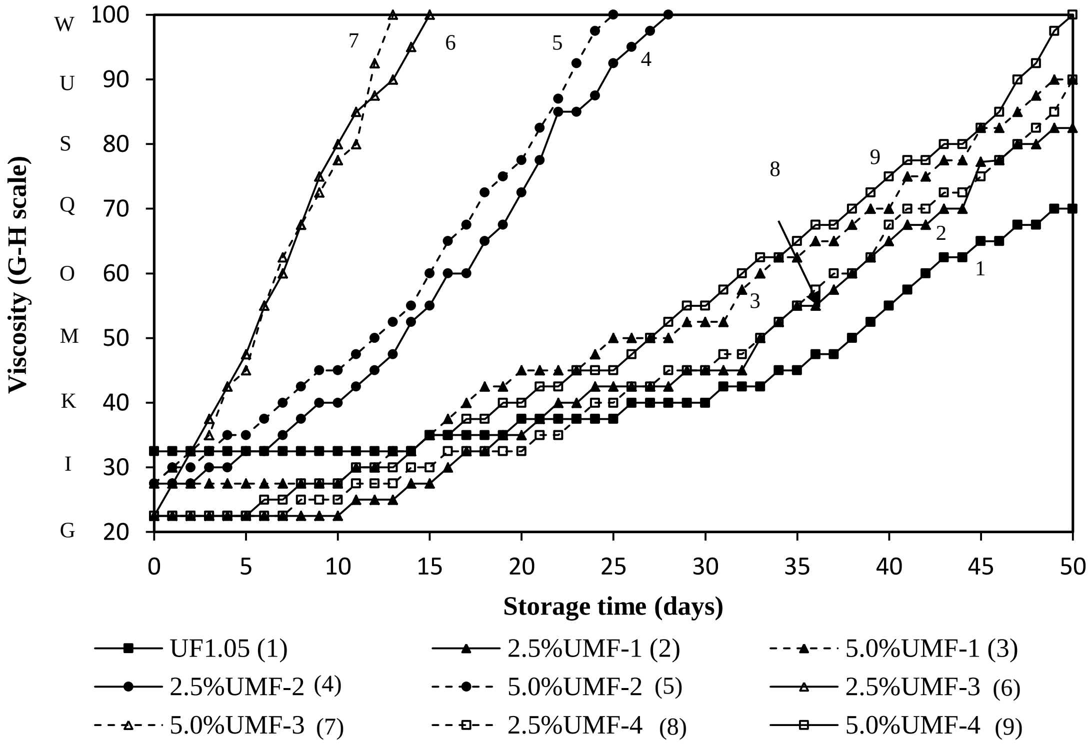

Fig. 3. Viscosity increases of UF and UMF resins observed during storage at 30 °C

Table 4. Pot Lives (h) of Catalyzed Resins with Different Catalysts and Levels Measured at 30 °C

Catalyst Level	0.5%		1.0%	1.5%	2.0%
Catalyst kind	A	B	B	B	B
UF1.05	8.25	0.2	—	—	—
2.5%UMF-1	—	10.5	8.75	6.50	3.75
5.0%UMF-1	—	10.5	9.25	6.75	3.75
2.5%UMF-4	—	12+	9.00	7.25	3.75
5.0%UMF-4	—	12+	9.25	7.25	4.25

Gel Time of Catalyzed Resins Measured at 100 °C

The gel times of catalyzed resins measured at 100 °C are shown in Table 5. Gel times became shorter with increasing catalyst levels and also with catalyst B, which is stronger than catalyst A. Resin UF1.05 showed shorter gel times than all UMF resins. Furthermore, resins UMF-1 generally showed shorter gel times in comparison with resins UMF-4, as indicated by the negative difference values. Gel times are an indication of the curing speed of resins, and all UMF resins appeared to cure more slowly and become comparable with resin UF 1.05 only at 2.0% level of Catalyst B, the stronger catalyst. The shorter gel times of resins UMF-1 compared to resins UMF-4, although the differences were relatively small, appear to be related to the higher levels of solid particles of oligomeric MF resin components present in the resins.

Table 5. Gel Times (s) of Resins with Catalysts A and B at Various Levels Measured at 100 °C

Catalyst Level	0.5%		1.0%		1.5%		2.0%		2.5%		3.0%	
Catalyst kind	A	B	A	B	A	B	A	B	A	B	A	B
Resin UF1.05	131	105	103	80	85	65	86	64	—	—	—	—
Resin 2.5%UMF-1	212 /-7	175 /-12	183 /-18	180 /8	175 /-4	152 /-10	146 /-25	134 /-12	145 /-22	124 /-14	212 /-7	175 /-12
Resin 5.0%UMF-1	242 /19	188 /-16	201 /4	165 /-14	171 /-7	152 /-16	157 /-13	136 /-26	162 /-6	131 /-26	242 /19	188 /-16

Notes: Values separated by a slash (/) indicate increases or decreases in comparison with data from resin UMF-4 reported in a previous article (Mao *et al.* 2013).

Gel and Cure Times of Catalyzed Resins Measured with a Rheometer

The gel and cure times of catalyzed resins measured on a rheometer in the dynamic mechanical analyzer (DMA) mode are reported in Table 6. The resin sample was heated from room temperature to the target isothermal temperature, 120 ^{o}C or 145 ^{o}C, in about 50 s and then held for 25 min. The moisture in the resin sample was mostly evaporated by the time it reached the curing temperature, making the test results different from the (liquid) gel time results discussed above. The results more likely reflect the resin curing parameters effective in the hot-pressing of boards. Gel times and cure time values were obtained from the storage and tan delta curves (Gillham *et al.* 1974; Laza *et al.* 1999; Young No and Kim 2005; Mao *et al.* 2013).

The gel time and cure time results, shown in Table 6, were shortened with increasing curing temperatures and also with higher catalyst levels, as expected. UMF resins with 2.5% melamine levels generally showed shorter gel and cure times than those with the 5.0% melamine level, indicating the slower curing effects of melamine as observed in the pot lives and gel times of catalyzed resins discussed above. Resins UMF-1 showed slightly longer gel times but slightly shorter cure times in comparison with resins UMF-4, possibly indicating a faster curing of resins UMF-1 because the resins' MF components are more fully substituted with hydroxymethyl groups than in resins UMF-4.

Table 6. Gel Times and Cure Times (s) Obtained under Isothermal Conditions at Different Catalyst Levels by Rheometry

Resin	Catalyst	Catalyst Level (%)	Gel Time (s)		Cure Time (s)	
			120 ^{o}C	145 ^{o}C	120 ^{o}C	145 ^{o}C
UF1.05	A	0.5	152	109	265	—
	B	1	—	—	—	—
2.5% UMF-1	B	0.5	132/15	101/6	207/ -3	132/-2
		1	117/ 1	90/ 3	174/-11	120/-20
		1.5	96/20	82/ 1	175/-28	120/-20
		2	88/ 7	74/ 0	139/ -6	101/-16
5.0% UMF-1	B	0.5	175/17	116/14	226/-74	166/-49
		1	166/47	118/30	207/-20	133/-24
		1.5	127/15	110/22	206/23	121/ 1
		2	105/11	96/15	182/ 2	123/-14

Notes: The values separated by slash (/) indicate the increases or decreases in comparison with data of Resins 2.5% and 5.0%UMF-4 reported in the previous report (Mao *et al.* 2013).

Particleboard Test Results

Particleboard test results are shown in Table 7, arranged according to the board numbers shown in Table 1. The control particleboards, made with resin UF1.05 in the face layer and resins UF1.05, 1.15, and 1.25 in the core layers with catalyst A (boards 1-3) (Mao *et al*. 2013), represent the range of UF resin uses in the industry, with the last resin combination, resin UF1.25 in the core-layer, being the most common. However, the free formaldehyde content (FC) values with this mole ratio were about 16 mg/100 g dry board, which corresponds to a formaldehyde emission (FE) value of more than 0.20 ppm in the large-scale chamber test method (Schwab *et al.* 2012), which is significantly higher than the new emission limits of 0.09 ppm.

Table 7. Formaldehyde Content and Physical Property Test Results for Particleboards

	Formaldehyde Content mg/100g dry board		Physical Properties of Particleboards Average (3.0 and 3.5 min press time)				
Board No.	Hot press time		IB (psi)	MOR (psi)	MOE (kpsi)	24 h Thickness Swell (%)	24 h Water Absorption (%)
	3.0 min	3.5 min					
1	7.9	8.0	58.0	940	141	29.1	76.6
2	13.6	12.8	74.4	1295	180	20.9	58.5
3	16.8	15.9	90.4	1495	202	18.5	51.2
4	8.0 / 0.2	7.7 / 0.4	82.2 / 7.8	1327 / -28	186 / 4	26.1 / -2.6	57.2 / -3.8
5	7.2 / 0.5	6.5 / 0.4	92.5 / -4.3	1438 /-92	219 / 4	22.0 / -3.1	56.8 / -5.1
6	6.4 / 0.2	6.1 / 0.1	85.1 / 7.0	1338 /-27	202 / 19	24.7 / -2.6	58.9 / -6.0
7	6.0 / 0.3	5.5 / 0.1	78.7 / 6.9	1223 / -62	191 / 6	26.5 / -0.5	63.7 / -7.6
8	8.2 / 0.2	7.4 / 0.3	108.5 /17.6	1740 / 100	245 / 18	24.8 / -2.0	62.6 / -6.0
9	7.2 / 0.1	6.3 / 0.3	114.9 / -9.4	1713 / -7	230 / -5	22.1 / -1.5	57.4 / -7.9
10	6.4 / 0.2	6.0 / 0.2	111.8 / -1.2	1770 / -125	240 / -10	20.1 / -2.2	63.9 / -10.8
11	5.5 / -0.1	5.3 / 0.1	105.5 / 2.3	1670 / 60	233 / 11	22.3 / -0.2	66.6 / -7.0
12	6.7 / 0.0	6.2 / 0.1	115.8 / -0.5	1832 / 17	256 / -6	14.5 / -2.3	45.6 / -4.0
13	6.5 / -0.1	6.1 / 0.2	119.3 / 3.0	1759 / 124	228 / 3	15.1 / -3.6	47.3 / -4.9
14	7.5 / 0.1	7.0 / 0.2	122.9 / -4.9	2038 / 113	272 / -1	14.2 / -2.5	40.0 / -1.3
15	7.2 / 0.2	6.4 / 0.5	127.9 / -6.4	2087 / -73	286 / -13	14.5 / -1.6	39.7 / -2.3

Notes: Two values separated by a slash (/) indicate increases or decreases in comparison with data from resin UMF-4 reported in a previous article (Mao *et al.* 2013).

Particleboards bonded with resin UF1.05 in the face layer and resins 2.5%UMF-1 and 5.0%UMF-1 in the core layer with various levels of catalyst B (boards 4-11) showed lower FC values of 5.3 to 8.2 mg/100 g dry boards, decreasing with increasing levels of melamine and catalyst and also with longer hot-press times. Most of these FC values correspond to the E1 class of European Standards. Resin 2.5%UMF-1 used in the core-layer showed acceptable IB values with a catalyst B level of 1.0%. Higher catalyst levels of 1.5% and 2.0% tended to show lower IB values and poorer water-soak test values, which was an effect of over-catalyzing. The IB, MOR/MOE, and water-soak values of particleboards with resin 5.0%UMF-1 used in the core layer showed significant improvements over those using resin 2.5%UMF-1. Further, in comparison with boards bonded with resins UMF-4, the differences were generally small in physical strength values, but the FC values were slightly worse (higher). The water-soak thickness swell and water absorption values slightly improved, indicating that the resin synthesis method of resins UMF-1 might find some applications in the industry. This use of UMF resins only in the core layer of boards is a lower cost alternative than using UMF resins in both layers.

Particleboards made with resin 2.5%UMF-1 in the face layer at 0.5 to 1.0% catalyst levels and resin 5.0%UMF-1 in the core layers at the 1.0% catalyst level (boards 12-13) showed similar FC values of 6.1 to 6.7 mg/100 g dry boards, and the IB, MOR/MOE, water-soak thickness swell, and water-absorption values were improved due to the use of resin 2.5%UMF-1 instead of resin UF1.05 in the face layer. On the other hand, only small improvements in FC values were obtained. In comparison with boards bonded with resins UMF-4 at the same melamine levels, the results were generally similar, as FC values were slightly worse (higher) and the physical strength, thickness swell, and water absorption values were slightly better.

Particleboards made with resin 5.0%UMF-1 in the face layer at the 0.5 to 1.0% catalyst B level and resin 5.0%UMF-1 in the core layers at the 1.0% catalyst B level (boards 14-15) showed similar FC values of 6.4 to 7.5 mg/100 g dry boards with higher IB, bending, and water-soak tests values due to the higher melamine contents in the face-layer resins.

The FC values were similar to the E1 class of European Standards. The bending test values indicated that the catalyst level of face-layer resin 5.0%UMF1.05 had higher values at the 0.5% catalyst level than at the 1.0% catalyst level, indicating that the catalyst levels of UMF resins should be adjusted not only for different melamine levels in the resin but also for which layer of boards it is used in.

In comparison with boards bonded with resins UMF-4 at the same melamine levels, the results are generally similar and the FC values were slightly worse (higher), but the physical strength changed slightly and the thickness swell and water absorption values improved slightly.

Overall, the test results from particleboards indicate that resins UMF-1 and UMF-4 performed with some differences in FC values and water-soak test values, which could be traced to the differences in resins' physical and structural differences, resulting from the synthesis procedures. It may be that the formaldehyde released during hot-pressing may be more effectively captured by the free melamine present in resins UMF-4, while the melamine in resins UMF-1 fully reacts with formaldehyde in the resin stage and therefore is more efficient as a bonding agent and has better water-soak test properties.

CONCLUSIONS

1. UMF resins made by adding melamine at three different points in the first alkaline step all resulted in cloudy resins and showed higher hydroxylmethyl and methylene-ether group levels and lower methylene group levels compared with UMF resins made by adding melamine in the last alkaline step of UF resin synthesis.
2. UMF resins made by adding melamine at the beginning of the first alkaline step (resins UMF-1) and in the last alkaline step of synthesis procedure (resins UMF-4) showed adequate storage lives of 2 to 3 weeks, albeit slightly shorter storage lives than UF resins.
3. UMF resins made by adding melamine at the middle and end of the first alkaline step (resins UMF-2 and -3) of the synthesis procedure showed poor storage lives and therefore the synthesis procedures did not offer any practical usefulness.
4. UMF resins were found to require stronger, free acid-containing catalysts at appropriate levels depending on the melamine levels and the layer of boards to be applied on for low formaldehyde contents and optimum physical performance values of boards.
5. Particleboards made with resins UMF-1 showed slightly higher formaldehyde content values and slightly improved water-soak test values over those bonded with resins UMF-4; thus, the two different resin synthesis procedures may be considered equally useful.

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