Investigation of Low Mole Ratio UF and UMF Resins Aimed at Lowering the Formaldehyde Emission Potential of Wood Composite Boards

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Urea-melamine-formaldehyde (UMF) resins with 2.5% and 5.0% melamine levels added at the beginning of the third step of the typical urea-formaldehyde (UF) synthesis procedure were synthesized with an F/(U+M) mole ratio of 1.05 and evaluated as particleboard binders to investigate the positive effects of melamine on the formaldehyde content and physical performance of boards. Resins were tested for storage properties and analyzed by ^{13}C NMR. Curing catalysts were studied, curing rates were measured, and laboratory particleboards were prepared and tested for formaldehyde contents as well as strength and water-soak test values. The UMF resins resulted in slower curing rates but had adequate board strength values. The formaldehyde content values were within the newly created California emission law (5.2 to 8.0 mg/100 g board). Another objective of this work was to establish the baseline performance of these resins for use in subsequent studies that will aim to reveal the effects of methylene-ether group contents on formaldehyde emissions.

Keywords: Urea-formaldehyde; Urea-melamine-formaldehyde; Particleboards

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INTRODUCTION

Urea-formaldehyde (UF) resins are the primary binder resins of interior-grade wood composite boards, such as particleboard, medium-density fiberboard, and hardwood plywood. One current challenge is to reduce or eliminate the relatively high formaldehyde emission levels of boards that arise due to the UF resin binders. Formaldehyde is a human carcinogen (IARC 2004; EPA 2009), and exposure has been known to cause various health problems (Cruz 2007).

The emission levels are regulated by state and federal laws (California Air Resources Board 2008; U. S. Senate Bill 2011). Further, the formaldehyde released from wood composite boards has been known to be a significant burden on the environment (California Air Resources Board 2007). The new California and Federal laws lowered the permissible formaldehyde emission levels of particleboards to less than 0.09 ppm as measured by the large-chamber method (Standard A208.1 2009; ASTM E1333 2010), which is less than one-half of the previous values.

The formaldehyde emission levels of boards depend primarily on UF resin factors and secondarily on board hot-pressing and after-treatment parameters (Christiansen and Anderson 1989). The major resin-related factor is the formaldehyde/urea (F/U) mole ratio used in the resin syntheses (Myers 1984; Myers and Koutsky 1990; Go 1991). An average face- and core-layer mole ratio of about 1.15 has been the industry standard until recently, resulting in boards having adequate physical strength properties and large-chamber formaldehyde emission values of 0.15 to 0.20 ppm, which has been within the industry standards until recently (Dunky 1998). Lowering the F/U ratio of resins further, especially in the core layer, will lower formaldehyde emission levels, but it will also decrease the board strength properties and result in longer hot-pressing times (Sigvartsen and Dunky 2006). Therefore, the approach of lowering the F/U mole ratio of resin has reached to the limit in spite of much effort (Sigvartsen and Dunky 2006; Lukkaronien and Dunky 2006), although some companies have reportedly met the new emission requirements by using mole ratios lower than 1.0.

The current published approach for formaldehyde emission reduction is the modification of UF resins with low levels of melamine (M) in the form of (liquid) urea-melamine-formaldehyde (UMF) resins (Tohmura *et al.* 2001; Zanetti and Pizzi 2003; No and Kim 2004, 2005, 2007; Park *et al.* 2009; Sun *et al.* 2011). These research reports have shown that UMF resin binders can give boards that have higher physical properties and low formaldehyde emission values, but little attention has been paid to the curing rates, storage, and pot lives of such resins, or ways of maximizing the desirable effects of melamine. Melamine has a higher functionality (≥ 3) than urea, and this difference implies that it has more functional groups available to react with formaldehyde, to result in lower free formaldehyde contents when compared with the same mole ratio UF resins. Melamine reacts with formaldehyde in a manner similar to that of urea to form hydroxymethylmelamines with up to six hydroxymethyl groups, but the subsequent curing reaction goes optimally only in the F/M ratio range of about 1.8 to 2.0 (Wirpsza and Brezezinski 1973). The reaction is expected to proceed less optimally as the mole ratio is lowered to the range of 1.15 to 1.05 of UMF resins. Further, dimers or trimers of hydroxymethylmelamines that can form in low F/(U+M) mole ratio resins may result in short storage lives of resins due to poor solubility in water (Wirpsza and Brezezinski 1973).

There are various key parameters to be investigated with respect to obtaining the maximum efficiency of melamine: base UF resin synthesis procedure, melamine level, point of melamine addition, final F/(U+M) mole ratio, and acid catalyst kind and level. In this work, the typical industry procedure was employed for base UF resin synthesis (Kim and Amos 1990). The reaction starts with a hydroxymethylation step, reacting 2.0 to 2.4 moles of formaldehyde with one mole of urea in a weakly alkaline pH to form various monomeric mono-, di-, and tri-hydroxymethyl-ureas. The polymerization reaction is then carried out in the second step under weakly acidic conditions, forming methylene (80%) and methylene-ether (20%) groups of oligomeric species with approximately 5 to 20 urea units. When the target viscosity is reached, the pH value is raised to the 7.0 to 8.0 range. In the third step, while cooling the reaction batch, a second portion of urea is added over a period of about 30 min and the cooling is continued until reaching room temperature. The free formaldehyde remaining in the resin reacts with the second portion of urea to form, in part, monomeric hydroxymethylureas. The finished UF resin synthesized by the typical procedure, thus, consists of free urea, monomeric hydroxymethylureas, and oligomeric species. Various other non-typical synthesis procedures for UF resins appear to be used (Gu *et al.* 1995; Park *et al.* 2006).

One major source of formaldehyde emissions could be the free formaldehyde content of finished typical UF resins made at an F/U ratio of 1.15, which remains at about

0.5% based on liquid resin weight (Kim and Amos 1990). The residual formaldehyde in resins is not necessarily un-reacted; rather it results from the reversibility of hydroxyl-methylation reactions between urea and formaldehyde (De Jong and De Jonge 1952a; Kim and Amos 1990). This reversibility increases in severity with increases in temperature (De Jong and De Jonge 1952a), as in the hot-pressing of boards. Further, methylene groups are the backbones of cured UF polymer structures and have little direct bearing on the formaldehyde emission potential of boards, whereas methylene-ether groups have been proposed to break down during hot-pressing of boards, yielding either methylene groups and formaldehyde or two hydroxymethyl groups in the presence of water (Wirpsza and Brezezinsky 1973). If this breakage occurs in the later stages of the curing process, the freed formaldehyde is likely to remain free in boards. Thus, methylene-ether groups might play an important role in the formaldehyde emissions. However, this aspect has been given little attention until now in the research community. In a sequel paper, the effects of higher methylene-ether group levels will be investigated (Mao *et al.* 2013).

UMF resins, due to the higher functionality of melamine, would react with more formaldehyde and also increase strength properties of boards (Sigvartsen and Dunky 2006; Lukkaronien and Dunky 2006), but the F/(U+M) mole ratio of resins has been known to be lowered to the 1.05-0.95 range to meet the new emission law levels with the possibility of longer hot-press times. The melamine content and its point of addition in UMF resin synthesis. In this study, 2.5% and 5.0% melamine levels based on the liquid resin weight were selected, which correspond to 3.94% and 7.87%, based on the resin solids content, and the melamine was added at the beginning of the third step under the mildly alkaline pH condition, before the addition of the second portion of urea.

Another factor regarding UMF resins is the slower curing rates compared with UF resins at the same mole ratio due to the higher basicity of melamine’s amino groups (No and Kim 2005). Thus, the commonly used ammonium sulfate type catalysts have been reported to be insufficient for UMF resins (Dunky 1998; Sigvartsen and Dunky 2006), and a stronger catalyst system based on ammonium sulfate and a free strong acid was also used.

UF resins on curing increase in viscosity and then go through gelation and vitrification stages to become a stiff solid as commonly measured by a dynamic mechanical analyzer or rheometer, resulting in gel times and cure times (Ebewele 1995; Umemura *et al.* 1996; No and Kim 2005). Quantitative ^{13}C NMR spectroscopy has been used to determine the molecular structure of uncured UF resins (Kim 2000, 2001; Kim *et al.* 2001, 2003).

In the present study, control UF resin samples and UMF resins having 2.5% and 5.0% melamine contents at F/(U+M) mole ratios of 1.05 were made and studied for storage stability, catalyzed resin stability, curing rates, and other characteristics and then evaluated by manufacturing and testing of laboratory particleboards including the free formaldehyde contents. The objectives were to identify the melamine levels and associated resin curing parameters needed in meeting the current formaldehyde emission levels as particleboard binders. Another objective was to obtain the baseline resin properties and binder performance data for the typical UF resin synthesis procedure, to be used in sequel studies aimed at the effects of uron and linear type methylene-ether group contents in resins.

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 for resin syntheses. Sulfuric acid of 8% concentration and sodium hydroxide solution of 4% and 25% concentrations were used as pH adjusters. Mixed pine wood particles (face layer and core layer) used in the industrial particleboard production and a wax emulsion with a 50% 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 as resin curing catalysts.

Resin Syntheses

UMF resins having melamine contents of 2.5%, and 5.0% based on the weight of liquid resins with an F/(U+M) mole ratio of 1.05 and UF control resins with an F/U mole ratios of 1.05, 1.15, and 1.25 were synthesized as described below.

Urea-formaldehyde-concentrate (UFC) was first made. 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 were made according to the typical resin synthesis procedure discussed above. In the first stage, the UFC (1508.1 g) was added to the 2 L reactor, the pH was adjusted to 8.0 with sodium hydroxide solution, and the reaction mixture was heated to 70 ^{o}C. Next, the first urea portion (348.4 g) was slowly added until the F/U mole ratio reached 2.0. Then the temperature was raised to 90 ^{o}C and maintained for 30 min at pH 8.0. In the second stage, the solution pH was adjusted to 4.75 with 8% sulfuric acid solution, and the solution viscosity was checked every 15 min using the Gardner-Holdt (G-H) method until it reached the desired viscosity of P-Q (1 hour and 25 min.). In the third stage, the pH was adjusted to 8.0 with sodium hydroxide solution, and the second portion of urea (567.4 g) was added, reaching to an F/U mole ratio of 1.05, giving Resin UF1.05. The resin was cooled to room temperature with a final viscosity of I-J on the G-H scale. Two other UF resins of higher mole ratios were similarly synthesized by adjusting the amount of second urea to 464.3 g and 376.9 g, respectively, to have an F/U mole ratio of 1.15 for Resin UF1.15 and an F/U ratio of 1.25 for Resin UF1.25, with final viscosities of H-I and I-J, respectively.

UMF resins having 2.5% and 5.0% melamine levels and a final F/(U+M) mole ratio of 1.05 were synthesized similarly to the control Resin UF 1.05 described above until the end of the second step. In the third step, at pH 8.0, for 2.5% melamine level, additional melamine (61.4 g) was added, and the reaction mixture was maintained at 90 ^{o}C at pH 8.0 for 60 min. Then, the second urea portion (537.9 g) was added and the reaction mixture was cooled to room temperature with a final viscosity of G-H according to the G-H scale, resulting in Resin 2.5%UMF1.05. For 5.0% melamine level, the same procedure was followed, using different amounts of melamine (124.5 g) and a second urea portion (507.5 g), resulting in Resin 5.0%UMF1.05 with a final viscosity of G-H on the G-H scale.

Resin Physical Property Measurements

Non-volatile solids contents (in triplicates) and specific gravities of resins were measured using standard procedures. The storage stability of resins was measured by placing resin samples in a convection oven at 30 ^{o}C and checking the viscosity daily for 50 days.

Chemical Structure Determinations

Chemical structure determinations of selected resins were done by ^{13}C NMR, carried out on a Techmag 400-2 NMR Instrument from Spectral Data Services, Inc., Champaign, IL, USA. For each NMR test, 2.0 g of resin sample was mixed with 1.0 g of deuterium oxide. A 12 µs pulse width and a 10 s pulse delay were used for quantitative results. About 400 scans were accumulated for each resin sample. Spectral peaks of urea carbonyls, reacted and un-reacted melamine triazine carbons, and all methylenic carbons were integrated under the same scale factor, and the integration values were quantified as group percentages. Urea carbonyls were separately integrated according to free urea, mono-substituted urea, di-/tri-substituted urea, and cyclic urea.

Pot-lives and Gel Times of Catalyzed Resins

Gel times of resins catalyzed using various levels of catalysts were measured in triplicates by heating in a glass tube at 100 ^{o}C and stirring continuously until the resin set to a solid. Pot-lives of resins catalyzed at various catalyst levels were measured in duplicates at 30 ^{o}C by checking the viscosity at every 15 min for 12 h.

Gel Times and Curing Times by Rheometer

Gel times and curing times of catalyzed resins were carried out in duplicates on an oscillatory rheometer (AR1500ex, TA Instruments Corp., DE, USA) with an 8 mm diameter probe at test temperatures of 90 ^{o}C, 120 ^{o}C, 135 ^{o}C, and 145 ^{o}C. The resin sample was allowed to balance at 20 ^{o}C for 10 s, heated to the target temperature in 50 s, and time sweeps were performed at a frequency of 1.0 Hz and strain of 1.0%.

Particleboard Manufacturing

Particleboards were made in the laboratory using the blending parameters shown in Table 1. Wood particles were dried to 5.0% moisture content and put in a rotating blender. Then wax and catalyzed resin were successively sprayed in using an air-atomizing nozzle within a blending time of approximately 15 min. Face particles and core particles were blended separately. Blended particles were weighed and laid on a steel plate in a box to form three-layer mats with a 1:2:1 weight ratio for 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 target parameters were as follows: resin content of 9.0%, wax content of 1.0%, mat moisture content of 8.0% based on 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	1.05	A	0.5	UF	1.05	A	0.5
2						1.15		
3						1.25		
4	UF	1.05	A	0.5	2.5% UMF	1.05	B	0.5
5								1.0
6								1.5
7								2.0
8	UF	1.05	A	0.5	5.0% UMF	1.05	B	0.5
9								1.0
10								1.5
11								2.0
12	2.5% UMF	1.05	B	0.5	5.0% UMF	1.05	B	1.0
13				1.0				
14	5.0% UMF	1.05	B	0.5	5.0% UMF	1.05	B	1.0
15				1.0				

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). Water-soak thickness swelling (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 of boards were measured after about three months of hot-pressing of boards 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 the boards after hot-pressing. Because of this unexpected waiting period, each test sample was sealed at the edges with duct tape, wrapped in saran film, and put in a sealed plastic bag. All samples were kept in a refrigerator at 4 ^{o}C until the testing. The formaldehyde content decreases of the boards from the long storage appeared minimal in comparison with reported data of UF resin-bonded boards obtained in 1-2 weeks of board preparation (No and Kim 2005). The tests were carried out according to the European standard method (EN120 2001). Test board samples had moisture contents of about 3.0% and the resultant FC data were not corrected, although the standards are based on 6.5% moisture content of boards.

RESULTS AND DISCUSSION

Resin Physical Properties

The synthesized resins showed pH values of 8.0, specific gravity values of 1.262 to 1.271, viscosity values of G-H to I-J on the G-H scale, and solids content values of

62.29 to 63.78%. The obtained test values were generally as expected from the synthesis procedures used and were also within the range of industrial values. The small property differences would make little differences in comparing the resins' bonding or formaldehyde emission potential values.

Resin Chemical Structures

Chemical structures of resin UF1.05 and resin 5.0%UMF1.05 from ^{13}C-NMR are summarized in Table 2, with the spectrum of the latter resin shown in Fig. 1, as an example. Chemical shift values were referenced to the free urea peak at 164.0 ppm. The overall results were very similar to previous reports, and signals were assigned to functional carbon groups, as cited in typical references (Kim 2000, 2001; Kim *et al.* 2001, 2003): 47.4, 53.9, and 60.1 ppm to methylenes of types I, II, and III methylenes, respectively; 69.5, 75.7, and 79.1 ppm to methylene-ethers of types I, II, and III, respectively; and 65.2 and 72.0 ppm to types I and II hydroxymethyl groups, respectively. Briefly, I, II, and III types of methylene and methylene-ether groups are defined by whether the two urea nitrogen groups bonded with them are substituted with 0, 1, or 2 formaldehyde-derived groups, respectively. Similarly, I and II types of hydroxymethyl groups are defined by whether the urea nitrogen group bonded with them has no or another formaldehyde-derived groups, 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, tri-substituted ureas, respectively. Signals of melamine triazine carbons and mono-, di-substituted melamine triazine carbons occurred at 167.1-168.1 ppm. The small signal at 50.4 ppm is due to methanol. The methylenic groups expected of melamine-formaldehyde components were not differentiated from those of UF resin components. The carbon group peak intensities were integrated and percentage values based on total urea and formaldehyde derived carbons, respectively, were calculated. The calculated F/U mole ratios (total -CH_2- groups/total urea and melamine carbons) were only slightly lower than the charged F/U mole ratio of 1.05. The degrees of polymerization of both resins were low at about 1.92, partly due to the low F/U mole ratios and the large amounts of the second urea portion used.

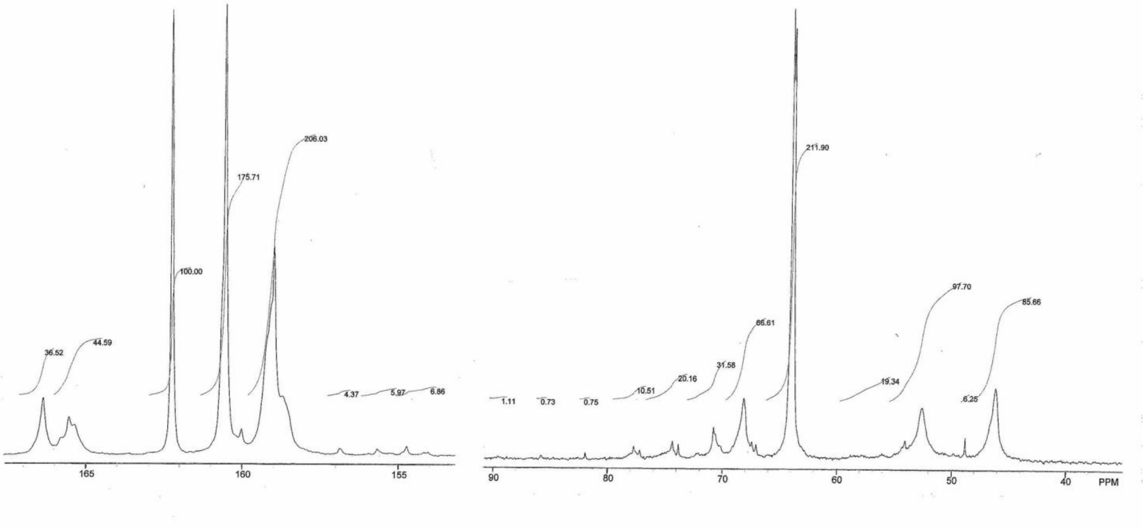

Fig. 1. ^{13}C NMR Spectra of Resin 5.0%UMF1.05 in water

The new findings from the ^{13}C NMR data were two-fold: first, Resin 5%UMF1.05 showed that 55.0% of melamine reacted with formaldehyde and 45.0% melamine remained, indicating a relatively low concentration of formaldehyde available at the point of addition. The un-reacted melamine in the resin would tend to come out as precipitates to shorten storage times, since melamine itself has very little solubility in water. The optimum efficiency of added melamine would be obtained when it reacts with 2 to 3 formaldehyde molecules. Since the melamine addition point selected in this study led to 45% un-reacted melamine, the full utilization of the higher cost melamine may not be realized. Investigation of other points of melamine addition might be fruitful.

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

Carbon Groups	Resin UF1.05 (%)	Resin 5% UMF1.05 (%)
Free urea	21.38	20.04
Monosubstituted urea	31.96	35.22
Di, trisubstituted urea	43.69	41.29
Cyclic urea	2.97	3.45
Total urea	**100.0**	**100.0**
Free melamine		45.03
Mono, di-sub melamine		54.97
Total melamine		**100.0**
Free formaldehyde	0.60	0.47
Total hydroxylmethyl	**43.30**	**44.59**
Type I	34.46	38.81
Type II	8.84	5.78
Total methylene-ether	**17.92**	**17.82**
Type I	11.71	12.20
Type II	4.59	3.68
Type III	1.62	1.92
Total methylene	**38.18**	**37.12**
Type I	14.95	15.69
Type II	19.96	17.89
Type III	3.28	3.54
Total CH_2	**100.0**	**100.0**
CH_2/CO	**1.023**	**1.038**
Degree of polymerization	1.931	1.915

Notes:

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

The second finding from the ^{13}C NMR data was the fact that most methylene-ether groups were formed in UF resins, and the addition of melamine in the third step of resin synthesis as used in this work did not affect the total methylene-ether group contents, which are potential sources of formaldehyde emissions remaining in UMF resins. Another interesting result is that Resin 5.0%UMF1.05 had slightly higher hydroxylmethyl group content than that of Resin UF1.05, wherein Type I hydroxylmethyl group increased from 34.46% to 38.81% and Type II hydroxylmethyl group decreased from 8.84% to 5.78%. These changes appear to indicate that the added melamine reacted not only with the free formaldehyde present but also with that which was slowly formed from the de-hydroxymethylation reaction of types I and II hydroxylmethyl groups of UF components. The increased content of the mono-substituted urea from 31.96% to 35.22% could be the result of losing type I hydroxylmethyl groups of UF components to melamine. During the resin synthesis, it was also observed that the addition of melamine to the reaction mixture lowered the viscosity from P-Q to N-O on the G-H scale after 1.0 h of reaction, in agreement with the migration of hydroxymethyl groups from the polymeric UF resin components to melamine. Overall, melamine appears to form more enduring bonds with formaldehyde in hydroxymethylmelamines compared with urea. This deduction agrees with the fact that UMF resins have been known to result in improvements in the bond strength and water-soak thickness swelling values for wood composite boards. Overall, the ^{13}C NMR results indicated that UMF resins are very similar to those of typical UF resins, with minor variations occurring due to melamine addition. The ^{13}C NMR data will also be used as the baseline in the planned subsequent studies for identifying small but meaningful structural differences affected by changes in resin synthesis variables.

Storage stability curves of resins at 30 °C are shown in Fig. 2 with viscosity increases of resin samples occurred over a period of 50 days. Resins 2.5%UMF1.05 and 5.0% UMF1.05 remained clear for a few days and then turned cloudy, indicating the precipitation of free melamine or melamine-formaldehyde reaction products, which would affect the viscosity storage stability negatively.

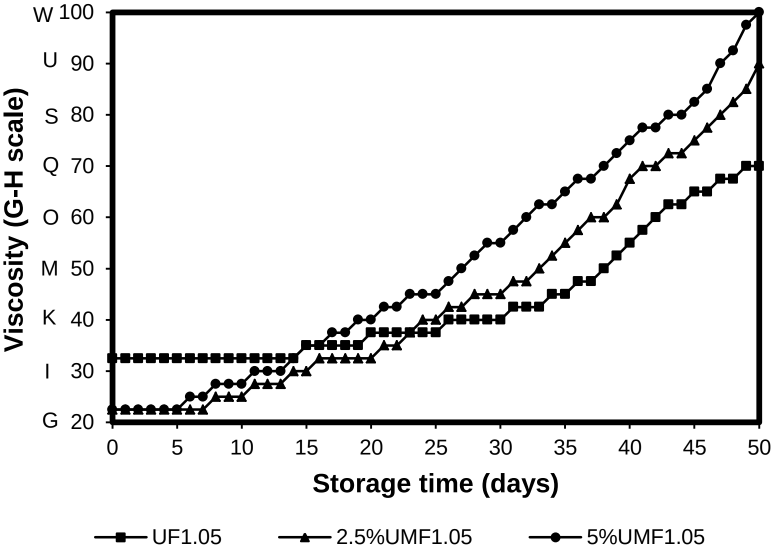

Fig. 2. Viscosity increases of UF and UMF resins observed during storage at 30 °C

Resin UF1.05 showed the highest storage stability, while Resin 2.5%UMF1.05 showed a higher stability than Resin 5.0%UMF1.05, indicating that storage stability decreased with increasing levels of melamine. To illustrate this, if the viscosity K on the G-H scale is considered to be the maximum value for a good spraying, Resin UF1.05 has a storage life of 31 days, Resin 2.5%UMF1.05 has 24 days, and Resin 5.0%UMF1.05 has 19 days of storage lives. Thus, the choice of melamine level for use in UMF resins could partly hinge on the storage life required for the particular plant. Free melamine or low mole ratio melamine-formaldehyde reaction products formed in resin synthesis are poorly soluble in water at room temperature (Wirpsza and Brezezinski 1973). They tend to come out of the water phase of resin during storage to form a milky appearance, accompanied with viscosity increases and with solid particles precipitating out in the end. Common UF resins' general storage behavior is similar, but the melamine components appear to accelerate the process due to the initiating effect of precipitated particles.

The pot-lives of catalyzed resins measured at 30 ^{o}C are shown in Fig. 3. Assuming that a viscosity of S on the G-H scale is the target level, UMF resins with a 2% level of catalyst B showed pot-lives of about 3.5 h, whereas those with 0.5% catalyst showed about 10.5 h. Resin UF1.05 gelled in 15 min with 0.5% catalyst B, indicating that catalyst B is not appropriate for UF resins. In industrial board manufacturing plants the resin is catalyzed and then soon sprayed onto wood particles. The mat is then promptly formed and hot-pressed in about 30 min, but the gelation of the applied resin should not be advancing too quickly before the hot-pressing.

It appears that both UMF resins catalyzed at 1.0% to 1.5% levels of Catalyst B would have comparable pot-lives with Resin UF1.05 catalyzed at a 0.5% level of Catalyst A. Thus, no particular problem is expected for UMF resins regarding the necessary pot-lives for practical applications.

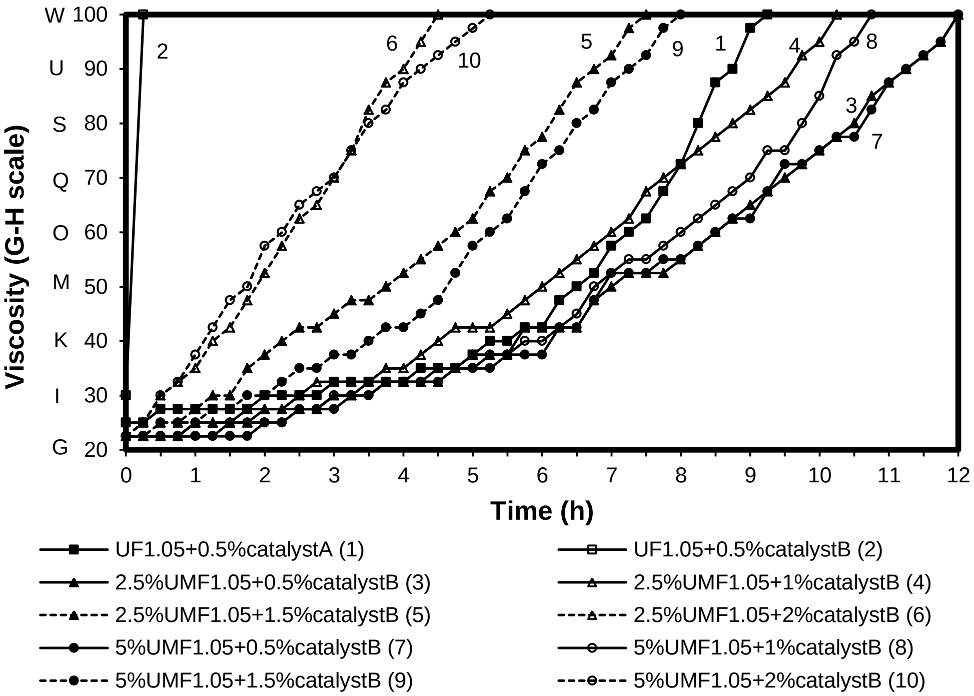

Fig. 3. Pot-lives of catalyzed UF and UMF resins with different catalysts and contents

Gel times of catalyzed resins measured at 100 ^{o}C are shown in Table 3. Gel times were shorter with increasing catalyst contents and were also shorter with Catalyst B than Catalyst A, reflecting the free sulfuric acid content in Catalyst B. Resin UF1.05 showed shorter gel times than Resin 2.5%UMF1.05, which has shorter gel times than Resin 5.0%UMF1.05, indicating that melamine increases the gel time even with the stronger Catalyst B. Thus, UMF resins (even with Catalyst B) would cure significantly slower than UF resins, indicating that melamine ties the acid species and delay the onset of curing reactions.

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%		2.0%		2.5%		3.0%
Catalyst Kind	A	B	A	B	A	B	A	B	A	B	B
Resin UF1.05	131	105	103	80	85	65	86	64	---	---	---
Resin 2.5%UMF1.05	219	187	201	172	179	162	169	146	167	138	139
Resin 5.0%UMF1.05	223	204	197	179	184	168	169	162	168	157	158

Gel and cure times of catalyzed resins measured with the rheometer in the dynamic mechanical analyzer (DMA) mode are reported in Table 4. In these tests, the resin sample was heated from room temperature to the target isothermal temperatures of 90^{o}C, *etc*. in about 50 s and then held for 25 min. The moisture in the resin sample would be mostly gone when it reached the curing temperature, and this fact makes such tests different from the gel time results discussed above. The tests more likely reflect the resin curing times in hot-pressing of boards. In typical runs, storage modulus, loss modulus, and tan δ curves were obtained *vs*. elapsed time. The gel time was taken as the time needed to reach to the maximum value of tan δ, and the cure time is defined as the time the storage modulus curve in the maximum slope region meets the tangent drawn from its maximum value at the end of the run (Gillham *et al.* 1974; Laza *et al.* 1999; No and Kim 2005). All resin samples showed tan δ values of about 0.10 at the end of curing, indicating that typical extents of vitrification were achieved in the tests (No and Kim 2005).

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

Resin Type	Catalyst Type	Catalyst Level (%)	Gel Time (s)				Cure Time (s)			
			90^{o}C	120^{o}C	135^{o}C	145^{o}C	90^{o}C	120^{o}C	135^{o}C	145^{o}C
UF 1.05	A	0.5	186	152	128	109	400	265	180	---
	B	0.5	60	---	---	---	137	---	---	---
2.5% UMF 1.05	B	0.5	181	117	102	95	525	210	165	130
		1.0	123	116	88	87	333	185	133	140
		1.5	122	116	87	81	333	203	152	140
		2.0	87	81	81	74	253	145	123	117
5.0% UMF 1.05	B	0.5	176	158	102	102	483	300	242	215
		1.0	123	119	95	88	325	227	187	157
		1.5	115	112	96	88	325	183	207	120
		2.0	96	94	91	81	275	180	147	135

The gel time and cure time results in Table 4 were shortened with increasing curing temperatures and also with higher catalyst levels, as was expected. Resin 2.5%UMF1.05 generally showed shorter gel and cure times than Resin 5.0%UMF1.05, indicating the slower curing effects of melamine, as observed in pot-life and gel times of catalyzed resins discussed above. In industrial hot-pressing of particleboards, the extent of resin curing in the core layer is the key to the internal bond strength values. The core layer temperature normally reaches the range 140 ^{o}C to 150 ^{o}C within about 150 to 180 s of pressing time for a typical 0.5 inch-thick mat (Wang *et al.* 2003). The gel and cure time values of 109 s and ~180 s for Resin UF1.05 with typical Catalyst A measured at 145 ^{o}C appear to indicate that the UF resin could hold boards well at the end of hot-pressing times of about 3 min. The similar values obtained for Resins 2.5%UMF1.05 and 5.0%UMF resin1.05 with Catalyst B at 1.0% to 2.0% levels appear to meet the same hot-pressing time criterion. Catalyst B at 0.5% levels appeared to be somewhat weaker.

Particleboard test results are shown in Table 5. The data are arranged according to the board numbers shown in Table 1, as discussed below. 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) represent the range of UF resin uses in the industry. The last resin combination, Resin UF1.25 in the core-layer, is more commonly used to achieve short hot-pressing times and good physical properties of boards (Go 1991). However, the formaldehyde content (FC) value with this mole ratio was about 16 mg/100 g board, which was the typical value of boards manufactured in the industry before the enactment of the new formaldehyde emission laws (Go, 1991) . This FC value corresponds to a formaldehyde emission (FE) value of about 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. Resins UF 1.15 and 1.05 in the core-layers lowered the FC values to the range 8 to 13 mg/100 g, but the boards showed lower IB and bending strength values due to insufficient extents of cross-linking in the cured UF resins.

Table 5. Formaldehyde Content 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	7.9	8.0	48.6	58.0	940	141	29.1	76.6
2	13.6	12.8	49.7	74.4	1295	180	20.9	58.5
3	16.8	15.9	50.8	90.4	1495	202	18.5	51.2
4	7.8	7.3	50.6	74.4	1355	182	28.7	61.0
5	6.7	6.1	50.8	96.8	1530	215	25.1	61.9
6	6.2	6.0	50.5	78.1	1365	183	27.3	64.9
7	5.7	5.4	50.4	71.8	1285	185	27.0	71.3
8	8.0	7.1	51.2	90.9	1640	227	26.8	68.6
9	7.3	6.0	51.5	124.3	1720	235	23.6	65.3
10	6.2	5.8	51.3	113.0	1895	250	22.3	74.7
11	5.6	5.2	50.8	103.2	1610	222	22.1	73.6
12	6.7	6.1	51.7	116.3	1815	262	16.8	49.6
13	6.6	5.9	50.9	116.3	1635	225	18.7	52.2
14	7.4	6.8	51.3	127.8	1925	273	16.7	41.3
15	7.0	5.9	52.0	134.3	2160	299	16.1	42.0

Note: Board number refers to the numbers in Table 1

Particleboards made with incorporation of Resin UF1.05 in the face-layer and Resin 2.5%UMF1.05 in the core-layer with various contents of Catalyst B (Boards 4 to 7) showed lower FC values of 6 to 8 mg/100 g boards with acceptable IB values when using catalyst B at a 1.0% level in the core layer. These FC values correspond to the E1 class of European Standards. The longer press time of 3.5 min showed slightly lower FC values, as expected. The UMF resin required the stronger catalyst B, of which free acid content needs to be considered with respect to its long-term wood degradation potential (Myers 1985). The UMF resins' curing rates were found to be too slow when using the common Catalyst A under the laboratory conditions. Use of higher levels (1.5% and 2.0%) of Catalyst B tended to show lower IB values and poorer water-soak test values, which are attributed to over-catalyzing effects. The approach of using a UF resin in the face layer and a UMF resin in the core layer is based on lowering the overall resin cost and using the UMF resin having higher formaldehyde reaction capacity in the core layer to capture the free formaldehyde accumulating during the hot-pressing.

Particleboards made with Resin UF1.05 in the face layer and 5%UMF1.05 at various levels of Catalyst B (Boards 8-11) showed FC values of 5.2 to 8.0 mg/100 g boards with acceptable IB values only with 1.0 to 1.5% levels of Catalyst B. These FC values are slight improvements over Resin 2.5%UMF1.05 used as core-layer resin discussed above but similarly correspond to E1 Class of European Standards. IB and bending strength values and water-soak test values improved over Resin UF1.05 or Resin 2.5%UMF1.05 used in the core-layer discussed above. Thus, the positive effects of the increased melamine level in the resin are mainly of board physical properties. The overall mole ratios of UMF resins appear to be the principal determinant for FC values.

Particleboards made with incorporation of Resin 2.5%UMF1.05 in the face layer and 5.0%UMF1.05 in the core layers at the 1.0% B catalyst level (Boards 12-13) showed similar FC values of 5.9 to 6.7 mg/100 g boards with acceptable IB values. The FC values were slight improvements over using Resin UF1.05 in the face layer (Boards 8-11) and similarly correspond to the E1 class of European Standards. The main advantage of using the UMF resin in face-layer resins is the improved water-soak thickness swell and water-absorption values. On the other hand, IB and bending test values indicated that the catalyst level in the face layer Resin 2.5%UMF1.05 showed higher values at 0.5% catalyst level than at the 1.0% catalyst level, indicating that the catalyst levels of UMF resins also should be adjusted according to the layer of the boards to which the resin is added.

Boards made with Resin 5%UMF1.05 in both face- and core-layers at 0.5 to 1.0% levels of Catalyst B (Boards 14-15) showed similar FC values of 5.9 to 7.4 mg/100 g boards with relatively good IB, bending strength, and water-soak test values. These FC values did not improve over the values of using Resin 2.5%UMF1.05 in the face discussed above (Boards 12-13). However, IB and bending strength values and water-soak test values of boards were improved further due to the extra melamine level in the face-layer UMF resin. The 1.0% catalyst content in the face layer appears to perform better than 0.5% level, indicating again the need of adjusting the catalyst content according to the melamine level of UMF resins and board layers. The relatively good physical properties of boards resulting from the use of Resin 5.0%UMF1.05 appear to indicate that the mole ratio could be lowered further to 1.00 or below to lower the FC values of boards, although the catalyst strength level and the hot-pressing time may have to be increased. The resin's storage stability also might get worse.

Overall, boards made with the longer press time of 3.5 min showed slightly lower FC values than 3.0 min press times, indicating the dependence of formaldehyde values on the expulsion of steam during hot pressing. It should be also noted that industrial boards made with the same resins and the same hot-pressing temperature and time would show lower IB strength and higher FC values than the boards made in the laboratory because of the larger sizes of boards in the industry. The moisture in the mat, which includes the free formaldehyde generated from resins during hot-pressing, takes longer times to get expelled from larger boards, and the industry prefers to keep the hot-pressing times as short as possible in order to maximize productivity. The approach of using UMF resins studied in this work for lowering the formaldehyde contents (or emission values) of boards could be effective to meet the European E1 class or the current U. S. large-chamber emission law levels if longer hot-pressing times and stronger catalysts are to be accepted. Investigation results of other resin synthesis variables, such as other melamine addition points or methylene-ether group content controls, will be published in subsequent papers, using the results of this study as the baseline.

CONCLUSIONS

1. The urea-melamine-formaldehyde (UMF) resins made from typical UF resins by modifying with 2.5% and 5.0% level melamine at a mole ratio of 1.05 were found to be adequate as core-layer binders for particleboard. The formaldehyde contents (emission potentials) of boards met the requirements of the E1 Class by European Standards.

2. The UMF resins needed to be catalyzed with stronger, free acid-containing catalysts at appropriate levels, depending on the melamine levels and also on the layers of boards to be applied. Curing rates of UMF resins were still slower than those of typical UF resins.

3. Use of the UMF resins in both the face- and core-layers of particleboards resulted in significantly improved strength and water-soak test values of boards.

4. The chemical structures of the UMF resins were very similar to those of typical UF resins, in agreement with the mode of melamine addition used in this study. About 55% of the added melamine reacted with formaldehyde. The methylene-ether contents of UMF resins were similar to those of typical UF resins, and are thus a possible source of formaldehyde emissions.

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