

Syntheses of Diethylene Tricarbamide–Formaldehyde and Copolymer Resins and Their Low Formaldehyde-Emitting Binder Performance of Wood Composite Board

Moon G. Kim
Sang-yeop Lee
Badamkhand Sukhbaatar

Abstract

Diethylene tricarbamide–formaldehyde (DF) resins were investigated for syntheses at low mole ratios and at about 60 percent resin solids levels in water as low formaldehyde-emitting binders of wood composite boards. Tri-functional monomer D was shown to react readily with formaldehyde to form hydroxymethyl groups that then react to form methylene bonds between molecules to form DF resins of water-soluble oligomeric condensation products, similar to urea-formaldehyde (UF) resins. DF resins showed a better storage life and longer pot life than, and similar cure times as, UF resins. DF resins also bonded laboratory particleboard as effectively as UF resins in terms of hot-pressing parameters and resultant boards' physical properties, while the formaldehyde content (FC) values of boards were lower by about 75 percent than UF resins, at about 2.3 to 4.4 mg/100 g wood by the Perforator method, significantly below the current regulation levels. Copolymer resins made with up to 15 percent urea substitutions performed equally well as particleboard binders with only slightly increased FC values, indicating some cost savings possible for industry. Copolymer resins made with up to 25 percent melamine also performed well with similarly low FC values and improved the physical properties of boards, indicating some lowering of loading levels of resin solids possible for industry, especially in the formulating of face layer resins. DF and copolymer resins are considered to be adaptable in current resin and board manufacturing plants to produce wood composite boards with a low formaldehyde emission potentials and without loss of productivity and board quality, a problem present in the current wood composites manufacturing industries.

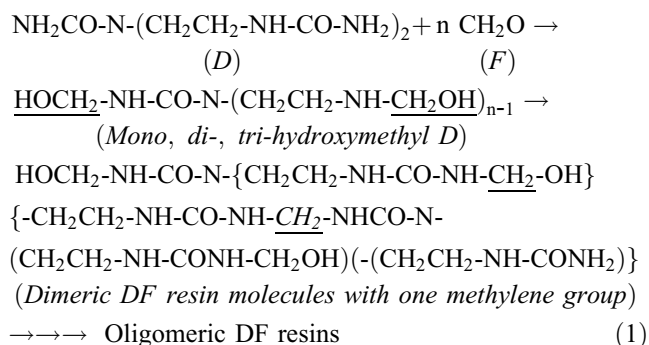
Annual usage of urea-formaldehyde (UF) resins amounts to 3.3 billion pounds in North America and 15.8 billion pounds worldwide, mostly as binders for interior-grade wood composite boards, such as particleboard, medium-density fiberboard (MDF), and hardwood plywood (Innovation Group 2006, Kennedy 2006). However, UF resin-bonded wood composite boards entail formaldehyde emission problems, unresolved or only partially resolved until recently (Go 1991, Graves 1993, Sigvartsen and Dunky 2006). The emission values in the recent past ranged from about 0.15 to 0.20 ppm by the standard Small Chamber test method (Kim et al. 2003, No and Kim 2007), far higher than US federal and state formaldehyde emission regulation limits (State of California 2007, Senate Bill 2011). The new law also introduced new definitions of “no-formaldehyde-added resins” and “ultra-low formaldehyde-emitting res-

ins” classes that aim at board emission values less than 0.04 ppm in the future. European and Japanese governments are also aiming at the ultra-low formaldehyde-emitting wood composite boards (Sigvartsen and Dunky 2006).

The authors are, respectively, Professor Emeritus, Former Postdoctoral Research Associate, and Former Graduate Student, Dept. of Sustainable Bioproducts, College of Forest Resources and Forestry and Wildlife Research Center, Mississippi State Univ., Mississippi State, Mississippi (mkim1941@gmail.com [corresponding author], lsy6709.mpresin@gmail.com, sbadmaa@gmail.com). This paper was received for publication in November 2017. Article no. 17-00074.

©Forest Products Society 2019.
Forest Prod. J. 68(3):236–255.
doi:10.13073/FPJ-D-17-00074

UF resins are manufactured by reacting urea (U) and formaldehyde (F), in which various hydroxymethylureas are initially formed, and they then react further during resin synthesis and curing processes among themselves to form methylene bridge groups between urea units to form higher-molecular-weight thermosetting resin polymers. Here, the initial formation reaction of hydroxymethyl groups is slightly reversible, resulting in resins having small amounts of formaldehyde that remain unreacted; due to this reversibility, some additional formaldehyde generated during the curing of resin in boards leads to the formaldehyde emission problems (De Jong and De Jong 1952a, 1952b, 1953; Myers 1983, 1990). Suppression of the reverse reaction of hydroxymethyl groups is possible only by increasing the urea amide group content of resins by, for example, adding more urea; that is, lowering the F/U mole ratio of resins. This method has been used to the utmost extent in industry, but the emission values are still significant, and the hot-pressing speed of boards decreased and board strength values deteriorated due to the reduced cross-linking capacity of resins (Plath 1967, Go 1991, Graves 1993). In theory, the F/U mole ratio of UF resins needs to be greater than 1.0 to result in cross-linked thermosetting network polymers, and an increase in mole ratio would increase the board strength values (Flory 1953). A recent laboratory report indicates that UF resins for the core layer of boards with an F/U mole ratio of 1.05 or lower may produce boards that meet current formaldehyde emission regulation levels (Mao et al. 2013c), but the curing speed and board strength values are reduced significantly from those of UF resins made with F/U mole ratios of 1.15 to 1.25. Use of tri-functional melamine (M) at low levels in UF resins in the form of urea-melamine-formaldehyde (UMF) resins can result in some improvements in board strength properties, but this approach is also limited in the effectiveness of emission reduction due to the slower curing speed and the fact that high levels of melamine are difficult to incorporate into liquid UMF resin formulations due to the limited storage stability of the resulting resins (Kim, unpublished data, 2013). This dilemma, encountered in raising the urea content of UF resins to increase the amide group content, was conceived to be resolvable by using a new monomer, diethylene tricarbamide (D), which has three carbamide groups in the molecule, as reported in the companion paper (Kim 2019) and in the US patent literature (Kim 2013), and as shown in the following resin synthesis scheme:



Monomer compound D was found to be synthesizable in high yields in the laboratory using various organic solvents as the reaction medium by reacting diethylene triamine, $\text{NH}(\text{CH}_2\text{CH}_2\text{-NH}_2)_2$ (DA), with urea. Despite the current

high selling price of this raw material DA (\$1.75/lb), the author concluded that a high-volume manufacture of monomer D for a new application might be feasible at a lower price, since DA, in turn, is currently manufactured in large volumes using low-cost starting materials: ethylene and ammonia. On this premise, the authors investigated syntheses of various DF resins and copolymer DUF and DMF resins by adding, respectively, urea and melamine to DF resins and tested them for effectiveness as particleboard binders in the laboratory, including their formaldehyde emission potentials.

Experimental Materials

Monomer material D used in this study was obtained in experiments carried out in various organic solvents reported in the companion paper (Kim 2019). Different batches of D were all washed with warm methanol and had melting points in the range of 215°C to 220°C. A formaldehyde solution of 50 percent concentration, donated by Georgia-Pacific Corp. (Taylorsville, MS), was used for resin syntheses. Mixed pine and hardwood particles (face layer and core layer) used in the industrial particleboard plant and wax emulsion with a 50 percent solid content were generously donated by Roseburg Forest Products Corp. (Louisville, MS). A catalyst (25% ammonium sulfate solution in water) made in the laboratory was used as resin curing catalysts.

Resin syntheses

General procedure.—Three-neck flasks of various sizes were used as reactors, equipped with a stirrer, thermometer, addition funnel, heating mantle, and pH meter; pH adjustments were made by dropwise addition of 8.0% sodium hydroxide or 4.0 percent sulfuric acid solution to the reaction mixture while stirring during reaction. Synthesized resins were cooled to room temperature and stored at 4°C in the refrigerator until use and warmed up to room temperature before testing or use. The following DF resins and copolymer DUF and DMF resins were synthesized for testing of polymeric resin formations and for use as binders in particleboard preparations. Also, control UF and UMF resins were synthesized according to reported procedures (Williams 1983, No and Kim 2007) to use for comparative testing of binder performance. The naming methods used for synthesized resins in this work are as follows and a summary of resin synthesis experiments is reported in Table 1:

1. Resin kind designations are followed by the resins' overall formaldehyde mole ratio; for example, Resin DF1.15 indicates that the DF resin's overall F/D mole ratio is 1.15.
2. For copolymer resins, the resin name is preceded by a weight percentage value of D or melamine; for example, Resin 83.0%DUF1.25 indicates that its D/(D + U) weight ratio is 83.0 percent with an overall F/(D + U) mole ratio of 1.25.
3. Resin 15.0%UMF1.15 indicates that its M/(U + M) weight ratio is 15.0 percent with an overall F/(M + U) mole ratio of 1.15, and Resin 14.3%DMF1.20 indicates that its M/(D + M) weight ratio is 14.3 percent with an overall F/(D + M) mole ratio of 1.20.

Control UF resins (#1).—The typical UF resin (Williams 1983) was prepared as follows. In the first step, 3,150 g of

Table 1.—Summary of resin synthesis experiments.^a

Resin type	Exp. #	Comonomer content	Resin synthesis methods of low-mole-ratio resins ^b
UF	1		Base UF resin with F/U = 2.10; low-mole-ratio UF resins obtained by adding U
UMF	2	~15.0% M	Reacting M and U with base UF2.10 to F/(U + M) = 1.35; repeat to 1.25, 1.15, and 1.05
DF	3a		Stepwise addition of D to F to obtain F/D = 2.41, 1.80, 1.55, 1.45, 1.35, and 1.25
	3b		One-time addition of D to F; F/D = 1.25; similar reactions to obtain F/D = 1.20 and 1.10
	3c		Reacted F and D to DF5.0; reacted D and DF5.0 to F/D = 2.20 and 1.50; reacted U with DF1.50 to 93.9%DUF1.20 and 91.4%DUF1.10
	3d, 3e		Extra-low DF by adding D to low-mole-ratio DF resins to F/D = 0.80 and 0.60
DF 3.00	4		DF resin reaction done with Ca(OH) ₂ as catalyst, a reference resin material
DUF	5	~94%–84% D	Added U to DF1.65 sequentially to F/(D + U) = 1.35, 1.15, 1.05, 1.00, and 0.95
	6	~82%–79% D	Reacted F and D to F/D = 2.10 or 2.25 and sequentially adding U to obtain F/(D + U) = 1.25, 1.15, and 1.05
	7	~83%–77% D	Reacted D with UF2.10 and extra F to F/(D + U) = 1.40 and then added sequentially more to obtain F/(D + U) = 1.30, 1.25, and 1.15
	8	~90%–93% D	Reacted D with UF2.10 and extra F to 90.0%DUF1.55, then added sequentially more D to obtain F/(D + U) = 1.45, 1.35, 1.25, and 1.15
DMF	9	~7.5% M	DF2.17 is made and added M to F/(D + M) = 1.77, then added D to F/(D + M) = 1.25
	10	~8.8% M	M and D together are reacted with F to obtain F/(D + M) = 1.10
	11	~10% M	DF1.80 is made by Method 3a, M is added to F/(D + M) = 1.40, then added minor amounts of U to obtain F/(D + M + U) = 1.35, 1.25, and 1.15
	12	~15.0% M	DF1.92 is made by Method 3a, M is reacted to F/(D + M) = 1.45, then, consecutively, minor amounts of M and D are added to obtain F/(D + M) = 1.35, 1.25, and 1.15
	13	~15% M	DF1.59 is made by Method 3a, and M is added to F/(D + M) = 1.20
	14	~14.3% M	DF1.80 is made by Method 3b, M is added to F/(D + M) = 1.33, then D is added to F/(D + M) = 1.20
	15	~17.5% M	DF1.74 is made by Method 3a, and M is added to F/(D + M) = 1.25
	16	~20.0%, 18.0% M	DF2.28 is made by Method 3b, and M is added to F/(D + M) = 1.15 and 1.05
	17	~25.0% M	DF2.80 is made by Method 3b, M is added to F/(D + M) = 1.45, then D is added to F/(D + M) = 1.15
	18	~30.0% M	DF3.20 is made by Method 3b, M is added to F/(D + M) = 1.36, then D is added to F/(D + M) = 1.05
	19	~35.0% M	DF3.20 is made by Method 3b, M is added to F/(D + M) = 1.27, then D is added to F/(D + M) = 1.05
	20	~50.0% M	D and M together are reacted with F to F/(D + M) = 1.54, then D is reacted to F/(D + M) = 1.05

^a UF = urea-formaldehyde; UMF = urea-melamine-formaldehyde; DF = diethylene tricarbamide-formaldehyde; F = formaldehyde; U = urea; M = melamine; D = diethylene tricarbamide.

^b Methods of reactions: 50% F, U, M, and D were reacted in water at pH 7.0 to 8.5 at about 60°C to 90°C; resins to be tested for binders are in mole ranges of 1.05 to 1.55 with viscosity values of HK and resin solids levels of 59.0 to 63.0 percent; pH adjustments were made with 8.0 percent NaOH solution.

50 percent formaldehyde solution was charged into a stirred reactor, the pH was adjusted to 7.5 to 8.0 with an 8 percent sodium hydroxide solution, and the reactor was heated to 70°C. Then 1,500 g of urea was added in such a rate that the temperature did not fall below 70°C (initial F/U ratio 2.10). Then the reaction exotherm and heating control were used to raise the temperature to 90°C, and the temperature was maintained by intermittent cooling and heating for 30 minutes while maintaining the pH at 7.2 to 8.0. Then, in the second step, using 8 percent sulfuric acid solution, the pH was lowered to 4.5 to 5.0, and the temperature was raised to 95°C, which was maintained for about 110 minutes to reach the target viscosity of WX by the Gardner-Holdt (G-H) scale, or about 500 cP. Then 8 percent sodium hydroxide solution was added to adjust the pH to 7.5 to 8.0. This intermediate product, Resin UF 2.10, was sometimes cooled to room temperature and used in parts for copolymer resin syntheses. Then, after the batch was cooled to room temperature, it was divided into smaller amounts of about 300 to 400 g and to each was added the second urea (U₂) in appropriate amounts to bring the overall F/U ratio to the target mole ratios of 1.25 to 0.95, and the mixtures were, respectively, stirred and heated back to 70°C and held for 30 minutes and cooled to room temperature with stirring. The final viscosity of resins ranged from H to K by the G-H scale initially, and the resin solids contents ranged from 60 to 63 percent.

Control UMF resins made with 15 percent melamine content by weight (#2).—First, 600.0 g of intermediate Resin UF 2.10 obtained above was taken in a stirred reactor and adjusted to a pH of 8.10, and 48.9 g of melamine was added and heated to 86°C and held for 20 minutes at pH 7.8 and cooled to 60°C; then 83.56 g of urea was added and stirred for 15 minutes while allowing the temperature to fall to 45°C. Then 160 g of resin sample was taken as 15%UMF1.35 with viscosity J. To the residue was added 3.06 g of melamine, and the mixture was heated at 80°C for 20 minutes and then cooled to 60°C, and 17.33 g of urea was added, stirred, and cooled to 45°C, then 160 g of resin sample was taken as 15%UMF1.25 with viscosity J. To the residue was added 2.61 g of melamine, and the mixture was heated at 80°C for 20 minutes and then cooled to 60°C, and 14.82 g of urea was added, stirred, and cooled to 45°C, and 160 g of resin sample was taken as 15%UMF1.15 with viscosity J. To the residue were added 2.00 g of melamine and 20 g of water, and the mixture was heated at 80°C for 20 minutes and then cooled to 60°C, and 11.4 g of urea was added, stirred, and cooled to 45°C and then cooled to room temperature, and the resin (~323 g) was taken as 15%UMF1.05 with viscosity F. The resin solid contents of these resins ranged from 60 to 65 percent.

Low-mole-ratio DF resins by stepwise addition of D (#3a).—One hundred and sixty-two grams of 50.0 percent formaldehyde solution (2.70 moles) and 100.0 g of water were charged into a stirred reactor and the pH of the reaction

mixture was adjusted to 8.5 with an 8 percent sodium hydroxide solution, followed by heating to 85°C. Then 260 g of first D (1.1206 moles) was added at such a rate that the temperature did not fall below 70°C to reach the initial F/D ratio of 2.41. Then the reaction exotherm and heating control were used to raise the temperature to 85°C to 88°C, which was maintained by intermittent cooling and heating. The viscosity began to increase from D to J by the G-H scale in 90 minutes. Then 88.0 g of second D and 60 g of water were added to attain a mole ratio of $F/(D_1 + D_2) = 1.80$, by which the temperature was lowered to about 70°C and the viscosity lowered to G. Then, the pH was readjusted to 7.2 to 8.0, and heating was applied to increase the temperature back to 85°C to 88°C. The viscosity increased to IJ in 45 minutes, after which 56.0 g of third D and 30.0 g of water were added [$D_1 + D_2 + D_3 = 1.55$]. Then the reaction was continued to reach viscosity I in 35 minutes, after which the reaction was stopped by the removal of heating and then cooling to room temperature. Taken was 160 g of this resin as Resin DF1.55, clear, viscosity I. To the residual resin were added 22.07 g of D and 14.0 g of water, heated to and maintained at 80°C for 15 minutes to result in DF resin with $F/D = 1.45$ with viscosity I. Taken was 160 g of this resin as Resin DF1.45. To the residue were added 18.9 g of D and 12.5 g of water and heated at 80°C for 15 minutes to result in viscosity I, and taken was 160 g of this resin as Resin DF1.35. To the residue were added 14.8 g of D and 10.0 g of water and heated to 80°C for 15 minutes to result in viscosity I, and taken was 120 g of this resin as Resin DF1.25. To the residue were added 18.3 g of D and 12.0 g of water and heated to 80°C for 15 minutes to result in viscosity I, and taken was all of the resin (~238.5g) as Resin DF1.15. The resin solids contents ranged from 60 to 62 percent, and pH was adjusted to 7.5 to 7.8.

Low-mole-ratio DF resins by one-time addition of D to formaldehyde solution (#3b).—First, 70.3 g of 50 percent formaldehyde solution and 102.0 g of water were taken into a reactor, and the pH was adjusted to 8.0 and heated to 60°C, followed by adding 217.5 g of D ($F/D = 1.25$). Then the reaction mixture was heated to and maintained at 90°C for 35 minutes and cooled to room temperature to obtain Resin DF1.25 with viscosity J, pH 6.8, and resin solids content of 60.6 percent; a similar procedure used 67.5 g of 50 percent formaldehyde solution, 103.8 g of water, and 217.5 g of D to result in Resin DF1.20 with viscosity J, pH 6.8, and resin solids content of 60.5 percent; a similar procedure used 61.87 g of 50 percent formaldehyde solution, 107.2 g of water, and 217.5 g of D to result in Resin DF1.10 with viscosity HI, pH 7.24, and resin solids content of 60.5 percent. In addition, 77.6 g of resin DF1.20 was taken and added with 1.022 g of urea to obtain Resin 97.7%DUF1.10 with viscosity HI, pH 6.9, and resin solids content of 61.2 percent.

Low-mole-ratio DF resins using an intermediate product DF5.0 (#3c)—Similar to the product “UF Concentrates” used in the UF resin industries, an intermediate product DF5.0 was first made: 3,030.0 g of 50 percent formaldehyde solution (50.50 moles) was taken into a stirred reactor, and the pH was adjusted to 8.40 and heated to 70°C. Then 2,343.2 g of D (10.1 moles) was added over a period of 50 minutes while maintaining the temperature between 70°C and 85°C. The reaction mixture was maintained at 85°C for 25 minutes, after which it became clear; after the heating mantle was removed, it was allowed to cool to room

temperature to obtain intermediate product DF5.0 with viscosity B and pH 7.4 and a long storage stability. Then 319.2 g of DF5.0 and 200.0 g of water were taken into a reactor, the pH was adjusted to 7.43, and the mixture was heated to 45°C; added was 88.57 g of D ($F/D = 2.20$), followed by heating the reaction mixture to 90°C for 10 minutes. The reaction mixture became clear, after which 73.88 g of second D was added ($F/D = 1.50$) and maintained at 90°C for 40 minutes to reach to viscosity HI, followed by cooling to room temperature to give Resin DF1.50 with viscosity I, pH 7.3, and resin solids content of 60.5 percent. Then two 84.4-g portions of Resin DF1.50 were taken and 3.0 and 4.36 g of urea was added to obtain, respectively, Resin 93.9%DUF1.20 with viscosity HI, pH 7.8, and resin solids content of 61.3 percent, and Resin 91.4%DUF1.10 with viscosity HI, pH 7.4, and resin solids content of 61.7 percent.

Scavenger-type resin DF0.80 using intermediate product DF5.0 (#3d).—Similarly, 201.5 g of DF5.0 and 294.0 g of water were taken into a stirred reactor, the pH was adjusted to 8.4, and the mixture was heated to 70°C, and 455.9 g of D ($F/D = 0.80$) was added, followed by heating the mixture to 90°C for 15 minutes. It then took 1.5 hours at 90°C for the reaction mixture to clear, and then the reaction continued for 1.0 hour and was cooled to room temperature to result in Resin DF0.80 with viscosity DE, pH 7.2, and resin solids content of 60.0 percent.

Scavenger-type Resin DF0.60 (#3e).—Sixty grams of 50 percent formaldehyde and 221.0 g of water were taken into a stirred reactor, the pH was adjusted to 8.4, and the mixture was heated to 70°C, and 232.0 g of first D ($F/D = 1.00$) was added, followed by heating the mixture to 90°C for 15 minutes. The reaction mixture soon cleared, and 100.0 g of second D ($F/D = 0.70$) was added over a period of 15 minutes. Then it took 25 minutes at 90°C to clear. Then 54.6 g of third D was added, which took 2.5 hours to clear, resulting in, after cooling, Resin DF0.60 with viscosity B, pH 7.2, and resin solids content of 60.0 percent.

Resin DF3.00 (#4).—This resin was made according to a reported procedure (Bentoniere and Rowland 1979) as follows: 510.0 g of water, 104.5 g of 50.0 percent formaldehyde solution (1.74 mole), 135.0 g of D (0.58 mole), and 2.50 g of calcium hydroxide were mixed in a stirred reactor and reacted for 23 hours at room temperature, followed by introduction of a slow stream of carbon dioxide for 30 minutes, during which time the pH value was reduced from 11.0 to 7.0. The reaction mixture was filtered of solid precipitates of calcium carbonate, and the resulting liquid was evaporated on a rotary evaporator at 80°C until the residue weighed 270.0 g to give the resin with a resin solids content of 59.0 percent and viscosity D.

Low-mole-ratio DUF resins having ~90 percent D by weight by adding urea (#5).—First, 96.7 g of 50 percent formaldehyde solution and 113.0 g of water were taken into a stirred reactor, the pH was adjusted to 9.12, and heating was begun. At 60°C, 232.0 g of D ($F/D = 1.65$) was added, the reaction mixture was heated to 90°C, and the pH allowed to drift down. The reaction mixture’s viscosity gradually increased: D at 25 minutes and G at 45 minutes. At 55 minutes of reaction time, it was cooled to 60°C, and 13.4 g of urea was added. Then 200.0 g of this resin was taken as Resin 94.5%DUF1.35 with viscosity J, pH 6.9, and resin solids content of 58.1 percent; to the remainder of the resin batch was added 7.11 g of urea; 100.0 g of this resin was

taken as Resin 89.9%DUF1.15 with viscosity I, pH 7.0, and resin solids content of 58.6 percent. The remainder of the resin batch was divided into three 60.0-g portions, and 1.06, 1.65, and 2.32 g of urea was added to obtain, respectively, Resins 87.2%UDF1.05, 85.6%UDF1.00, and 84.0%UDF0.95 with viscosity I, pH 7.2, and resin solids contents ranging from 59.1 to 61.9 percent.

Low-mole-ratio DUF resins having ~80 percent D by weight by adding urea (#6).—First, 123.1 g of 50 percent formaldehyde solution and 75.1 g of water were taken into a stirred reactor, and the pH was adjusted to 7.30, and heating was begun. At 60°C, 232.0 g of D (F/D = 2.10) was added, and the reaction mixture was heated to 85°C and the pH allowed to drift down during the reaction. The reaction mixture's viscosity gradually increased to M at 60 minutes of reaction time, after which it was cooled to 60°C, and 49.6 g of urea was added to obtain Resin 82.4%DUF1.15 with viscosity K, pH 7.0, and resin solids content of 60.7 percent. A 150.0-g portion of the resin was taken, and 3.25 g of urea was added to obtain Resin 79.5%DUF1.05, with viscosity J, pH 7.2, and resin solids content of 61.5 percent. Another similar procedure was carried out for a larger-scale experiment using 1,080.0 g of 50 percent formaldehyde solution, 780.0 g of water, and 1,856.0 g of D (F/D = 2.25). The first phase of the reaction was carried out at pH 7.0 to 8.0 at 90°C until a resin viscosity of JK was reached (80 minutes), followed by cooling to 60°C and adding 384.0 g of urea, resulting in 4,100 g of Resin 83.0%DUF1.25 with viscosity GH and resin solids content of 60.8 percent.

Low-mole-ratio DUF resins having ~80.0 percent D by weight using UF2.10 (#7).—One hundred and eighty-five grams of intermediate Resin UF2.10 were taken into a stirred reactor, and 66.7 g of 50 percent formaldehyde solution and 120.0 g of water were added, the pH was adjusted to 7.80, and the mixture was heated to 60°C. Then 300.0 g of D was added, and the reaction mixture was heated to 90°C and held for 40 minutes, after which the viscosity reached I. Then the reaction mixture was cooled to room temperature and 307.0 g of this resin sample was taken as Resin 83.3%DUF1.40 with viscosity IJ, pH 7.0, and resin solids content of 60.8 percent. The remainder was divided into three 120-g portions, and 1.90, 4.10, and 5.33 g of urea was added to result in, respectively, Resin 81.0%DUF1.30 with viscosity IJ, pH 7.1, and resin solids content of 62.2 percent; Resin 79.7%DUF1.25 with viscosity I, pH 7.2, and resin solids content of 64.0 percent; and Resin 77.0%DUF1.15 with resin viscosity I, pH 7.2, and resin solids content of 65.1 percent.

Low-mole-ratio DUF resins having ~90 percent D by weight using UF2.10 (#8).—One hundred and fifty grams of intermediate Resin UF2.10 were taken into a stirred reactor, and 147.9 g of 50 percent formaldehyde solution and 200.0 g of water were added, and the pH was adjusted to 7.80. Then, 300.0 g of D was added, and the reaction mixture was heated to 90°C and held for 40 minutes, after which the viscosity reached GH. Then 135.4 g of D and 100 g of water was added and heated back to 90°C and held for 30 minutes, after which the viscosity reached HI, followed by cooling to room temperature, and 200 g of this resin sample was taken as Resin 90.0%DUF1.55 with viscosity IJ, pH 7.0, and resin solids content of 60.4 percent. To the residual resin were added 34.61 g of D and 20.0 g of water and treated similarly at 90°C for 10 minutes and cooled to 60°C; 200 g of this resin sample was taken as Resin 90.8%DUF1.45 with

viscosity I, pH 7.2, and resin solids content of 61.0 percent. With the residual resin, a similar reaction was carried out by adding 32.96 g of D and 50 g of water and 160 g of this resin was taken as Resin 91.6%DUF1.35 with viscosity IJ, pH 7.1, and resin solids content of 61.3 percent. With the residual resin, a similar reaction was carried out using 29.44 g of D and 30 g of water and 200 g of this resin sample was taken as Resin 92.4%DUF1.25 with viscosity I, pH 7.2, and resin solids content of 61.4 percent. With the residual resin, a similar reaction was carried out using 27.80 g of D and 10 g of water to obtain (~438 g) Resin 93.1%DUF1.15 with viscosity IJ, pH 7.2, and resin solids content of 61.0 percent.

Low-mole-ratio 7.5 percent melamine-containing DMF resin (#9).—One hundred and one grams of 50 percent formaldehyde solution and 80.0 g of first water were taken into a stirred reactor, the pH was adjusted to 8.60, and 180.0 g of first D (F/D = 2.17) was added, followed by heating the reaction mixture to 90°C, which was then held for 15 minutes, followed by adding 22.0 g of melamine (F/[D + M] = 1.77) and heating back to and holding at 90°C for 15 minutes. Then 92.0 g of second D and 55.0 g of second water were added. The reaction mixture was then held at 90°C for 35 minutes to reach to viscosity H, after which it was cooled to room temperature, giving Resin 7.5%DMF1.25 with resin viscosity I, pH 7.0, and resin solids content of 60.8 percent.

Low-mole-ratio 8.8 percent melamine-containing DMF resin (#10).—First, 155.8 g of 50 percent formaldehyde solution and 240 g of water were taken into a stirred reactor, the pH was adjusted to 8.60, and the mixture was heated to 60°C. Then, 465.0 g of D and 45.0 g of melamine (F/[D + M] = 1.10) were added and heated back to 85°C and held for 30 minutes, after which the reaction mixture reached viscosity F. The reaction mixture was then cooled to room temperature to give Resin 8.8%DMF1.10 with viscosity G, pH 7.8, and resin solids content of 61.0 percent.

Low-mole-ratio ~10 percent melamine-containing DMF resins by adding minor amounts of urea (#11).—One hundred and sixty-two grams of 50 percent formaldehyde solution and 100.0 g of first water were taken into a stirred reactor, the pH was adjusted to 8.20, and 260 g of first D (F/D = 2.41) was added, followed by heating the mixture to 90°C, which was then held for 40 minutes to reach viscosity JK. Then, 60 g of second water and 88.0 g of second D (F/D = 1.80) were added, and the temperature was maintained at 80°C for 30.0 minutes to obtain viscosity KL, after which 60 g of third water, 22 g of third D, and 42.0 g of melamine (F/[D + M] = 1.40) were added and the pH adjusted to 8.70; the temperature was maintained at 85°C for 35 minutes to obtain viscosity GH. The reaction mixture was cooled to room temperature to result in 740.2 g of DMF resin with a mole ratio of 1.40. Three 180-g portions of this resin were taken and added to each of 1.03, 3.33, and 6.04 g of urea, respectively, to obtain resins having F/(D + M + U) mole ratios of 1.35, 1.25, and 1.15, wherein the melamine content was 10.1, 10.1, and 9.6 percent, respectively, with viscosity values of I to IJ and resin solids content in the range of 60.1 to 61.2 percent.

Low-mole-ratio 15 percent melamine-containing DMF resins (#12).—First, 139.1 g of 50 percent formaldehyde solution and 80.0 g of water were added into a stirred reactor, and the pH was adjusted to 8.40, followed by adding 210.0 g of D (F/D = 2.56). Then, the reaction mixture was heated to 90°C and held for 45 minutes, during which time

the viscosity of reaction mixture increased gradually from $\sim A_1$ to IJ. Then, 70 g of D ($F/D = 1.92$) and 70.0 g of water were added, and heating was continued at the same temperature for 35 minutes, followed by cooling to 50°C to result in viscosity H. Then 49.4 g of melamine ($F/(D + M) = 1.45$) was added and heated back to 90°C and held for 30 minutes, after which the reaction mixture became clear. Then the heating was removed and the mixture allowed to cool down to 60°C, the pH was adjusted to 8.00, and 120.0 g of resin sample was taken as Resin 15%DMF1.45 with viscosity L. To the residue were added 2.83 g of melamine, 16.0 g of D, and 20.0 g of water, and the mixture was heated back to 85°C and held for 5 minutes, after which the reaction mixture became clear, followed by cooling to 60°C. Then, 120 g of resin sample was taken as Resin 15%DMF1.35 with viscosity J. The residue was similarly treated with 2.75 g of melamine, 15.58 g of D, and 20 g of water to obtain Resin 15%DMF1.25 and taken 120 g of resin sample. The residue was similarly treated with 1.57 g of melamine, 8.91 g of D, and 10 g of water to obtain Resin 15%DMF1.15 (~ 356 g). All resins were adjusted to a pH of 7.5, and resin solids contents were in the range of 60.1 to 62.0 percent.

Low-mole-ratio 15 percent melamine-containing DMF resin (#13).—One hundred and forty-four grams of 50 percent formaldehyde solution and 120.0 g of first water were taken into a stirred reactor, the pH was adjusted to 8.5, heating to 50°C was begun, followed by adding 232.0 g of first D ($F/D = 2.40$) and heating to 90°C. After 60 minutes at that temperature, the reaction mixture reached viscosity EF, after which were added 118.0 g of second D ($F/D = 1.59$) and 25.0 g of second water and the mixture was heated to 80°C. After 40 minutes of reaction time, the reaction mixture became clear, and pH value reached 6.21 with viscosity HI. The pH of the reaction mixture was adjusted to 8.6, and 62.0 g of melamine was added before heating back to 80°C was begun. After 120.0 minutes of reaction time, the reaction mixture became clear, and 40.0 g of water was added and held at 80°C for 20.0 minutes, followed by cooling to room temperature to yield Resin 15%DMF1.20 with viscosity K, pH 7.1, and resin solids content of 60.8 percent.

Low-mole-ratio 14 percent melamine-containing DMF resin (#14).—First, 376.3 g of 50 percent formaldehyde solution and 491.7 g of water were taken into a stirred reactor, the pH was adjusted to 8.5, the mixture was heated to 50°C, and 808.0 g of first D ($F/D = 1.80$) was added and heated to 87°C. After 35 minutes at the temperature, the reaction mixture became clear and reached to viscosity EF, after which 155.0 g of melamine was added and reacted at the same temperature for 20 minutes to get the reaction mixture clear ($F/[D + M] = 1.33$). Then, 119 g of second D ($F/[D + M] = 1.20$) was added and heated to 87°C. After 10 minutes of reaction, the reaction mixture became clear and was cooled to room temperature, resulting in Resin 14.3%DMF1.20 with viscosity D, pH 7.5, and resin solids content of 59.6 percent.

Low-mole-ratio 17.5 percent melamine-containing DMF resin (#15).—Using a procedure similar to the resin synthesis above, 122.5 g of 50 percent formaldehyde solution, 180.0 g of first D ($F/D = 2.63$), 92.0 g of second D ($F/D = 1.74$), 80.0 g of first water, 65.0 g of second water, and 58.0 g of melamine were reacted to obtain Resin

17.5%DMF1.25 with viscosity J, pH 7.18, and solids content of 60.0 percent.

Low-mole-ratio 20 percent and 18 percent melamine-containing DMF resins (#16).—First, 118.1 g of 50 percent formaldehyde solution and 155 g of water were taken into a stirred reactor, the pH was adjusted to 8.3, the mixture was heated to 80°C, and then 200.0 g of first D ($F/D = 2.28$) was added. After 10.0 minutes, the reaction mixture reached 90°C and became clear after another 10 minutes. The reaction mixture was then quickly cooled to 50°C, and pH was checked at 6.5 and adjusted to 9.20, followed by adding 68.0 g of melamine ($F/[D + M] = 1.40$), and heating back quickly to 90°C was begun. After about 20 minutes, the reaction mixture became clear, and 72.0 g of second D was added. After 10 minutes of reaction time, the reaction mixture became clear and was cooled down to room temperature and 350.0 g of resin was taken as Resin 20.0%DMF1.15 with viscosity F, pH 7.5, and resin solids content of 60.0 percent. To the residue were added 16.2 g of D and 11.0 g of water and the mixture was heated at 80°C for 10 minutes, followed by cooling down to room temperature to result in Resin 18.0%DMF1.05 with viscosity GH, pH 7.2, and resin solids content of 60.2 percent.

Low-mole-ratio 25 percent melamine-containing DMF resin (#17).—First, 130.7 g of 50 percent formaldehyde solution and 80 g of water were taken into a stirred reactor, the pH adjusted to 8.8, and the mixture heated to 70°C. Then, 180.0 g of first D ($F/D = 2.80$) was added. After 10.0 minutes of reaction time, the reaction mixture reached 90°C and became clear in another 10 minutes. The reaction mixture was then quickly cooled to 80°C, and pH was checked at 6.5 and adjusted to 8.8, followed by adding 68.0 g of melamine ($F/[D + M] = 1.45$), and heating back quickly to 90°C was begun. After about 25 minutes, the reaction mixture became clear, and 92.0 g of second D and 82.0 g of second water was added, followed by heating back to 90°C. After 15 minutes, the reaction mixture became clear and cooled down to give Resin 25.0%DMF1.15 with viscosity J, pH 7.1, and resin solids content of 60.6 percent.

Low-mole-ratio 30 percent melamine-containing DMF resin (#18).—Using a procedure similar to the procedure of resin synthesis above, 132.2 g of 50 percent formaldehyde solution, 160.0 g of first D ($F/D = 3.20$), and 89.0 g of first water; 116.6 g of melamine ($F/[D + M] = 1.36$), and 89.0 g of second water; and 112.0 g of second D were reacted to obtain Resin 30.0%DMF1.05 with viscosity H, pH 7.12, and solids content of 60.0 percent.

Low-mole-ratio 35 percent melamine-containing DMF resin (#19).—Using a procedure similar to the procedure of resin synthesis above, 146.9 g of 50 percent formaldehyde solution, 180 g of first D ($F/D = 3.20$), and 95.0 g of first water; 146.0 g of melamine ($F/[DM] = 1.27$); and 92 g of second D, and 94.0 g of second water were reacted to obtain Resin 35.0%DMF1.05 with viscosity KL, pH 7.18, and solids content of 56.0 percent.

Low-mole-ratio 50 percent melamine-containing DMF resin (#20).—First, 146.9 g of 50 percent formaldehyde solution and 144.3 g of first water were taken into a stirred reactor, the pH was adjusted to 9.20 and the mixture was heated to 60°C. Then, 20.4 g of first D and 190.0 g of melamine ($F/[D + M] = 1.54$) were added, followed by heating to 90°C. With pH maintained at 7.9 to 8.2, the temperature was maintained at 90°C for 65 minutes, after which the reaction mixture became clear. Then 170.0 g of

second D and 20.0 g of second water was added, and the temperature was kept at 90°C for 15 minutes, after which the reaction mixture became clear, and then was cooled to give Resin 50.0%DMF1.05 with viscosity EF and pH 8.1. The resin sample gelled in 4 days on standing at room temperature, and another sample advanced to a thick syrup in 5 days in the refrigerator. The resin was not examined further.

Physical and chemical property measurements of synthesized resins

General tests of synthesized resins.—Nonvolatile solids contents were measured in duplicates using the standard procedures: 1 g of resin sample, catalyzed and baked for 2 hours at 125°C. Free formaldehyde content (FC) of resins were determined by the usual hydroxylamine method. Viscosity of resins was measured with the G-H bubble tube method at 25°C in a water bath.

Chemical structure determinations.—¹³C NMR analyses of resins DF1.25, DF1.75, and 14.3%DMF1.20 were obtained using a Techmag 400-2 NMR Instrument from Spectral Data Services, Inc. (Champaign, IL, USA). In this test, 2.0 g of resin sample was mixed with 1.0 g of deuterium oxide. A sample of Resin 83.0%DUF1.25 was run with DMSO-d₆ as solvent. A 12-μs pulse width and 10-second pulse delay were used for quantitative results. About 400 scans were accumulated for each resin sample, resultant spectral peaks were integrated, and functional group values were analyzed in the same way as used for UF resin analyses reported by our laboratory (Kim et al. 2003).

Shelf lives of resins and pot lives and gel times of catalyzed resins.—Shelf lives of resins were measured by standing the G-H viscosity measuring sample tubes at room temperature and checking viscosity values daily at 25°C in a water bath. Gel times of resins catalyzed with 1.0 percent of catalyst addition were measured in triplicates by heating in a glass tube at 100°C while stirring continuously until the resin set to a solid. Pot lives of catalyzed resins were measured in G-H viscosity tubes in duplicates placed in an oven at 30°C by checking viscosity changes for 30 hours.

Curing tests of catalyzed resins.—Gel and cure tests were done on a DMA983 (TA Instruments, New Castle, DE, USA); approximately 25 mg of resin catalyzed with 1.0 percent of catalyst addition was evenly impregnated on a piece of fiberglass braid (16.15 by 10.95 by 0.12-mm dimension), and the impregnated braid was clamped horizontally between two DMA arms in the heating chamber, the rigidity reading was zeroed for cancellation of the braid effect, and the heating/curing of resin was initiated. A fixed displacement mode with 0.80-mm amplitude and 0.4-Hz oscillation frequency was used. The temperature program started with an equilibration wait at 30°C, followed by increasing the temperature at a rate of 50°C/min to 120°C and then holding at that temperature for 20 minutes. The force needed to rock the arms was monitored and calculated into stiffness (G') and loss modulus (G'') values, and the ratio of the two values was calculated as *tan delta* values.

Particleboard manufacturing and testing for binder performance of synthesized resins

Laboratory particleboards of 22 by 22 by 0.5-inch dimensions.—Boards were made with resins selected among

synthesized resins along with some commercial UF or UMF (CUMF) resins from unknown suppliers obtained from a nearby PB manufacturing plant in Mississippi. Wood particles were dried to 4.0 to 5.0 percent moisture content, and a measured amount was put into a rotating blender, and 1.0 percent wax solids and 8.0 percent catalyzed resin solids were successively sprayed in using an air-atomizing nozzle placed within the blender drum within approximately 15 minutes. Face layer particles and core layer 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, and bottom layers. Two mats were made; one was pressed for 3.0 minutes and the other for 3.5 minutes. The press closing rate was initially 0.5 inch/s to a mat thickness of 1.0 inch and then 0.03 inch/s to reach the target board thickness of 0.5 inch in a Dieffenbacher press. The pressed boards were cooled at room temperature for 1 day. Other target parameters were as follows: mat moisture content of 8.0 to 10 percent based on oven dried wood weight, board dimensions of 22 by 22 by 0.5 inches, board density of 50.0 pounds per cubic foot (pcf), and press temperature of 350°F. Boards were cut into physical test samples using the same pattern and also taken 6 by 6-inch formaldehyde test samples. Physical test samples were allowed to equilibrate in a room at 60 percent relative humidity for 1 week.

Laboratory particleboards of 6 by 6 by 0.5-inch dimensions.—Boards were also made in duplicates in the second part of study on a 6 by 6-inch laboratory hot press. Board preparation parameters were the same as above except that the target resin solids loading level was increased to 10 percent and resin/wax-wood mixing was done by hand using a spatula in a plastic beaker. Target board densities were 50.0 pcf, and testing of boards was limited to water-soak tests for which the first boards were used and FC tests were done with the second boards. Data of boards having poor water-soak test values were discarded and repeated when necessary.

FC test of boards.—The Perforator Extraction method (EN 120 2001) was followed with tests starting after 1 day of standing of boards at room temperature from board manufacturing. The 6 by 6-inch samples cut from larger boards or made on the small press that were to be tested after more than 1 day of standing were wrapped tight in Saran film, put in a sealed plastic bag, and kept in a refrigerator at 4°C until the day of testing. Tests were completed usually within 4 days of board manufacturing. Cutting boards into small test pieces was done about 0.5 hour prior to testing. Board samples tested had moisture contents of about 3.0 percent, and the resultant FC data were not corrected, although the standards are based on 6.5 percent moisture content of boards.

Physical and mechanical testing of particleboards.—Equilibrated boards were tested for internal bond (IB) strength (eight test pieces) and bending strengths (modulus of rupture and modulus of elasticity) (four test pieces) on an Instron machine (Norwood, MA, USA). Board densities were measured by measuring dimensions and weights of bending test samples. Water-soak thickness swelling and water absorption values (two test pieces) were measured at 20°C in a water bath according to ASTM D 1037-93. The 6 by 6-inch boards made on the small press were cut into two 2 by 2-inch samples and tested for 24-hour water-soak properties at 20°C in a water bath.

Results and Discussion

Synthesis reaction characteristics of DF resins in comparison with UF and UMF resin systems

An earlier report indicated that D reacts readily with formaldehyde with a base catalyst to form resin-like monomeric materials at an F/D mole ratio of 3.0, as shown above in the one resin synthesis procedure (Bentoniere and Rowland 1979). In our exploratory experiments, compound D was found to be sparingly soluble in water at room temperature but increasingly more soluble at higher temperatures; also that (1) D readily dissolves in 50 percent formaldehyde solution above 60°C under a mild alkaline pH of 7.0 or higher, indicating its ready reaction with formaldehyde to form hydroxymethyl groups; (2) the pH value of the resin synthesis reaction mixture slowly decreased from the initial set value of about 7.5 to 8.5 down to about 6.2 by itself during resin syntheses, similarly as in the first alkaline stage cook of UF resins (Kim, unpublished data, 2013); and (3) DF resins increased in viscosity relatively rapidly in this very mild acidic pH range, indicating a ready polymer formation through the formation of methylene bonds (Eq. 1). This pH range is quite different than UF resins, for which it needs to be acidified to pH 4.0 to 5.0 by adding an acid to advance the polymerization. The resultant (aqueous) DF resins were found to behave well, were clear, and were easily washable with water, unlike UF or UMF resins, of which dimers or trimers can often result in precipitates that are difficult to wash. It was found also that because there is no need of an acidification step and because DF oligomers are well soluble in water, the F/D mole ratio value in the polymerization step of DF resins can be any value above about 1.10, in contrast to UF resin systems, where the F/U mole ratio in the acidic polymerization step needs to be above about 1.80 to avoid formation of water-insoluble oligomers that disrupt further polymerization reactions (Kim and Amos 1990).

DF resin syntheses.—DF resins can be synthesized readily by either one-step or stepwise addition of D to the formaldehyde solution in mild alkaline/acidic pH ranges to reach the target F/D mole ratio values of 1.10 to 1.25 without an acidification step to pH 4 to 5. An acidification step is a must for UF resins, and changing the pH to the basic side for a urea addition in the middle of the acidic polymerization step is very difficult to carry out for various reasons (Kim 2013). It was also noted that the dissolution speed of D decreases as the resin mole ratio is decreased, similarly as observed in the addition of melamine in UMF resin syntheses (Kim 2013). One synthesis parameter that can affect resin-cooking characteristics is the mole ratio value effective in the polymerization step, and in DF resins, the type of phase disturbance observable in UF resins with F/U ratio values below about 1.80 was not observed for all mole ratios. Overall, the resultant differences in resin polymer properties arising from the different ways of adding D during resin synthesis could be different molecular-weight distributions, a useful parameter but not investigated in detail in this preliminary study. It is also noted that the pH of the reaction mixture that has gone down to about 6.2 by itself during the reaction, once the finished resin is cooled to room temperature, comes back to close to 7.0, which can be adjusted further by adding sodium hydroxide solution.

The starting F/D ratio is a parameter that would affect various resin characteristics; one extreme value of 5.00 was

examined, where the viscosity advancement was shown to be stalling, indicating that the polymerization reaction is inhibited as in UF resin synthesis at an initial F/U mole ratio of about 2.6 or higher (Kim and Amos 1990). Thus, intermediate Resin DF5.0 was shown to be viscosity stable for several months as expected and appeared useful as a stable formaldehyde source akin to the “UF Concentrates,” a technology used in UF resin manufacturing industries. This approach was tested in syntheses of scavenge-type DF resin products, in which mole ratios are significantly below 1.0. This type of DF resin appears feasible only if longer reaction times are used, although their effectiveness as scavengers was not investigated. Overall, D appears to behave just like urea but with a higher functionality in resin syntheses, as expected.

Copolymer DUF resins syntheses.—DUF copolymer resins, which could provide lower-cost alternatives, were synthesized at 10 to 20 percent urea levels by weight by advancing the DF resin components with an appropriate intermediate F/D mole ratio to an appropriate degree of polymerization, followed by adding urea and further reaction. In order to avoid a second shot of formaldehyde addition during resin cooking, the starting F/D mole ratio was precalculated based on the amount of urea to be added to reach to the target F/(D + U) mole ratio values, respectively, with about 10 and 20 percent levels of urea by weight. In this type of urea addition, the resins are expected to have all urea components be in monomeric forms and DF resin components in polymeric forms. In the second approach, the urea component was replaced with the polymerized intermediate Resin UF2.10 for syntheses of DUF resins at about 10 to 20 percent levels of urea. This second approach results in resins having most UF components in polymeric forms.

Copolymer DMF resins syntheses.—One difficulty in syntheses of UMF resins at low formaldehyde mole ratio values has been known to be the limited storage stability of resulting UMF resins due to the tendency of forming insoluble precipitates of oligomeric MF components, often leading to two-phase resin systems of short storage lives (Mao et al. 2013c). This can occur often if the addition point of melamine is such that MF components have to go through the pH range of 5.0 or below, the effective pH range needed for polymerization of UF components. Addition of melamine in UMF resins, therefore, has been commonly done after the acidic UF polymerization stage is over in the mild alkaline pH of 7.0 or higher, though the storage stability of UMF resins is still limited, especially at low mole ratios, and this restricts melamine levels in useful UMF resins to about 15 percent by weight relative to urea. On the other hand, since the pH range required in the polymerization stage of DF resins is only between about 6.0 and 7.0, melamine can be added at any point in syntheses of DMF resins with melamine levels of between 7.5 and 50.0 percent relative to the weight of D. However, since melamine itself is only sparingly soluble in water and therefore needs formaldehyde to react and go into solution, the melamine addition points in resin syntheses were accordingly varied to have some formaldehyde be available for reaction: in the beginning with D, in the middle point with a part of second D, and at the tail end of resin synthesis. In most cases, the resulting resins came out clear and were generally more stable than UMF resins in similar overall mole ratio ranges. Further, DMF resins containing 20 to 50 percent melamine

levels were synthesized by adding melamine in the first part of synthesis to allow an ample amount of formaldehyde to be available for melamine to react with, followed by adding more D with water. Overall, although the storage stability of DMF resins appeared better than UMF resins at equal melamine levels, melamine level effects on resin stability became increasingly apparent at 30 to 50 percent melamine levels, as shown, for example, by Resin 50%DMF1.05, which gelled in 4 days on standing at room temperature, and a similar thing happened after 5 days in the refrigerator.

Extent of polymerization and mole ratio of resins.—In this investigation, most DF, DUF, and DMF resins with low formaldehyde mole ratios in the range of 1.10 to 1.25 were synthesized in order to discover resin systems that can give the lowest possible FC values of boards. The extent of polymerization of resins, a major curing rate-determining parameter, was kept in the similar ranges by keeping resin solids contents in the narrow range of 60 to 62 percent by using appropriate amounts of water and also by keeping the ending viscosity value in the similar narrow ranges of H to K (G-H scale). Although the extent of polymerization is normally made higher for core-layer resins for fast pressing times and lower for face-layer resins to prevent pre-cure problems, this aspect of resin synthesis was not investigated in detail.

¹³C NMR structure determination of synthesized resins.—¹³C NMR spectra of Resins DF1.75, DF1.25, 83.0%DUF1.25, and 14.3%DMF1.20 are reported, respectively, in Figures 1A and 1B, Figures 2A and 2B, and Figures 3A and 3B and Figures 4A and 4B, and the spectral analysis data are collected in Table 2, including NMR data of UF resins and compound D for comparison. For compound D, there are shown two types of ethylene carbons in a 1:1 ratio (38.53; 47.44 ppm) and two types of carbonyl carbons in a 1:2 ratio (158.7; 159.6 ppm). In DF resins, these carbons were shifted by the introduction of formaldehyde-derived methylene or hydroxymethyl groups to the carbamide nitrogen atoms within the expected ranges in comparison with UF resins (Levy and Nelson 1972, Tomita and Hatono 1978). On the other hand, the formaldehyde-derived groups of DF, DUF, and DMF resins also show minor changes in chemical shift values from those of UF resins due to the presence of ethylene carbons in the molecule. The chemical shift values of formaldehyde-derived groups of DF and copolymer resins are hydroxymethyl (~63.6; 72 ppm), methylene-ether (~69.5; 74.0; 78.0 ppm), methylene (~46.5; 53.0 ppm), and free formaldehyde (~81.5 ppm) groups, which are all slightly different from those of UF resins (Kim and Amos 1990). This result leads to the conclusion that DF and copolymer resins are of similar chemical and polymeric structures as those of UF resins. A note to make in the quantitative estimation of the type I methylene group at 46.6 ppm in DF and copolymer resins is that the peak completely overlaps with one of the high-intensity ethylene carbons, discernible only as a shoulder peak and with the integration value not directly measurable. This integration problem is resolved by assuming the overlapping ethylene carbon value as equal to the integration value of another ethylene carbon peak at 37.44 ppm and subtracting it from the integration value of the overlapped peaks. Another note to make is the carbonyl carbon peaks of DF and copolymer resins appear in at least six major peaks, all relatively close to the two carbonyl carbon peaks of compound D and with their chemical shift

values appearing reasonable in view of the nitrogen atoms bonded to the hydroxymethyl or methylene groups in different ways. Detailed assignments of carbonyl carbons were not made at this time. Also, melamine carbons appeared as three broad peaks, and integration values indicate that more than a half of them reacted to form bonds to formaldehyde-derived groups.

However, some inaccuracy in peak integration values appears to be present, as shown by the high CH₂O/(D + U) ratio values of DF and DUF resins calculated directly from the integration values. It appears that there exists NMR sensitivity depression of carbonyl carbons, from which (D + U) integration mole values are derived, to result in raising the mole ratio values. Further, although the corresponding CH₂O/(D + M) value calculated for DMF resin resulted in a value close to the materials charge value, the melamine/D ratio came out lower at 0.13 versus the materials charge mole ratio of 0.37, indicating that melamine carbons are depressed more than DF resin's carbonyl carbons. These NMR effects are likely to be arising from the longer relaxation times of carbonyl and melamine carbons due to a lack of nearby hydrogen atoms in the molecules and different mobility of resin molecules due to high viscosities of resins (Levy and Craik 1984). These NMR problems need to be addressed in later studies to be able to define the accurate polymeric structure of DF resins, although it is natural to assume that branched polymer structures would be formed based on the tri-functionality of compound D. Also, it is not clear at this time whether there are copolymer bonds formed between D and urea or melamine molecules in the resin stage, though such bonds are expected to arise in the curing stage. Overall, NMR data lead to a conclusion that UF resin-like DF resin and DUF and DMF copolymer resin structures arise in resin syntheses.

Synthesis formulations of DF resins versus UF resins.—Table 3 shows the resin synthesis formulations based on making 100 g of DF and UF resins, having the same final mole ratio of 1.15 and the same resin solids levels of about 59 percent. It is readily seen that the amount of formaldehyde needed for DF resin is only 31 percent of that needed for UF resin due to the fact that the molecular weight of D (232) is 3.87 times greater than that of urea (60). Since adhesive resins are used in boards on the same weight basis, this fact would also indicate that cured DF resins' lifetime formaldehyde emission potentials are that much lower. The starting premise of this work of using a material of higher functionality (3) resulted in this formulation difference due to the two ethylene groups incorporated into the molecule of D.

Room temperature characteristics of DF and copolymer resins.—Synthesized DF and DUF and DMF copolymer resins at low F/D ratio values in resin solids ranges of 50 to 65 percent with viscosity values anywhere between D and X by the G-H scale were found to be clear and adequately stable for industrial uses somewhat better than current UF or UMF resins in most cases, as shown in Table 4 as viscosity increases of resins observed at room temperature over a period of 3 weeks. Resin storage stability of about 3 weeks is the common requirement in the US particleboard industry. Also, the free FC values of DF resins determined by the hydroxylamine method were less than 20 percent of the common values of UF resins at similar mole ratio values, which are also found in ¹³C NMR integration values in Table 1, in the 83- to 91-ppm region. This result is one

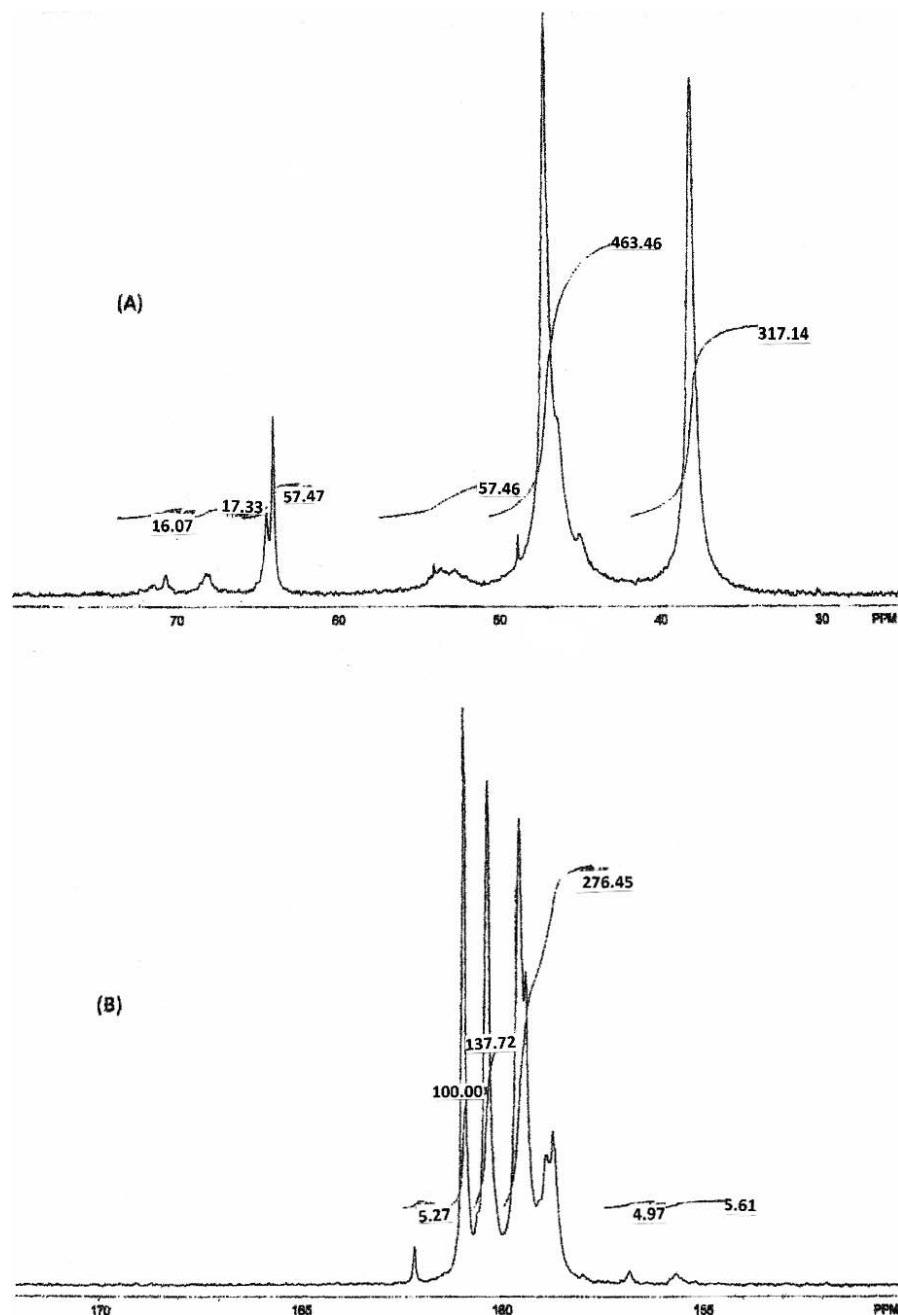


Figure 1.—¹³C NMR spectra of Resin DF1.25 with peak integration values: (A) aliphatic carbons and (B) carbonyl carbons.

validation for using a higher functionality monomer D. Also, it is noted that DMF resins synthesized with about 25 percent or higher melamine levels were found to have shortened storage lives, as shown in Table 3, but they might still be useful where the shelf-life requirement is less strict.

Pot lives and curing characteristics of DF and copolymer resins.—DF and copolymer resins were found to need ammonium sulfate-type acid latent catalysts for curing similarly as for UF resins. Gel times obtained with catalyzed DF and copolymer resins in Table 5 were comparable with those of UF resins at similar mole ratio values. Also shown in the table are the pot lives of catalyzed resins measured at 30°C, in which DF and copolymer resins show ample pot lives, longer than UF resins. Further, the curing pattern of

Resin DF1.75, shown as a time-temperature dynamic mechanical analysis (DMA) diagram in Figure 5, measured at 120°C according to a reported procedure (No and Kim 2005), presented the curing process with three curves: stiffness (rigidity), loss modulus, and tan delta (loss modulus/stiffness) curves. In DMA testing of thermosetting resins, the stiffness curve represents the emerging polymer networks that are conserving the exerting (dynamic) force, the loss modulus represents the uncured resinous phase that is mechanically associated with the polymer networks and thus is able to dissipate the energy of exerted force into heat energy, and the tan delta curve is simply their ratio (Lothouse and Burroughs 1978). In this test, both moduli are adjusted to be near at zero in the beginning, and

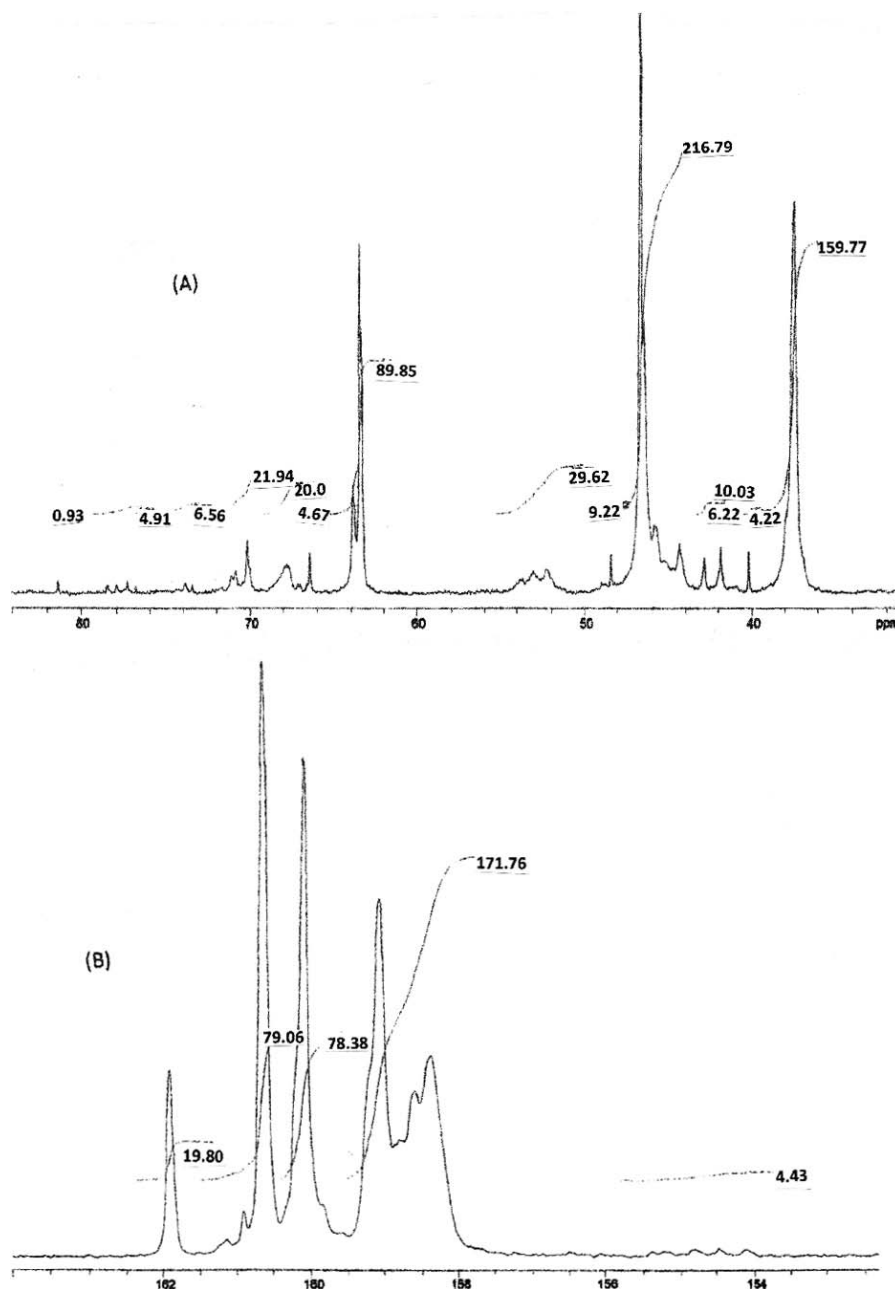


Figure 2.— ^{13}C NMR spectra of Resin DF1.75 with peak integration values: (A) aliphatic carbons and (B) carbonyl carbons.

therefore the starting tan delta value is not well defined, but as soon as some polymer networks emerge, that is, viscosity increases in this stage, the tan delta curve increases. In Figure 5, the tan delta curve arrives at a maximum with a value of about 1.4 at 2.0 minutes of cure time (i.e., the loss modulus increases faster than the stiffness (viscosity) curve in this period), and the maximum point indicates that some polymer networks are formed to span throughout the entire resin sample, that is, the gelation of resin sample is to be attained shortly after this point. The gelation point is typically defined to be where the tan delta value reaches 1.0 (Lofthouse and Burroughs 1978).

Then the curve decreases rapidly thereafter to pass through the 1.0 point and stabilizes at a value of about 0.5, which reflects the onset of the rubbery stage of resin

curing. The rubbery stage continues until it meets a broad maximum value of about 0.55 at 5 minutes. In this rubbery stage, the stiffness and loss moduli increase in parallel, indicating that the expanding polymer networks are also bringing resinous materials into the dynamic system, by association, to result in increased dissipation of the dynamic energy into heat energy. The broad maximum point attained indicates that the resinous phase available in the resin sample is reduced to such an extent that the expanding polymer networks add to the stiffness modulus but the loss modulus fails to begin increasing due to the lack of resinous materials. The test sample then starts to show more of the solid-like characters (i.e., the beginning of the vitrification stage), after which the tan delta curve decreases sharply (i.e., stiffness increases fast, and loss modulus also

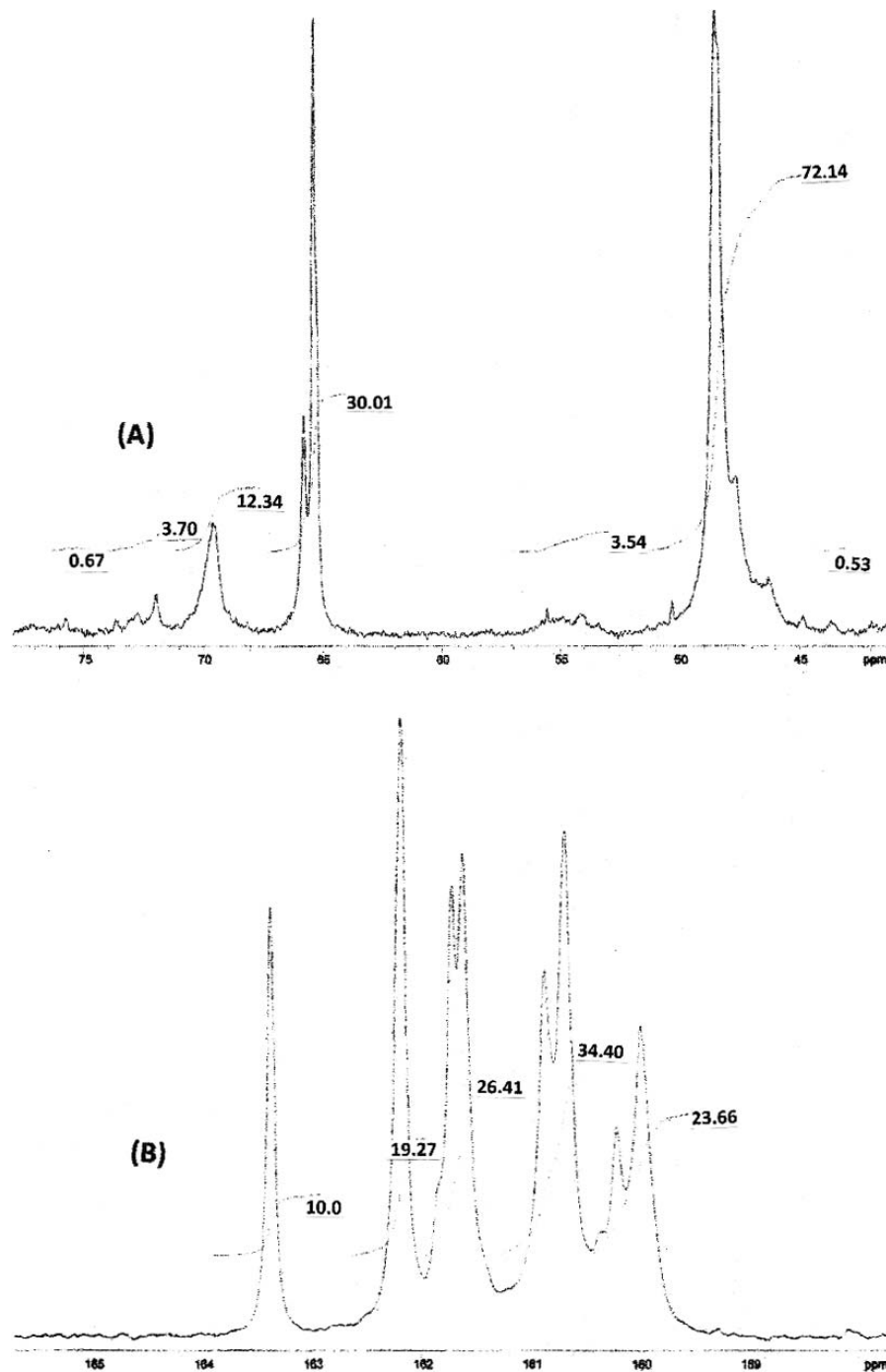


Figure 3.—¹³C NMR spectra of Resin 83.0%DUF1.25 with peak intergration values: (A) aliphatic carbons and (B) carbonyl carbons.

decreases), a rapid progression of vitrification process. A high stiffness value of about 1,300 GPa and a low tan delta value of 0.20 is reached at about 10 minutes of cure time, a completion of vitrification process. Afterward, the residual curing capacity in the resin sample allows a further, slow curing process to continue, and it reaches a stiffness value of 1,400 GPa and tan delta value of 0.15, measured at the curing temperature of 120°C, at 19 minutes. When the sample is cooled to room temperature, the stiffness will increase sharply, and tan delta value decrease substantially (although this was not measured in this study). The sample is considered to be fully cured at this point. Typical tan delta

values of 0.10 to 0.15 at room temperature are indicated for cured thermosetting polymers (Ferry 1980). Also, this DMA curing pattern of Resin DF1.75 is very similar to those of UF resins reported (No and Kim 2005). Overall, synthesized DF and copolymer resins were concluded to be closely similar in the curing speed and cured strength values with UF resins of similar mole ratios, indicating that generally known UF resins' hot-pressing parameters can be used for laboratory bonding of particleboard: a press temperature of 350°F and 3.0 or 3.5 minutes of press times for 0.5-inch-thick boards and so on.

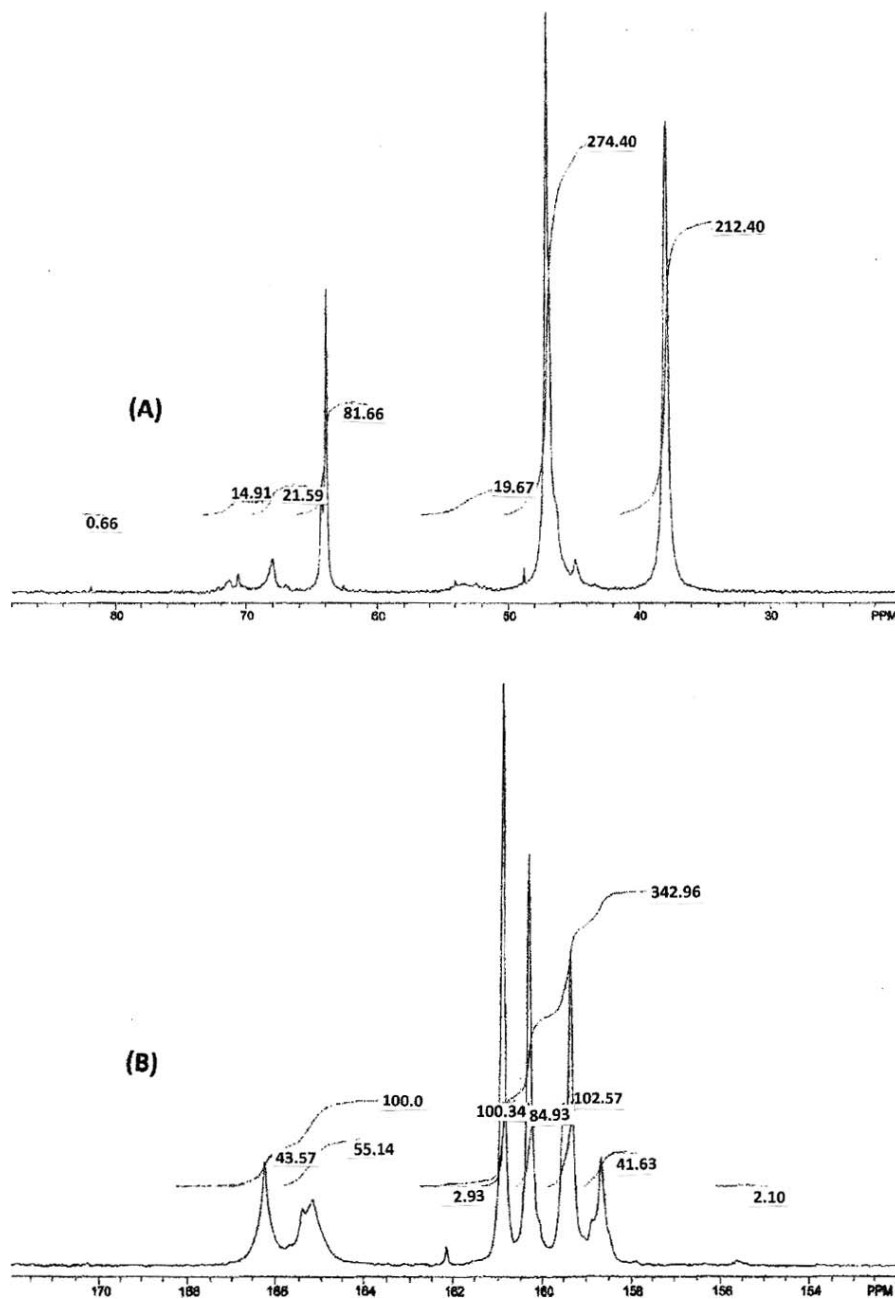


Figure 4.—¹³C NMR spectra of Resin 14.3%DMF1.20 with peak integration values: (A) aliphatic carbons and (B) carbonyl carbons.

Particleboard preparation.—Catalyzed DF resins' adequate pot lives allowed adequate resin and wax spraying efficiency and also ample mat-forming times as with UF resins. Further, the hot pressing of boards (22 by 22 by 0.5 inches) went well with the usual 8 to 12 percent mat moisture content values, and, further, the hot-pressing schedule and hot-pressing times were the same as those used for UF resins, indicating that DF resins would require, if any, only minimal modifications in the board manufacturing processes of industry. However, in the course of making and testing many 6 by 6 by 0.5-inch boards in the laboratory, it was noticed that DF resins need about 14 percent mat moisture contents in the face layers and that the optimum pressing temperature was about 275°F to 300°F versus 325°F to 350°F for UF resins, indicating DF resins'

slightly faster curing speeds in comparison with UF resins of similar resin mole ratios.

Test results of particleboards.—Test results of 22 by 22 by 0.5-inch laboratory boards are shown in Table 6. All boards showed similar board density values to allow board properties to be compared directly among themselves, and boards prepared for comparison using laboratory-synthesized UF resins gave satisfactory IB, modulus of elasticity, modulus of rupture, and 24-hour water-soak weight gain and thickness swelling values, as expected. Also, FC values of these boards were at 12 to 14 mg/100 g of wood, in agreement with reported values (Go 1991; Graves 1993; Kim et al. 2003; No and Kim 2004, 2007). Boards made with DF resins in both core and face layers and also those made with DF resins in the core layer and UF resins in face

Table 2.—¹³C NMR analysis results of various resins and compound D. Chemical shift values (parts per million [ppm]) and integration values in percentages among aliphatic groups and among carbonyl or melamine ring carbons (%).^a

Chemical groups	UF (ppm)	UF 1.15 ^b	DF 1.25	DF 1.75	14.3%DMF1.20	83.0%DUF1.25	DF/DMF (ppm)	D (ppm)
Formaldehyde-derived group (%)								
Free CH ₂ O	91.0	0.51	0	0	0	0		
	87.0	0.06	0	0	0	0		
	83.1	0.18	0	0.40	0.32	0	81.5	
Total		0.75	0	0.40	0.32	0		
Methylene-ether	79.1	1.67	0	2.12	0	0.86	78.0	
	75.1	4.24	0	2.97	0	2.40	74.0	
	69.5	10.46	5.90	8.65	10.0	15.97	69.0	
Total		16.37	5.90	13.74	10.0	19.23		
Hydroxymethyl	72.0	11.12	5.13	9.49	7.5	2.40	70–72	
	65.2	39.94	19.57	38.87	40.0	38.87	63.6	
	Total		42.06	24.70	48.39	47.5	41.27	
Methylene	60.1	4.60	0	0	0	0		
	53.9	21.83	19.56	12.81	9.8	4.58	52–54	
	47.4	14.35	49.32	24.66	30.0	34.82	46.46	
Total (G. total i) ^c		40.78 (712)	68.88 (293)	37.47 (235)	39.8 (200.5)	38.40 (77.3)		
Carbonyl carbons (%)								
Amide C=O carbons	164.0	16.51	1.01	5.70	1.1	10.00	161.9	159.6
	162.2	30.49	19.25	22.64	36.4	19.27	160.7	159.6
	160.7	50.18	26.52	22.44	25.8	28.41	160.1	159.6
	158.0	2.81	53.22	49.22	10.2	34.30	159.1	158.7
			53.22	49.22	19.7	23.65	158.6	158.7
(G. total i)			53.22	49.22	6.8		158.4	158.7
Melamine carbons					46.4		166.2	
					24.8		165.4	
					28.8		165.2	
(G. total i)					(37.9)			
M/D mole ratio					0.13			
(G. total i)		(606)	(519)	(349)	(540)			
Calculated CH ₂ O/(D + M + U)		1.17	1.70 ^d	2.02 ^d	1.11	1.70 ^d		
Ethylene carbons					Carbon (%)			
			50	50	50	50	46.67	47.44
			50	50	50	50	37.44	38.53

^a See Table 1 for abbreviations.

^b UF resin data from Kim et al. (2003) (15-day stored resin).

^c G. total i = total of actual integration values of formaldehyde-derived groups or carbonyl carbon or melamine carbons from which resin mole ratios were calculated. NMR data of compound D and Resin DUF 1.25 were obtained in DMSO-d₆, and chemical shift values (not shown) are slightly changed in comparison with those of other resins that were obtained neat (no solvent) or with D₂O as solvent.

^d These calculated values are greater than charged mole ratios due to lowered sensitivity of carbonyl groups than aliphatic groups.

layers show some scatter in the physical data, but they are judged to be comparable with boards bonded with UF resins.

On the other hand, FC values of boards bonded with DF resins in the core layer only or in core or face layers are reduced by 75 to 80 percent in comparison with same mole ratio UF resins: DF resin mole ratio values between 1.15 and 1.35 show FC content values of 2.3 to 4.4 mg/100 g of boards, significantly below the new emission standards of about 8.0 mg/100 g of wood (Athanasiadou et al. 2009). The fact that DF resins used in the core layer only or in both

face and core layers show similarly low FC values indicates that DF resins, which are expected to be higher in price than UF resins, can be used only in core layers to save overall resin costs. Further, four sets of test results of commercial (C) UF or CUMF resins derived as trial resin binders from nearby particleboard plants over a period of time, evaluated in this laboratory, showed low strength values and high FC values, reflecting the hectic transition period being experienced by the particleboard industry since the new formaldehyde emission regulations were published (State of California 2007; US Senate Bill 2011).

Table 3.—Comparison of formulations for syntheses of 100 g of DF and UF resins.^a

Mole ratio	Resins	D or urea weight (g)	50% formaldehyde solution (g)	Water (g)	Resin solids content (%)	Total resin weight (g)
1.15	DF	55.16	16.42	28.42	59.0	100.0
	UF	46.51	53.49	0	59.0	100.0

^a See Table 1 for abbreviations.

Table 4.—Stability of resins at room temperature (~22°C) measured by viscosity changes and formaldehyde contents of selected resins.^a

Days	0	3	4	5	6	7	8	10	12	14	17	20	21	23	24	CH ₂ O content
UF1.05	G				H		I	J			K		P			0.12%
DF1.15	F			G						G	G	GH				0.02%
15%UMF1.05	I	J		J				K		M			P			0.01%
7.5%DMF1.25	I													N		0.03%
15.0%DMF1.25	E													I		—
17.5%DMF1.15	E			EF					EF				I			—
25%DMF1.15	F	F			FG		GH	H			I					—
30%DMF1.05	I	IJ				J	K	K	L	MN	NO	R			T	—
35%DMF1.05	H	K	O			W										—
50%DMF1.05	D		T													—
80%DUF1.20	HI					HI		HI	I	IJ		J	K		KL	—

^a See Table 1 for abbreviations.

Table 5.—Pot lives observed by viscosity changes in hours at 30°C and gel times at 100°C of resins catalyzed with 1.0 percent ammonium sulfate solution (25%).^a

	0 h	2.25 h	6.0 h	10.5 h	17.5 h	24.0 h	30.0 h	Gel time (s)
DF1.10	D	E	EF	FG	I	J	J	91
DF1.15	D	E	F	GH	J	K	MN	75
DF1.25	E	F	GH	HI	P	TU	V	77
80%DUF1.20	E	F	G	H	O	Q	T	84
8.8%DMF1.10	D	E	G	J	N	RS	U	80
UF1.10	E	F	Gel					88

^a See Table 1 for abbreviations.

Table 7 shows the test results of synthesized DF and UF and 15% UMF resins used for bonding small 6 by 6 by 0.5-inch boards, conducted to confirm the results of the larger boards discussed above. Physical tests were limited to 24-hour water-soak tests done with two 2 by 2-inch samples, and FC values were obtained mostly 1 day after the board making. (FC test values obtained with boards that showed unsatisfactory water-soak test results of above 50 percent water absorption and 25 percent thickness swell values are omitted in this article.) Some variations appear to be involved in test results due to inconsistencies incurred in

hand-operated hot pressing and also in hand blending of resin/wax on wood. First, it is noted that FC test values of 6 by 6-inch boards in Table 7 (and all boards in subsequent Tables 8 and 9) are slightly higher than the results of larger boards in Table 6: this might be coming partly from the higher resin loading levels of 10.0 versus 8.0 percent used for larger boards. These FC values still confirm the overall capability of DF resins for formaldehyde emission reduction in comparison with those of UF resins of mole ratios of 1.15 to 0.95, which showed FC values in the range of 16.6 to 6.3 mg/100 g wood, and also with those of 15.0%UMF resins of

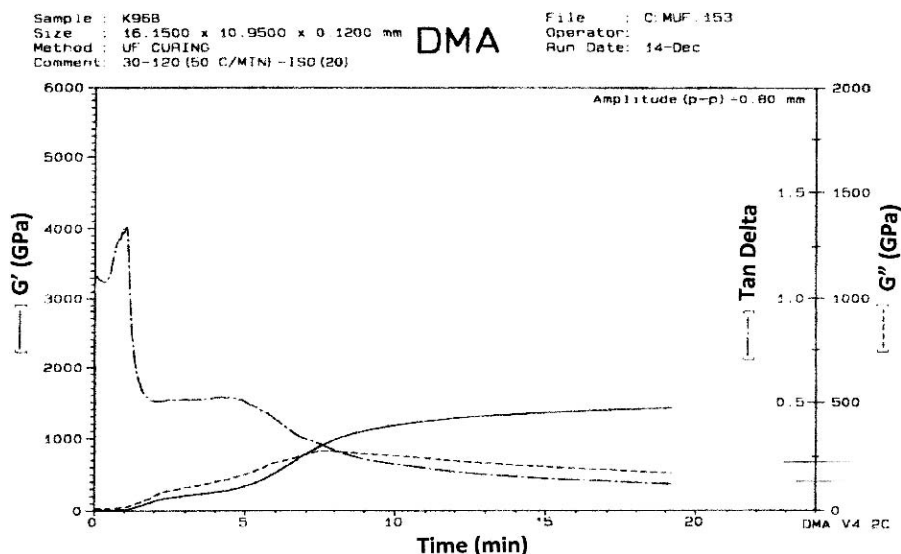


Figure 5.—Curing test of Resin DF1.75 on DMA983 using an isothermal scan at 120°C.

Table 6.—Test results of DF resins alone or in combination with UF resins in core and face layers of 22 by 22 by 0.5-inch laboratory boards: board density, internal bond (IB), 24-hour water absorption (WA) and thickness swell (TS), and formaldehyde contents (FC).^a

Face layer	Core layer ^b	Board density	IB (psi)	MOE (kpsi)	MOR (psi)	24-h WA (%)	24-h TS (%)	FC (mg/100 g)
UF1.05	UF1.10	0.77	123	280	1,559	54	19	12.8
	UF1.20	0.79	119	224	1,550	40	18	14.4
CUF	CUF	0.77	109	248	1,556	45	16	24.5
CUF	CUF	0.78	63	187	905	44	24	13.6
CUMF	CUMF	0.78	76	143	781	29	10	11.1
CUF	CUMF	0.79	72	135	932	40	18	8.5
DF1.30	DF1.40	0.78	104	256	1,377	39	20	3.0
DF1.25	DF1.25	0.80	160	297	2,196	42	15	1.8
DF1.20	DF1.20	0.78	94	225	1,259	43	17	1.6
UF1.05	DF1.10	0.77	100	210	1,056	48	20	2.3
	DF1.20	0.79	94	226	1,188	46	18	2.8
	DF1.30	0.79	139	142	1,362	45	18	3.9
	DF1.35 A	0.76	139	261	1,881	44	20	4.0
	DF1.35 B	0.78	148	246	1,781	47	22	4.4
	DF1.35 C	0.78	147	235	1,460	50	26	2.9
	DF1.35 D	0.76	142	250	1,777	54	20	3.9

^a See Table 1 for abbreviations. MOE = modulus of elasticity; MOR = modulus of rupture.

^b A, B, C, and D indicate different batches of DF resin preparation. Boards were pressed at 350°F for 3.0 and 3.5 minutes and averages obtained. Commercial UF (CUF) and CUMF resins are industrial UF or UMF resins that were going through mill trials in board plants in Mississippi in 2012.

mole ratios of 1.35 to 1.05, with FC values of 31.2 to 11.5 mg/100 g wood in this table. Another note to make is that FC values of boards bonded with DF resins having various mole ratio of 1.55 to 1.15 in the face and core layers show their dependency on the mole ratio of resins, similar to the results of UF or UMF resins, indicating that DF resins also have to contend with the reverse relationship between hot-pressing times and resin mole ratios in the case of seeking ultralow FC values.

Boards bonded with 15%UMF resins show FC values that are not much different than similar mole ratio UF

resins in Table 7, but their water-soak properties indicate sizable improvements over UF resins, partly agreeing with reported results of boards made with UF or UMF resins having low levels of melamine (Sun et al. 2011; Mao et al. 2013a, 2013b, 2013c). UMF resins having mole ratio values less than 1.0 could provide some advantage in practice, especially in formulating face-layer resins. Finally, we also examined a particleboard found in our wood shop and one particleboard and one MDF board sold as piece goods in nearby hardware stores. FC values of all boards were low as boards bonded with UF resins,

Table 7.—Test results of various DF, UF, and UMF resins as binders of 6 by 6 by 0.5-inch particleboards made by hot pressing at 350°F for 3.5 minutes and 50-pound-per-cubic-foot (pcf) target density.^a

Face resin mole ratio	Core resin mole ratio	24-h WA (%)	24-h TS (%)	Formaldehyde content (mg/100 g)
UF1.05	DF1.25	36.4	12.2	4.5
UF1.00	DF1.15	42.9	22.9	3.5
UF1.05	UF1.15	33.3	14.7	16.6
UF1.05 in face and core		28.8	11.7	12.2
		28.0	12.5	9.2
UF1.00 in face and core		35.4	12.7	8.6
UF0.95 in face and core		37.3	18.4	6.3
DF3.00 in face and core		14.4	5.6	61.6
DF1.55 in face and core		29.5	14.7	8.7
DF1.45 in face and core		47.7	22.4	7.0
DF1.35 in face and core		40.4	19.5	4.5
DF1.25 in face and core		39.7	26.8	4.5
DF1.15 in face and core		40.0	22.0	4.2
15%UMF1.35 in face and core		28.0	8.8	31.2
15%UMF1.25 in face and core		33.0	9.1	25.8
15%UMF1.15 in face and core		29.5	10.0	16.0
15%UMF1.05 in face and core		29.5	10.0	11.5
UF resin-bonded commercial boards		65.1	27.5	3.6 ^b
		16.6	7.6	5.9 ^c
		17.8	6.8	5.0 ^d

^a See Table 1 for abbreviations. WA = water absorption; TS = thickness swelling.

^b Particleboard, 40 pcf, old piece found in wood shop.

^c Particleboard, 50 pcf, piece good from Lowe's.

^d MDF, 37 pcf, piece good from Home Depot, all in June 2012.

Table 8.—Test results of DUF resins as binders of 6 by 6 by 0.5-inch particleboards made by hot pressing at 350°F for 3.5 minutes and 50-pound-per-cubic-foot target density.^a

Face resin mole ratio	Core resin mole ratio	24-h WA (%)	24-h TS (%)	Formaldehyde content (mg/100 g)
33.0%DUF1.15 ^b	66.0%DUF1.15	44.2	19.6	8.1
	50.0%DUF1.15	51.5	24.0	10.6
	33.0%DUF1.15	43.0	17.0	12.6
94.5%DUF1.35	84.0%DUF0.95	44.0	22.4	4.0
89.9%DUF1.15	89.9%DUF1.15	36.6	21.3	4.1
88.1%DUF1.15	85.3%DUF1.05	42.5	25.0	4.7
77.0%DUF1.15	77.0%DUF1.15	53.0	30.0	5.2
79.7%DUF1.25	79.7%DUF1.25	49.0	25.5	6.4
80.1%DUF1.35	72.2%DUF1.05	27.6	11.1	5.0
74.8%DUF1.15	72.2%DUF1.05	33.6	16.8	4.4
UF1.05	81.0%DUF1.30	22.3	14.9	8.7
	79.7%DUF1.25	30.8	14.8	7.5
	77.0%DUF1.15	33.5	19.2	8.3

^a See Table 1 for abbreviations. WA = water absorption; TS = thickness swelling.

^b 33.0%DUF1.15 means 33.0 percent D and 77.0 percent urea in the resin with an F/(D + U) ratio of 1.15 and so on.

indicating possibly that a long time elapsed since the boards were produced or that some treatments were done on them and a very low mole ratio resin used in case of the first board.

Table 8 shows the test results of selected synthesized DUF copolymer resins used for bonding 6 by 6 by 0.5-inch boards, conducted to find the effect of urea addition to DF resins to possibly find a way to lower the cost of DF resin.

Table 9.—Test results of DMF resins as binders of 6 by 6 by 0.5-inch particleboards made by hot pressing at 350°F for 3.5 minutes and 50-pound-per-cubic-foot target density.^a

Face resin mole ratio ^b	Core resin mole ratio	24-h WA (%)	24-hTS (%)	Formaldehyde content (mg/100 g)
15.0%DMF1.30 ^c	DF1.20	35.1	16.1	4.8
17.5%DMF1.15	7.5%DMF1.25	31.4	15.1	5.2
17.5%DMF1.25H	DF1.20	39.2	17.7	3.3
17.5%DMF1.25J	DF1.20	41.1	15.4	4.4
17.5%DMF1.25M	DF1.20	45.2	19.0	3.6
17.5%DMF1.30	DF1.20	35.1	16.1	4.3
25.0%DMF1.05	DF1.15	41.0	21.0	4.1
	17.5%DMF1.15	26.5	22.0	4.6
30.0%DMF1.05	DF1.25	30.1	15.9	4.8
35.0%DMF1.05	DF1.15	30.7	14.6	4.1
	17.5%DMF1.15	29.1	13.7	4.4
35.0%DMF1.05	17.5%DMF1.15	35.1	13.4	4.5
UF1.05	15.0%DMF1.15	40.7	14.1	4.6
Face and core resin	Mole ratio			
7.5%DMF	1.25	37.6	20.2	5.4
	1.40	40.0	21.0	7.8
10.2%DMF	1.35	45.2	23.8	5.2
	1.31	52.5	30.4	4.6
	1.25	46.6	24.4	4.8
	1.45	41.0	18.9	8.4
15.0%DMF	1.35	43.0	18.6	6.0
	1.25	44.9	14.9	4.2
	1.22	48.9	25.5	4.1
	1.20	47.7	22.9	4.2
	1.15	43.5	24.8	4.1
20.0%DMF	1.28	42.8	16.8	4.5
	1.15	43.5	24.8	4.1
25.0%DMF	1.15	33.3	13.9	4.2
30.0%DMF	1.10	26.7	12.8	4.2
	1.05	27.3	11.3	3.4
	1.00	30.6	11.9	2.6
	0.95	38.2	14.8	2.5
35.0%DMF	1.05	35.5	12.0	3.9

^a See Table 1 for abbreviations. WA = water absorption; TS = thickness swelling.

^b H, J, and M indicate different resin repeat batches.

^c 15.0%DMF1.30 means 15.0 percent melamine and 85.0 percent D in the resin with an F/(D + M) mole ratio of 1.30 and so on.

The results show that addition of urea by more than about 15 percent in either core or face-layer resins decreases the formaldehyde reduction efficiency significantly, raising the FC values of boards above about 5.0 mg/100 g wood. This effect, effected by relatively small urea addition levels, can be understood by the fact that a U/D ratio of 15 percent to 85 percent by weight, for example, means a ratio of about 40 percent to 60 percent by mole values, increasing the total formaldehyde charge in the synthesis of resin more than it appears. Also, the urea components variation of using pure urea or the intermediate Resin UF2.10 in DUF resin syntheses did not appear to make much difference in the FC values of boards.

Table 9 shows the test results of various synthesized DMF copolymer resins used for bonding 6 by 6 by 0.5-inch boards in the face and core layers or in combination with DF resins in core layers, conducted to find the effect of adding melamine at 7.5 to 35.0 percent levels to DF resins. The data indicate that FC values are not much affected by up to about 25 percent melamine levels in comparison with DF resins in mole ratio ranges of 1.15 to 1.30, giving FC values of about 3.3 to 5.2 mg/100 g wood, significantly below the new regulation limits (Athanasidou et al. 2009). With lower mole ratios and high melamine levels of resins, the FC values can go down to near 3.0 mg/100 g wood with decent water-soak properties. The positive effect on water-soak test values of melamine in DMF resins could be utilized for formulating face-layer resins and similarly for UMF resins in comparison with UF resins.

Historical perspectives on formaldehyde emission values of particleboard.—Table 10 shows the strength properties and formaldehyde emission values of particleboards reported in the literature for UF resins and 5 to 20 percent melamine-containing UMF resins with known (face-core) average mole ratio values. For UF resins, mole ratio values of 1.15 to 1.20 show relatively good strength values but high FC values of 13.0 to 23.0 mg/100 g wood, generally agreeing with the results of this study. At mole ratio values of 1.10 to 1.05, the IB strength values are poor, probably in the unacceptable ranges, and, for example, the FC value of

Resin UF0.95 still remains relatively high in the range of 6.0 mg/100 g boards. For boards made with UMF resins, which have been experimented mostly in the laboratory studies until recently, the board strength values remain relatively good at a mole ratio of 1.05, and FC values are in the range at about 7.0 mg/100 g boards, just on the borderline of the current regulation limit in the United States. However, the fact that resin mole ratios of 1.15 to 1.25 are known to be needed for core-layer resins in order to have the hot-pressing speed necessary to maintain the historical productivity of US particleboard and MDF manufacturing plants indicates that the emission problems are difficult to solve with resins of mole ratios 1.10 and below. In this regard, DF and copolymer resins appear to be fitting well to come in the industry with adequate resin mole ratios and very low FC values. An interesting note to make is the very high FC value of 61.3 mg/100 g wood reported in 1982 of an industrial particleboard (Roffael, et al. 1982), about ten times the current regulation limit values. The industry had come a long way to the recent past FC value of about 13 mg/100 g wood, which corresponds to only about 0.15 percent of the amount of formaldehyde used in the synthesis of resin. The fact that a small fraction of the formaldehyde used in resin syntheses causes a big emission problem, due to the reversibility of hydroxymethyl groups as reported (De Jong and De Jonge 1952a, 1952b, 1953), indicates the difficulties of the task at hand. Also, the data of DF and copolymer resins appear to be proving the underlying reversibility theory of hydroxymethyl groups in resins and the appropriateness of the approach taken in this study.

Conclusion

Synthesis procedures of DF resins were found to be relatively simple because of there being no need of an acidic pH adjustment step during the cook, and resulted mostly in clear stable resins under the various synthesis conditions. D can be added to aqueous formaldehyde solution all at once or in any number of portions to achieve any target F/D ratio values. D readily reacts with formaldehyde to form hydroxymethyl groups at above 60°C under mild alkaline

Table 10.—Small-chamber formaldehyde emission (FE-SC) values, perforator (FC) values, and physical property values of particleboards bonded with various-mole-ratio UF and UMF resins reported in the literature.^a

Resin mole ratio	UF resin					UMF resin					
	Formaldehyde content (mg/100 g)	FE-SC (ppm)	TS (%)	IB (psi)	Reference ^b	Melamine (%)	FC (mg/100 g)	FE-SC (ppm)	TS (%)	IB (psi)	Reference ^b
1.50	61.3				A						
1.40	32.7				A						
1.28						13.5		0.23	29.1	64	C
1.25	19.0	0.32	28.0	122	D	20.0	10.1	0.14	26.0	217	D
	26.0			120	B	10.0	13.0	0.17	26.0	138	D
1.15	13.0	0.16	32.0	119	D	20.0	7.0	0.10	25.0	189	D
	17.0	0.19		138	E	10.0	10.0	0.14	27.0	167	D
	18.0			105	B	15.0	16.0		10.1	—	D
1.10	13.0			80	B						
1.05	13.0			90	B	10.0	7.0	0.12	28.0	152	D
	7.0			79	B	5.0	7.0	—	16–27	90–134	F
0.95	6.0			42	B						

^a See Table 1 for abbreviations. TS = thickness swelling; IB = internal bond.

^b References: (A) Roffael et al. (1982) (industrial board); (B) Go (1991); (C) Sun et al. (2011); (D) No and Kim (2007); (E) Kim et al. (2003); (F) Mao et al. (2013a, 2013b, 2013c). All are lab boards except boards of reference A.

pH and further to form methylene bonds between molecules in the mild acidic pH range of 6.2 to 7.0, attained without pH adjustments, to result in viscosity increases to any target values. This result indicates that current resin manufacturing industries can carry out DF resin manufacturing without modification of resin reactors. DF polymers in finished resins are well soluble in water with little chance of phase separation during the storage of resins. DF resins show adequate storage lives at room temperature and also have curing parameters that are as fast as those of UF resins, indicating that current board manufacturing industries do not need any modification on their board hot-pressing lines. Particleboards bonded with DF resins used in the core layers only or in both core and face layers show similarly good physical properties as UF resins in the same mole ratio ranges, and FC values of boards bonded with DF resins are less than UF resins by about 75 to 80 percent. The FC values of 2.3 to 4.4 mg/100 g boards obtained with DF resins correspond to emission levels significantly below the current US regulation limits.

DUF and DMF copolymer resins were found to be synthesized also readily by adding urea or melamine, respectively, in the middle or later part of the synthesis of DF resins. DUF copolymer resins were limited to have up to about 15 percent urea by weight due to increases in the FC values of boards. DMF copolymer resins were found to be storage stable up to about 25 percent of melamine levels and performed well as particleboard binders. DMF resins did not show much improvement in FC values in comparison with DF resins, but some improvements in physical strength properties of boards were observed, indicating that some reduction of resin solids loading levels of boards would be possible in industry and thus reduce the FC values. Overall, the small FC values of boards bonded with DF and copolymer resins indicate that the reversibility of hydroxymethyl groups in resins is suppressed proportionately to the higher functionality of base monomer D, proving the underlying theory as well as the appropriateness of the approach taken in this study.

Acknowledgment

This research was funded in part through a research contract between MP Resins Inc. and the National Science Foundation SBIR program (IIP-0912773).

Literature Cited

- Athanassiadou, E., S. Tsiantzi, and C. Markessini. 2010. Producing panels with formaldehyde emission at wood level. *In: Proceedings of the 7th European Wood-Based Panel Symposium*, October 13–15, 2010; European Panel Federation and Wilhelm Klauwitz Institute, Hanover, Germany. pp. 110–117.
- Bentoniere, N. R. and S. P. Rowland. 1979. Durable-press cotton with improved retentions of strength and abrasion resistance via N-methylolpolyethyleneurea D. P. 2. *J. Appl. Polym. Sci.* 23:2567–2577.
- De Jong, J. I. and J. De Jonge. 1952a. The formation and decomposition of dimethylolurea. *Recl. Trav. Chim. Pays-Bas* 71:661–667.
- De Jong, J. I. and J. De Jonge. 1952b. The reaction of urea with formaldehyde. *Recl. Trav. Chim. Pays-Bas* 71:643–660.
- De Jong, J. I. and J. De Jonge. 1953. Kinetics of the formation of methylene linkages in solutions of urea and formaldehyde. *Recl. Trav. Chim. Pays-Bas* 72:139–157.
- European Committee for Standardization. 2001. Wood based panels—Determination of formaldehyde content—Extraction method called the perforator method. European Standard EN 120. European Committee for Standardization, Brussels.
- Ferry, J. D. 1980. *Viscoelastic Properties of Polymers*. 3rd ed. Wiley, New York.
- Flory, J. P. 1953. *Polymer Chemistry*. Cornell University Press, Ithaca, New York.
- Go, A. T. 1991. Low emitting particleboard UF resins. *In: Proceedings of the 25th International Particleboard and Composite Materials Symposium*, T. M. Maloney (Ed.); Washington State University, Pullman, Washington. pp. 285–289.
- Graves, G. 1993. Formaldehyde emission control via resin technology. *In: Proceedings of the 27th International Particleboard and Composite Materials Symposium*, T. M. Maloney (Ed.); Washington State University, Pullman, Washington. pp. 221–232.
- Innovation Group. 2006. *UF Resins: A Report on UF Resins*. Innovation Group, Morristown, New Jersey.
- Kennedy, H. J. 2006. The North American wood adhesives market. *In: Wood Adhesives 2005*. C. R. Frihart (Ed.). Forest Products Society, Madison, Wisconsin. pp. 33–38.
- Kim, M. G. 2013. Diethylene tricarbamide and diethylene tricarbamide-formaldehyde resins. US patent 8,604,239 B2.
- Kim, M. G., and L. W. Amos. 1990. Quantitative ¹³C NMR study of urea-formaldehyde resins in relation to the formaldehyde emission levels. *Ind. Eng. Chem. Res.* 29(2): 208–212.
- Kim, M. G., S.-Y. Lee, and B. Sukhbaatar. 2019. Syntheses of diethylene tricarbamide (DF) and copolymer resins and their low formaldehyde-emitting binder performance of wood composite board. *Forest Prod. J.* (in press).
- Kim, M. G., B. Y. No, S. M. Lee, and W.-S. Nieh. 2003. Examination of selected synthesis and room temperature storage parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C NMR spectroscopy. *J. Appl. Polym. Sci.* 89:1896–1917.
- Levy, G. C. and D. J. Craik. 1984. *In: Topics in Carbon-13 Spectroscopy*. Vol. 4. G. C. Levy (Ed.). Wiley Interscience, New York.
- Levy, G. C. and G. L. Nelson. 1972. *Carbon-13 NMR for Organic Chemists*. Wiley-Interscience, New York. pp. 38–135.
- Lofthouse, M. G. and P. J. Burroughs. 1978. Material testing by dynamic mechanical analysis. *J. Therm. Anal.* 13:439–453.
- Mao, A., E. B. Hassan, and M. G. Kim. 2013a. Investigation of UF and UMF resins aimed at lowering the formaldehyde emission potentials of wood composite boards. *BioResources* 8(2):2453–2469.
- Mao, A., E. B. Hassan, and M. G. Kim. 2013b. Low mole ratio UF and UMF resins entailing uron-type methylene-ether groups and their low formaldehyde emission potentials. *BioResources* 8(2):2470–2486.
- Mao, A. E. B. Hassan, and M. G. Kim. 2013c. Low mole ratio urea-melamine-formaldehyde resins entailing increased methylene-ether group contents and their formaldehyde emission potentials of wood composite boards. *BioResources* 8(3):4659–4675.
- Myers, G. E. 1983. Formaldehyde emission from particleboard and plywood paneling: measurement, mechanism, and products standards. *Forest Prod. J.* 33(5): 27–37.
- Myers, G. E. and J. A. Koutsky. 1990. Formaldehyde liberation and cure behavior of urea-formaldehyde resins. *Holzforschung* 44 (2):117–126.
- No, B. Y. and M. G. Kim. 2004. Syntheses and properties of low-level melamine-modified urea-melamine-formaldehyde resins. *J. Appl. Polym. Sci.* 93:2559–2569.
- No, B. Y. and M. G. Kim. 2005. Curing properties of low level melamine-modified urea-formaldehyde particleboard binder resins studied with dynamic mechanical analysis (DMA). *J. Appl. Polym. Sci.* 97:377–389.
- No, B. Y. and M. G. Kim. 2007. Evaluation of melamine-modified urea-formaldehyde (UMF) resins as particleboard binders. *J. Appl. Polym. Sci.* 106:4148–4156.
- Plath, L. 1967. Einfluss von Presszeit und Presstemperatur auf die Formaldehyd-Abspaltung. *Holz Roh- Werkst.* 25(2):63–67.
- Roffael, E., H. Miertzsch, and W. Menzel. 1982. Post treatment of particleboards for reduction of formaldehyde emission capacity. *Adhäsion* 26(3):18–23.
- Sigvartsen, T. and M. Dunky. 2006. New adhesive development to meet the challenges of tomorrow. *In: Wood Adhesives 2005*. C. R. Frihart (Ed.). Forest Products Society, Madison, Wisconsin. pp. 23–28.
- State of California. 2007. Proposed regulation order—Airborne toxic control measure to reduce formaldehyde emission from composite wood products. Section 93120. State of California, Sacramento.

- Sun, Q.-N., C.-Y. Hse, and T. F. Shupe. 2011. Characterization and performance of melamine enhanced urea formaldehyde resins for bonding southern pine particleboard. *J. Appl. Polym. Sci.* 119:3538–3543.
- Tomita, B. and S. Hatono. 1978. Urea-formaldehyde resins. III. Constitutional characterization by ^{13}C Fourier transform NMR spectroscopy. *Polym. Sci. Polym. Chem.* 16:2509–2525.
- US Senate Bill. 2011. The Formaldehyde Standards for Composite Wood Products Act (S. 1660). US Senate, Washington, D.C.
- Williams, J. H. 1983. Low emitting aqueous formulations of aminoplast resins and processes for manufacturing them. US patent 4,482,699.