

Syntheses and Properties of Low-Level Melamine-Modified Urea–Melamine–Formaldehyde Resins

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Received 5 January 2004; accepted 19 March 2004

DOI 10.1002/app.20778

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Syntheses of urea–melamine–formaldehyde (UMF) resins were studied using 2–12% melamine levels and UF base resins that were preadvanced to various different extents. The melamine reaction was carried out at pH 6.3 with F/(U + M) mole ratio of 2.1 until a target viscosity of V was reached (Gardener–Holdt) and then the second urea added at pH 8.0 to give a final F/(U + M) mole ratio of 1.15. Analyses with ^{13}C -NMR and viscosity measurements showed that MF components react fast and the UF components very slowly in the melamine reaction. Therefore, as the extent of preadvancement of UF base resin was decreased, the reaction time to reach the target viscosity became longer and the MF resin components showed high degrees of po-

lymerization. The overpolymerization of MF components resulted in increasingly more opaque resins, with viscosity remaining stable for more than a month. As the preadvancement of UF base resin was increased, the extent of advancement of MF components decreased, to give clearer resins, with viscosity slowly increasing at room temperature. Overall, preadvancing the UF base resin components to an appropriate extent was found to be a key to synthesizing various low-level melamine-modified UMF resins. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2559–2569, 2004

Key words: polycondensation; resins; thermosets; ^{13}C -NMR spectra of UMF resins; synthesis

INTRODUCTION

Urea–formaldehyde (UF) resins^{1–8} (Fig. 1) are the major binders for interior-grade wood composite boards, such as particleboard, medium density fiberboard, and hardwood plywood,⁹ and the drawbacks are low water resistance and emission of formaldehyde from the wood composite boards.^{10–13} The overall formaldehyde/urea (F/U) mole ratio used in manufacturing of UF resins, currently at a low value of about 1.15, has been the key parameter used to lower the formaldehyde emission. Lowering the F/U mole ratio would further decrease the formaldehyde emission but the bond strength and water resistance of boards would also decrease. The low F/U mole ratio of UF resins is necessitated by the low functionality of urea (≤ 2.3) that also limits the extent of crosslinking in curing of UF polymers.

Melamine, with a functionality of 3 or higher,¹⁴ has been used as a low-level copolymer component of particleboard binder-type UF resins by some North American manufacturers. With the rigid ring structure and reaction chemistry, similar to that of urea, these

urea–melamine–formaldehyde (UMF) resins have been claimed to enhance the water resistance and physical strength and also reduce the formaldehyde emission of boards.^{15–21} However, as will be described below, past research results on UMF resins failed to show a positive relationship, apparently because of the varying resin synthesis procedures used without recognizing the different chemistries for urea and melamine components. Current commercial melamine–urea–formaldehyde (MUF) resins, which are quite different from UMF resins, are normally synthesized with far higher levels of melamine (>50%), and used in different wood-bonding applications.¹⁴

The melamine–formaldehyde (MF) resin-forming reaction, often carried out at pH between 6 and 9, initially results in various hydroxymethylmelamines and then in dimers, trimers, and so forth, which precipitate out from the aqueous phase (Fig. 2). The resins are often spray-dried. The MF reaction is too fast at pH < 6. Somewhat stable, clear-liquid MF resins are obtained at pH 8.3–8.6¹⁴ because the formation of dimers and trimers is very slow at this pH range. Because UF components polymerize at a reasonable speed only at pH 4–5 or below, coreaction of MF and UF components in the usual manner would be impractical. Also, UF components can be polymerized to higher degrees without a phase separation because of their better compatibility with water. In past research on UMF resins, these differences in reactivity and solubility

Journal article No. FP-267 of the Forest and Wildlife Research Center, Mississippi State University.

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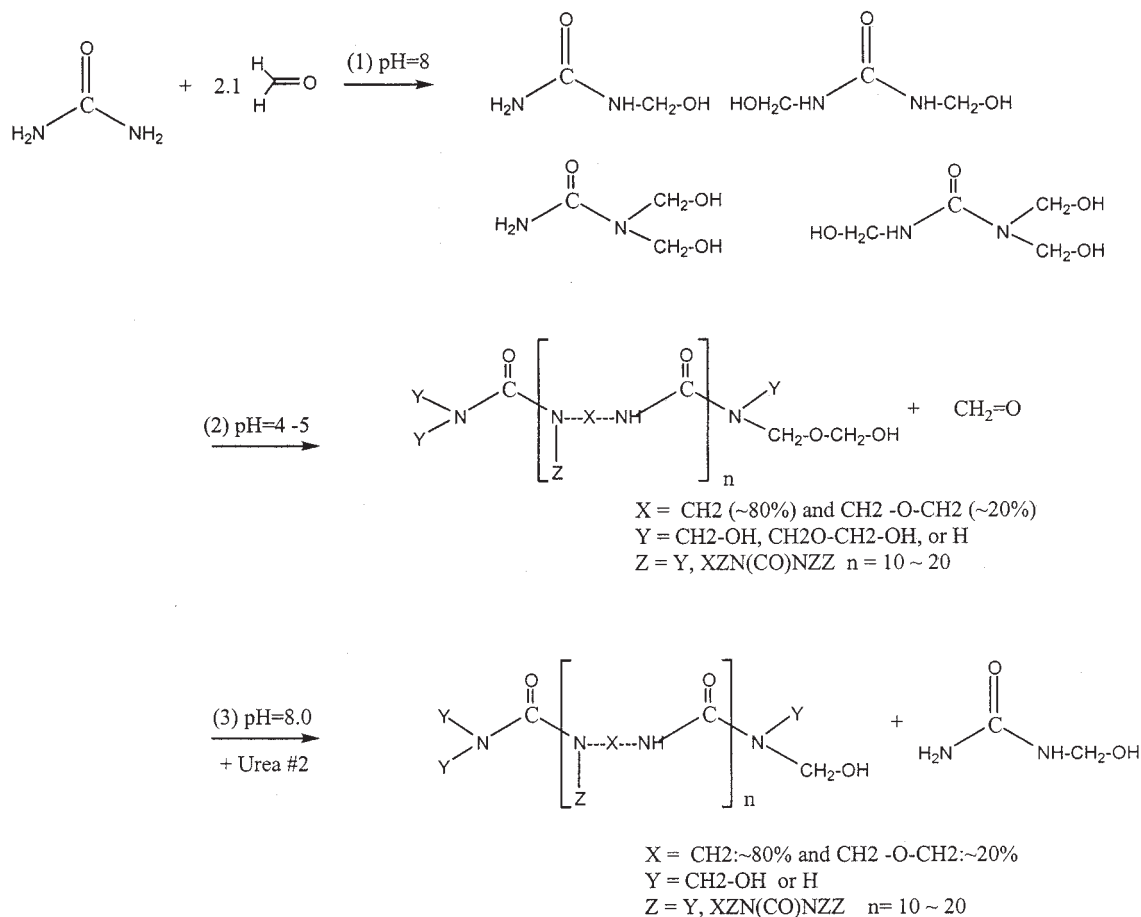


Figure 1 Synthesis steps of urea-formaldehyde resins.

between UF and MF components have been only slightly recognized. Often, melamine (M) and first urea (U₁) were simultaneously reacted with formaldehyde (F₁) from the beginning at pH 8–9 and then the reaction mixture's pH was allowed to decrease to about 6.2 to speed up the reaction.^{15,17} In this method, the UF components would advance very minimally because of the high pH and mainly the MF components would advance in obtaining the target extents of polymerization. In another method, the UF components are first advanced to the high degree commonly

used in synthesis of UF resins and then melamine was added with some more formaldehyde (F₂) and further reacted.^{15,21} In this method, MF components would advance only minimally or to varied extents. In both procedures, the (F₁ + F₂)/(U₁ + M) mole ratio is normally kept at 2–3 and the polymerization reaction carried out until a predetermined water dilutability is obtained. The water dilutability was determined mostly by the MF components. The second urea is then added to lower the (F₁ + F₂)/(U₁ + M + U₂) mole ratio to 0.7–1.3, which is another variable that affects the

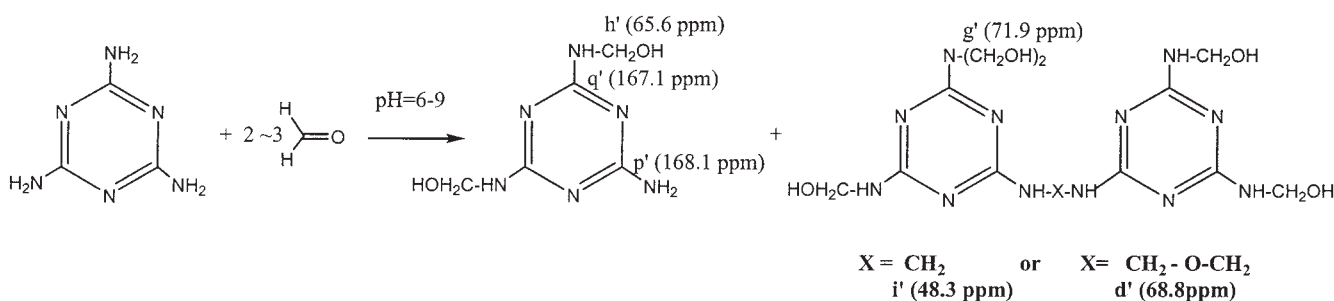


Figure 2 Melamine-formaldehyde resin system and their ¹³C-NMR chemical shift values.

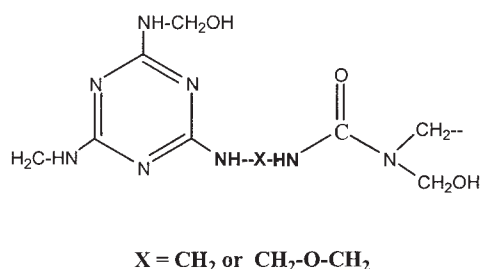


Figure 3 Copolymer formation of urea and melamine in UMF resins.

bonding and formaldehyde emission performances of boards.

In our recent research, the synthesis chemistry of UF resins has been well clarified.^{22–27} In manufacturing UF resins, the urea is added in two parts, the first urea (U_1) and the second urea (U_2) (Fig. 1). The first urea and formaldehyde are reacted at about 90°C in a weak alkaline pH at F/ U_1 mole ratio of about 2.10 to form hydroxymethylureas. Then, the reaction mixture is acidified to pH 4–5 and maintained at about 95°C to form methylene and methylene-ether bonds to result in UF polymers. In this second reaction step, some hydroxymethyl groups split off as formaldehyde, by the reverse reaction, attributed to the decreasing number of urea amide groups available within the resin system. The urea functionality attained under this typical UF resin synthesis condition is only about 2.3–2.5 and the freed formaldehyde amounts to about 0.28 mol/mol of first urea. Once the target viscosity is obtained, V-X (Gardener-Holdt) at resin solids level of 60–65% for particleboard binder-type resins, increasing the pH to 8.0 ends the reaction. Then, the reaction mixture is cooled to about 60–70°C, the second urea is added and mixed, and the mixture is cooled to room temperature with a final F/($U_1 + U_2$) ratio of about 1.15. During the cooling and storage period, the second urea reacts with the free formaldehyde present in the reaction mixture to form monomeric hydroxymethylureas (Fig. 1).

In past research, a reaction product of urea, melamine, and formaldehyde at pH 6.5 was shown to contain, by ¹³C-NMR analyses, methylene groups formed between urea and melamine, a result of copolymerization (Fig. 3).²⁸ In general, copolymers have been assumed to be formed in UMF and MUF resins. MUF resins are generally difficult to analyze because of insolubility. UMF resins synthesized with a F/($U + M$) mole ratio of 3.0, using the first procedure discussed above, showed a cloudiness in 30 min of cooking at pH 6.5.²⁹ The resultant resins, at 4–8% melamine levels, showed lower formaldehyde emission than that of control UF resin but the internal bond strength of particleboard remained about the same.¹⁷ UMF resins synthesized, using the second procedure

discussed above, resulted in lower formaldehyde emission of boards but the internal bond and water-soak thickness (TS) values sometimes deteriorated as the melamine level was increased from 9.5 to 34.4%.³⁰ Thus, either procedure failed to clearly show the advantages of incorporating melamine in UF resins, apparently because of the lack of controls for advancements of UF and MF components. It is also known that the curing of MF resins requires stronger catalysts and higher press temperatures, or longer press times, compared to UF resins because of the lower reactivity of the hydroxymethyl groups.¹⁴ Another possibility for the varying board performances of UMF resins observed could be the migration of hydroxymethyl groups of the polymeric UMF resin components to the second urea during the cooling and storage periods, as in UF resins.^{22–27} Overall, although showing the bonding and formaldehyde emission improvements that parallel the melamine levels of UMF resins would be a rather complex thesis, the extents of polymerization of UF and MF components appeared to be the key parameter. Therefore, various UMF resins were synthesized using UF base resins preadvanced to D, K, and S viscosity as well as A₂ and V, the latter two corresponding to the two typical procedures discussed above. The melamine level was varied over 2–12% based on the liquid resin weight, and the F/($U + M$) mole ratio kept at 2.1 during the polymerization and at 1.15 after the second urea addition. Other parameters were kept constant. The reaction times taken in resin syntheses were measured. Selected resin intermediates and finished resins were analyzed by ¹³C-NMR and finished resins examined for storage stability and other resin characteristics. Results of examining finished resins for their curing properties and particleboard bonding and formaldehyde emission performances will be published in sequel articles.

EXPERIMENTAL

Reagent-grade 98% urea and 99% melamine, and a fresh industrial-grade 50% aqueous formaldehyde solution from the Georgia-Pacific Corp. resin plant (Louisville, MS), kept at 60°C in the laboratory, were used. The pH adjustments were made using 8% sulfuric acid and 25% sodium hydroxide solutions, and Brookfield or Gardner-Holt viscometers used to measure the viscosity. A convection oven, gel timer, and specific gravity meter (Troemner Co., Philadelphia, PA) were used to measure other resin properties.

Synthesis of control UF resin

Following the known procedure,²³ a 50% aqueous formaldehyde solution (F) (1697 g) was charged to a stirred reactor, the pH was adjusted to 7.0–8.0, and the solution was heated to 70°C. Then, first urea (807

g) was added slowly while the reaction temperature was maintained at below 90°C ($F/U_1 = 2.1$). The temperature was increased to 90°C in 20 min and held for 30 min, after which the reaction mixture was adjusted to pH 4.6 to begin the polymerization. When the reaction mixture reached X viscosity in about 120 min, it was adjusted to pH 8.0, cooled to about 60°C, and second urea (668 g) was added and cooled further to room temperature, resulting in Resin UFA for control [$F/(U_1 + U_2) = 1.15$].

Synthesis of a UF resin intermediate at pH 6.3 for NMR comparison

Into a stirred reactor, a 50% aqueous formaldehyde solution (126 g) was charged, the pH was adjusted to 8.0, and the solution was heated to 70°C. Then, urea (60.0 g) was added slowly while the reaction temperature was maintained at <90°C ($F/U_1 = 2.1$). Then, the temperature was increased to 90°C in 20 min and held for 30 min (viscosity $\sim A_2$). Then, the pH was adjusted to 6.3 and the reaction mixture maintained at 90°C for 6 h. The reaction mixture became cloudy in 1 h and reached B viscosity only at the end of the reaction period. The reaction mixture was cooled to 60°C, the pH was adjusted to 8.0, second urea (49.6 g) was added and mixed well, and the mixture was cooled to room temperature to obtain Resin UFA₂BU₂ [$F/(U_1 + U_2) = 1.15$].

Synthesis of MF resin intermediates for NMR comparison

Into a stirred reactor, 50% aqueous formaldehyde (150.0 g) and water (20.0 g) were charged, the pH was adjusted to 7.0–8.0, and the mixture was heated to 80°C. Then, melamine (150.0 g) was added slowly while the reaction temperature was maintained at 80–90°C ($F/M = 2.1$). After the melamine had completely dissolved, the temperature was increased to 90°C in 20 min and held, while the pH was kept at 8.3–8.6. The water dilutability of the reaction mixture reached a value of 1 : 2, resin to water, in 70 min. The reaction product was cooled to 60°C and adjusted to pH 8.5 to give sample Resin MFa ($F/M = 2.1$) with O viscosity. A small sample taken was clear but gelled in 2 days at room temperature. Then, urea (59.0 g) was added and the reaction mixture mixed at pH 8.5 and then cooled to room temperature to give Resin MFU₂ [$F/(U + M) = 1.15$] with G viscosity, which was clear and stable at room temperature for about 10 days.

Synthesis of a UMF resin with 12% melamine added in the beginning

First, a 50% aqueous formaldehyde solution (1974 g) was charged to a stirred reactor, the pH was adjusted

to 7.0–8.0, and the solution was heated to 75–80°C. Then, first urea (710.0 g) and melamine (484.0 g; 12% based on finished resin weight) were added slowly while the reaction temperature was maintained at about 80°C [$F/(U_1 + M) = 2.1$]. After the urea and melamine had completely dissolved, the temperature was increased in 20 min to 85°C and maintained for 30 min. The pH was then adjusted to 6.7 and allowed to decrease by itself. The viscosity of the reaction mixture began at about A_2 and reached the target viscosity “V” in 65 min with the pH decreasing to 6.3. The pH was adjusted to 8.3 and the cooling began, after which a small sample was taken for NMR analysis, Resin UMF12A₂V. When the temperature reached 60°C, second urea (775.0 g) was added and the reaction mixture was mixed and cooled to room temperature, to obtain Resin UMF12A₂VU₂ [$F/(U_1 + U_2 + M) = 1.15$].

Synthesis of a UMF resin with 12% melamine with base UF resin preadvanced to V viscosity

A batch of the control UF resin described above was made until the polymerization reaction advanced to “V” viscosity, using 50% formaldehyde solution (1450 g) and first urea (690 g). To this UF base resin at pH 8.0, a 50% formaldehyde solution (F_2) (524 g), preadjusted pH to 8.0, and melamine (484 g; 12% based on finished resin weight) were added and reacted for 20 min at 85°C [$(F_1 + F_2)/(U_1 + M) = 2.1$]. The viscosity of the reaction mixture was J. Then, the pH was adjusted to 6.7 and allowed to decrease while maintaining the temperature at 85°C until the viscosity reached V, which took about 20 min. Then, the reaction mixture was adjusted to pH 8.0, cooled to 60°C, and an NMR sample was taken, Resin UMF12VV. Then, second urea (795.0 g) was added and the reaction mixture was mixed and cooled to room temperature, to obtain Resin UMF12VVU₂ [$(F_1 + F_2)/(U_1 + U_2 + M) = 1.15$].

Syntheses of UMF resins with 6% melamine with UF base resins preadvanced to two intermediate extents

Using a similar procedure used for control UF resin, 50% aqueous formaldehyde (1697 g) and first urea (807 g) were reacted ($F/U_1 = 2.1$) until the reaction mixture reached D viscosity. Then, the reaction mixture was adjusted to pH 8.0, 50% formaldehyde solution (F_2) (272 g), preadjusted to pH 8.0, and melamine (227 g; 6% based on finished resin weight) were added [$(F_1 + F_2)/(U_1 + M) = 2.1$]. The reaction mixture was heated at 85°C, while allowing the pH to decrease, until VW viscosity, adjusted to 8.0, and cooled to 60°C; urea (789 g) was then added and mixed, and the reaction product cooled to room temperature, to obtain Resin UMF6DVU₂ [$(F_1 + F_2)/(U_1 + U_2 + M) = 1.15$].

Another batch of resin was made using the same formulation and procedure except that the extent of reaction for the base UF resin was K viscosity, resulting in Resin UMF6KVU₂ [(F₁ + F₂)/(U₁ + U₂ + M) = 1.15].

Syntheses of UMF resins with 12% melamine with UF base resins preadvanced to two intermediate extents

The synthesis procedures similar to those described above for 6% melamine level resins were used. Thus, 50% aqueous formaldehyde solution (F₁) (1365 g) and first urea (649 g) (F/U₁ = 2.1), additional 50% formaldehyde solution (540 g), melamine (458 g; 12% based on the finished resin), and second urea (785 g) were used. Resin UMF12DVU₂ was obtained from the UF base resin viscosity D and Resin UMF12KVU₂ from the UF base resin viscosity K, both with (F₁ + F₂)/(U₁ + U₂ + M) = 1.15. Several samples were also taken during syntheses for NMR analysis: UF base resin at D viscosity, Resin UFD; after the melamine reaction mixture reached N viscosity, Resin UMF12DN; after the melamine reaction reached V viscosity, Resin UMF12DV. NMR samples were adjusted to pH 8.0 and cooled to room temperature.

Syntheses of UMF resins with various levels of melamine and UF base resins preadvanced to three intermediate extents

Using the resin synthesis procedures described above, UMF resins within the matrix of melamine levels and D, K, and S viscosity values of UF base resin were synthesized. The melamine levels were 2, 4, 8, and 10%, based on the liquid resin weight. The F/(U + M) mole ratio of the reaction mixture during the polymerization step was kept at 2.1 and the second urea added to obtain the finished resins with mole ratio of 1.15. Viscosity measurements were made during the resin syntheses and all resins were evaluated for storage stability by measuring the viscosity changes for 50 days at room-temperature storage.

Resin property tests

Nonvolatile resin solids contents were measured by heating 1.0 g of liquid resins at 110°C for 3 h in an oven. Gel times were measured at 100°C (boiling water) using a Sunshine gel timer. The catalyst was 0.5% ammonium sulfate (25%) solution in water for both nonvolatile solids content and gel time measurements. Specific gravity was measured using a specific gravity meter (Troemner Co.). The stability of resins was evaluated by storing resins (~ 400 g) in a plastic container at room temperature and measuring the viscosity daily.

¹³C-NMR spectroscopy

NMR resin samples were prepared by mixing liquid resins (2.0 g) and D₂O (1.0 g). Carbon spectra were obtained on a Techmag 360-MHz NMR spectrometer (Spectral Data Services, Inc., Champaign, IL) using a 12-μs pulse width and a 10-s pulse delay for quantitative results of methylenic groups, which showed T₁ values of 0.16 s or smaller by the inversion-recovery method.²³ About 400 scans were accumulated for each run. Peak integration values of urea carbonyls, melamine carbons, and methylenic carbons were separately summed and percentages calculated according to group types and substitution patterns.

RESULTS AND DISCUSSION

General characteristics of ¹³C-NMR of UMF resins

¹³C-NMR analysis of UF resins has been well established.^{21–26,32–36} ¹³C-NMR results of UMF resins and intermediates indicated the typical characteristics of UF resin components as shown by the various methylenic carbon and urea carbonyl group percentage values (Table I). The methylenic groups of UF resins have been classified as free and oligomeric formaldehyde; Types I, II, and III methylene-ether groups; Types I and II hydroxymethyl groups; and Types I, II, and III methylene groups (Fig. 4 and Table I). The integral values of these groups would define the polymer structures as described in previous reports.^{21,22} In general, the extent of polymerization, or the (methylene + 1/2 methylene-ether) bond content, increases as the resin system is advanced and the total free and oligomeric formaldehyde content decreases drastically after the addition of second urea. For the MF components, new peaks at 65.6 and 71.6 ppm appeared in UMF resins, the former assigned to Type I hydroxymethyl groups and the latter to Type II hydroxymethyl groups, from the similarity with those on UF resin components at 65.2 and 71.9 ppm, respectively. They were very close together and calculated together in this study. The methylene (48.3 ppm) and methylene-ether (68.8 ppm) groups on MF components [Figs. 2 and 5(a)] were broad and not differentiated from broad Type I methylene (47.4 ppm) and methylene-ether groups (69.5 ppm) on UF components. Therefore, it was difficult to form a conclusion whether any copolymerization occurred between urea and melamine units. Melamine ring carbons occurred at 167.1–168.1 ppm.³⁷

UF resin intermediate UFA₂BU₂

This UF resin intermediate, made by polymerizing at pH 6.3 and 90°C for 6 h of reaction at F/U₁ mole ratio of 2.1, became cloudy in the first hour of reaction and reached B viscosity only at the end of the reaction.

TABLE I
Percentage Values for Various Methylenic and Carbonyl Carbons of Urea Portions of UF and UMF
Resin Samples Determined by ^{13}C -NMR Spectroscopic Method^a

	Synthesized UF and UMF resin samples									
	Groups (ppm)	UMF12 A ₂ V	UMF12 A ₂ VU ₂	UFD*	UMF12 DN	UMF12 DV	UMF12 DVU ₂	UMF12 VVU ₂	UF A ₂ BU ₂	MFaU ₂
Free and oligomeric formaldehyde	91.0	0.59	0.41	0.56	0.61	0.42	0.34	0.33	0.65	0
	87.0	1.04	0	2.72	1.56	1.72	0.15	0.10	0	0.33
	83.1	1.56	0	2.98	2.74	3.52	0.17	0.19	0	0.25
	Total	3.19	0.41	6.26	4.91	5.66	0.66	0.62	0.65	0.58
Methylene-ether groups	79.1 (III)	0.93	0	1.02	1.56	1.99	1.24	1.85	2.64	0
	75.1 (II); 74.8*	4.26	3.93	5.04	7.03	7.63	5.66	4.43	6.62	3.43
	69.5 (I); 68.8*	19.15	20.50	8.39	12.14	12.10	11.85	9.76	18.20	16.14
	Total	24.34	24.43	14.45	20.73	21.72	18.25	16.04	27.46	19.57
Hydroxymethyl groups	71.9 (II); 71.6*	16.60	12.53	14.20	26.40	24.69	19.83	16.18	16.03	10.05
	65.2 (I); 65.6*	44.75	51.62	13.13	22.90	22.48	34.87	38.90	35.10	64.78
	Total	61.35	64.15	27.33	49.30	47.17	54.70	55.08	51.13	74.83
	60.1 (III)	0	0	3.13	2.19	2.84	1.82	0.94	2.03	0
Methylene groups	53.9 (II); 55.0*	7.17	6.66	14.64	16.02	15.69	15.79	17.16	10.48	1.87
	47.4 (I); 48.3*	3.96	4.35	5.83	6.86	6.87	8.29	10.16	8.25	5.02
	Total	11.13	11.01	23.60	25.07	25.40	25.90	28.26	20.76	6.89
	164.0	2.86	38.80	0	0	0	34.74	34.59	38.11	46.84
Urea carbonyl groups	162.2	30.02	30.21	6.07	9.67	11.03	21.36	23.06	19.84	44.59
	160.7	65.68	30.75	91.85	87.72	84.81	42.06	39.64	39.21	8.57
	158.0	1.45	0.24	2.08	2.60	4.16	1.84	2.70	2.84	0

^a Sample numbers were defined in the text and the chemical shift values are related to the chemical structures shown in Figure 4. The amount of formaldehyde in Resin UFD is smaller than that in others and its methylenic group percentage values were proportioned to make them comparable. For Resin UMF12 series, to convert the values into moles based on the first urea, multiply by 2.935. Chemical shift values of methylenic groups bonded to melamine are marked with asterisks. Melamine ring carbon peaks appeared at 167.1–168.1 ppm and are not included in this table.

After the addition of the second urea [$\text{F}/(\text{U}_1 + \text{U}_2) = 1.15$], the viscosity decreased to A₁. The ^{13}C -NMR results (Table I) showed a (methylene + 1/2 methylene-ether) bond content of 0.722, corresponding to an extent of polymerization 3.6, on average 0.12 group being formed per hour of reaction. The methylene : methylene-ether group ratio was 60 : 40, a higher ether group value compared to the ratio of 77 : 23 found for Resin UFD synthesized at pH 4.6 in about 30 min. These results indicate that the polymerization of UF components is very slow and more ether groups are formed at pH 6.3, both of which will apply for UF resin components in syntheses of UMF resins at or near pH 6.3. The role of methylene-ether bonds in UF resins is not well understood, but such a bond has been assumed to break and emit a mole of formaldehyde on curing.

Resin MFaU₂

MF resins synthesized with an F/M ratio of 2.5 at pH 6.3 in preliminary experiments quickly became cloudy and insoluble. In the synthesis of Resin MFaU₂ at pH

8.4, the reaction mixture remained clear and its water dilutability decreased slowly to 1 : 2 (resin : water) in 70 min of reaction. The sample taken before the addition of the second urea, Resin MFa (F/M = 2.1) with O viscosity, gelled overnight to indicate an appreciable reactivity of hydroxymethyl groups at pH 8.4. Resin MFaU₂ obtained by adding the second urea to Resin MFa [$\text{F}/(\text{M} + \text{U}) = 1.15$], showed G viscosity and remained clear at room temperature for at least 10 days, with the ending viscosity increased to P. The ^{13}C -NMR results of Resin MFaU₂ [Table I, Fig. 5(a)] indicated an overall (methylene + 1/2 methylene-ether) bond content of 0.415, mostly of Type I bonds. Because little polymerization would have occurred for the second urea components, the bond content value indicates that the melamine components have an extent of polymerization 1.71. This low extent of advancement appears necessary for MF components to remain in solution. Furthermore, the methylene : methylene-ether group ratio of Resin MFU₂ was 41 : 59, a high ether group content compared to that of UF resins. These reaction characteristics would apply for MF components in syntheses of UMF resins. The NMR

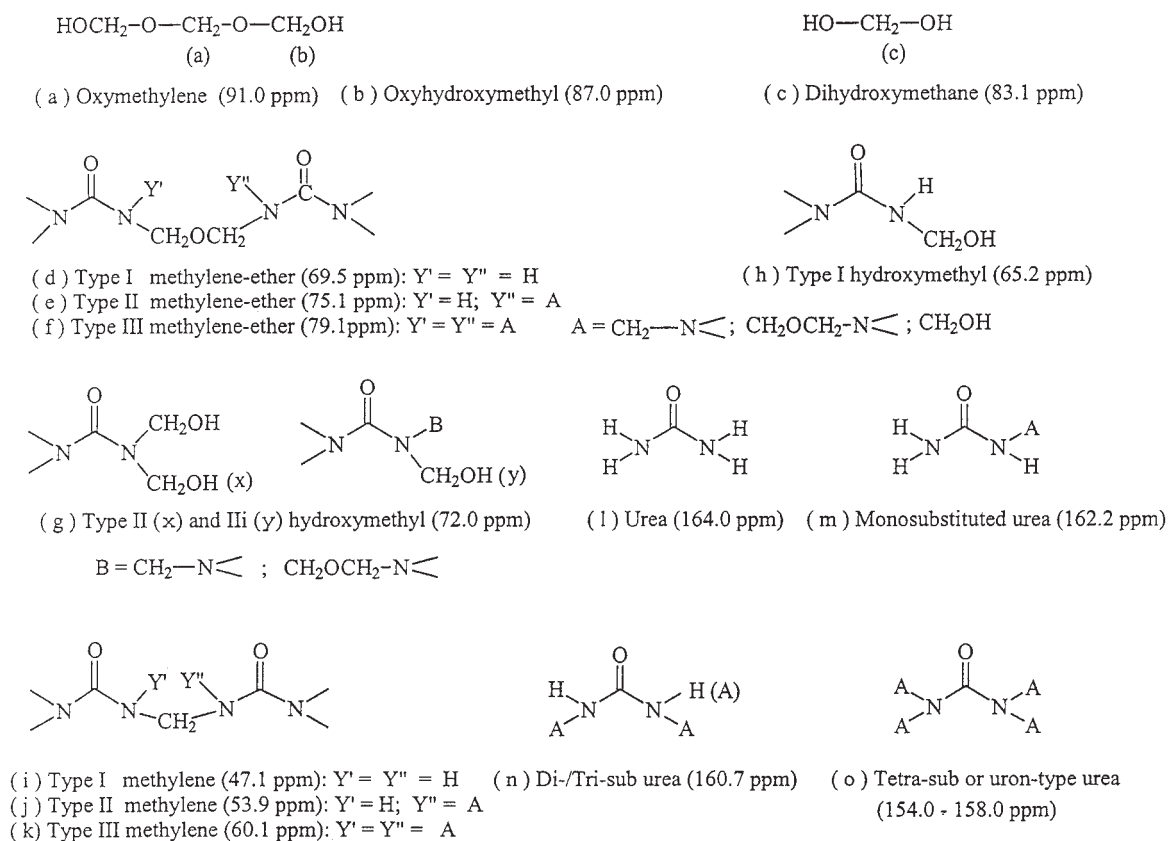


Figure 4 Chemical structures of UF resins and their ^{13}C -NMR chemical shift values.

results further indicated that the second urea added had reacted to form mono- and dihydroxymethylureas, consuming about 0.8 out of 2.5 mol of formaldehyde used in resin synthesis, leaving the balance 1.7 mol to be bonded to melamine molecules. Although a direct comparison was not made because of the premature gelation of Resin MFa, the results indicate that some of the hydroxymethyl groups, bonded to melamine molecules, migrated to the second urea [Fig. 6(a)] as in UF resins. This reversibility of hydroxymethyl groups of MF resin components has been little known, although it has been assumed to occur in curing of MF resins at elevated temperatures, especially for resins made with higher F/M ratios.¹⁴ The melamine ring carbons appeared at 167.15, 167.24, and 168.06 ppm, the first two peaks for di- and trisubstituted melamines and not well separated and the last peak for monosubstituted melamine. Overall, the Resin MFaU₂ synthesis experiment indicates that the reaction of MF components goes relatively fast even at pH 8.4 and will thus go faster at lower pH 6–7, where most UMF resin syntheses have been carried out in the past.

Resin UMF12D series intermediates

Samples UFD, UMF12DN, UMF12DV, and UMF12DVU₂ were obtained in synthesis of the last resin sample

using the base resin UFD: adding 12% melamine and reacting to N viscosity and V viscosity, respectively, and then adding the second urea. The ^{13}C -NMR spectra [Fig. 5(b)] and data (Table I) indicate the various reaction characteristics. The methylene/methylene-ether group content, adjusted for the second formaldehyde added with the melamine, gradually increased by 0.146 groups from Resin UFD to Resin MUF12DVU₂ per mole of the first urea. This increase constitutes 18.8% of the total methylene/methylene-ether group content 0.774/mol per mole of the first urea. Because polymerization of UF resin components would have progressed little in this stage, the methylene/methylene-ether group content increase would be mostly of the MF components, which translate into an extent of polymerization 1.58 for MF components. This value is comparable to that of Resin MFaU₂, discussed above, and indicates that the MF components remain soluble and translucent and would continue to polymerize to increase the resin viscosity at room temperature.

The free formaldehyde level was relatively high until the second urea addition (Table I), indicating that the formaldehyde ratio used, $(F_1 + F_2)/(U_1 + M) = 2.1$, was in excess with the melamine components having not fully reacted in this reaction period. Type I hydroxymethyl groups (~ 65.5 ppm) increased from 13 to 23% when the second formaldehyde and mel-

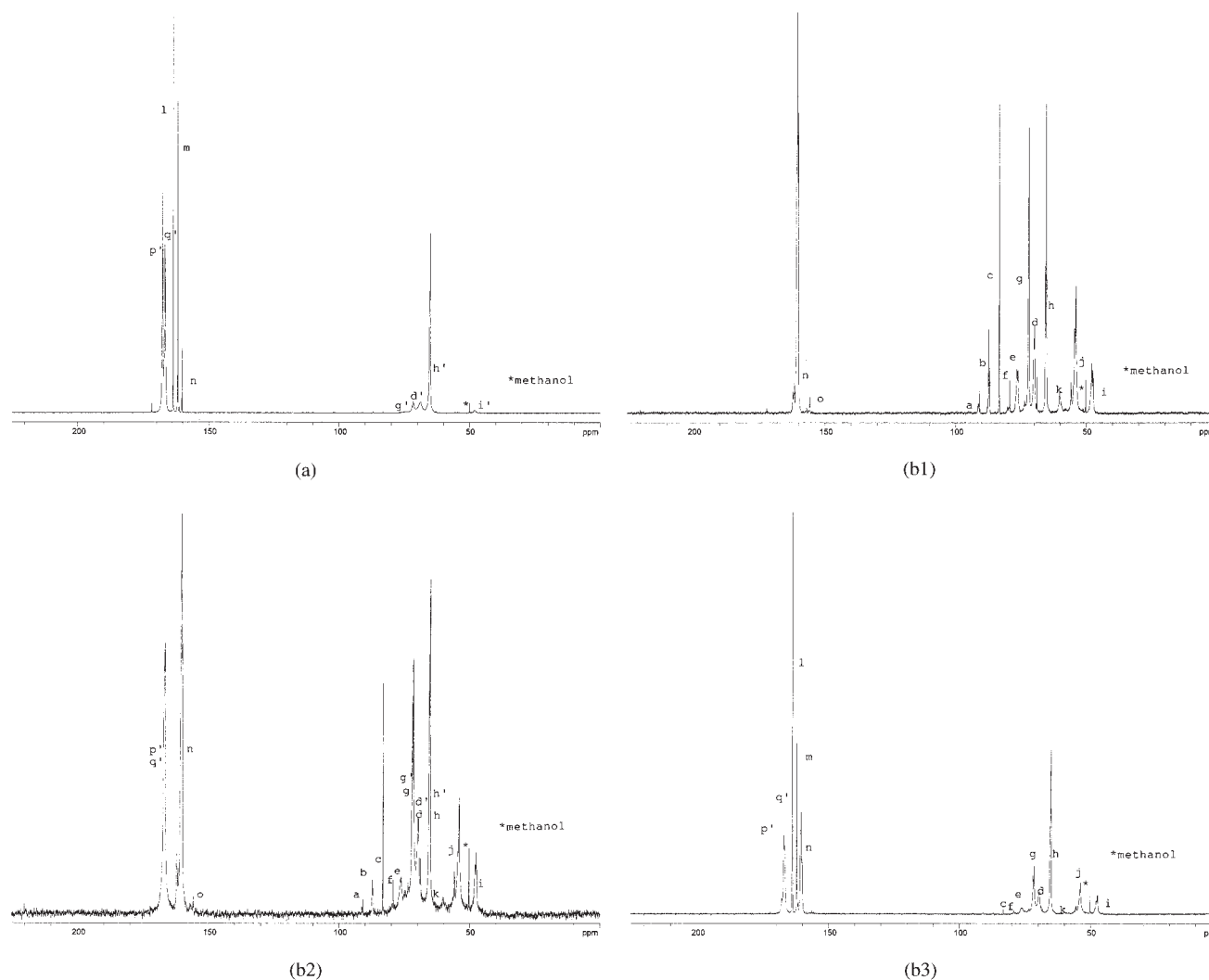


Figure 5 (a) ^{13}C -NMR spectrum of Resin MFaU₂ with chemical shifts indicated for various carbons shown in Figure 2. (b) ^{13}C -NMR spectra of Resin samples UFD(1), UMF12DV(2), and UMF12DVU₂(3) with chemical shifts indicated for various carbons shown in Figures 2 and 4.

amine were added and then further increased to 35% with the addition of the second urea [$(F_1 + F_2)/(U_1 + M + U_2) = 1.15$] as a result of reaction with formaldehyde. Type II hydroxymethyl groups of both UF and MF components (~ 72.0 ppm) similarly increased, but decreased after the second urea addition because of dissociation into formaldehyde and reaction with the second urea, as observed with Resin MFU₂ [Fig. 6(a)] discussed above. This migration of hydroxymethyl groups also resulted in decreasing Type II and Type III methylene and methylene-ether groups with addition of the second urea, similar to UF resins.

Resin UMF12A₂VU₂ made without preadvancement of UF base resin

With this UMF resin synthesis procedure, often used in previous research, the reaction with 12% melamine

and first urea with formaldehyde at pH 6.3 reached the target viscosity VW in about 60 min. The finished resin was cloudy. The reaction time, the longest compared with that of UMF resins synthesized with UF base resins, preadvanced to D, K, or S viscosity values, but was relatively short compared with UF resins, about 120 min at pH 4.6 (Fig. 8). ^{13}C -NMR results of the final resin and the sample taken before the addition of second urea (UMF12A₂V) (Table I) indicated a (methylene + 1/2 methylene-ether) bond content of 0.465 groups per mole of combined first urea and melamine, a DP value of 1.87. This synthesis procedure thus resulted in resins having a very low average molecular weight compared to the common DP value 10 for finished UF resins. On the other hand, because the UF components would have experienced only a small increase in the methylene/methylene-ether bond content (0.12 group) as discussed above, the

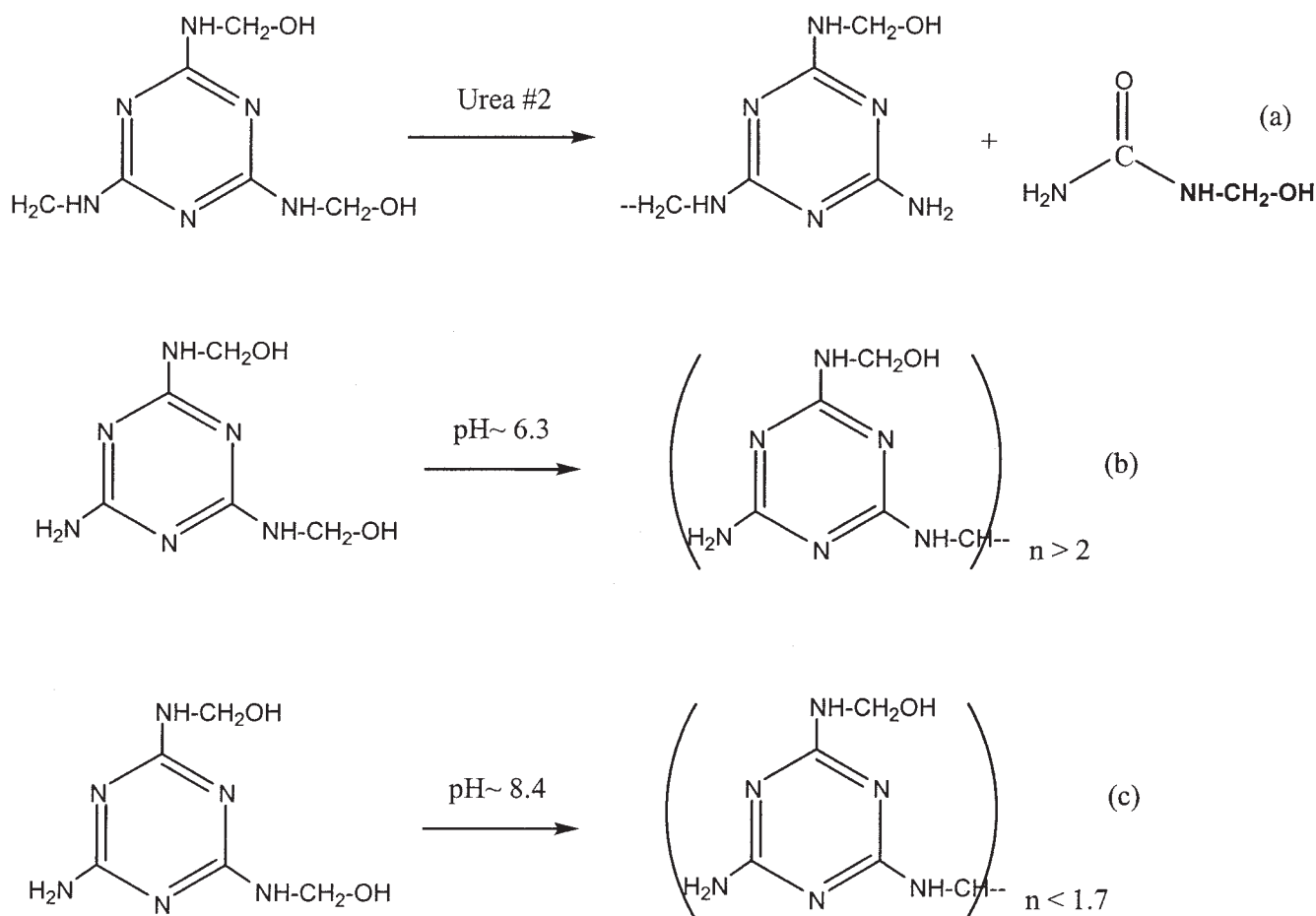


Figure 6 (a)–(c) Reaction schemes of melamine and formaldehyde resins.

balance of about 0.345 bond/0.336 mol of melamine for the MF components indicates a very high degree of polymerization value [Fig. 6(b)]. This overpolymerization of MF components in Resin UMF12A₂VU₂ is supported by the cloudy appearance. The resin's apparent viscosity showed a good stability for more than 30 days at room temperature. For the UMF resin synthesized with 2% melamine and no advancement of UF base resin, the final resin did not even reach the target viscosity in 5.5 h of reaction, apparently because of the lack of reactive, dissolved MF components. This resin's apparent viscosity similarly remained low and stable for more than 30 days (Fig. 7). With these UMF resins, the MF components polymerized to a point where they are no longer soluble and formed small particles that remain suspended in the low molecular weight UF components.

Resin UMF12VVU₂, made with UF base resin, advanced to full extent

With this second typical UMF resin synthesis procedure used in previous research, 12% melamine and the second formaldehyde were added to the UF compo-

nents, which was prepolymerized to V viscosity. The reaction time to the target viscosity V was short, about 20 min (Fig. 8), and resulted in a clear resin as ex-

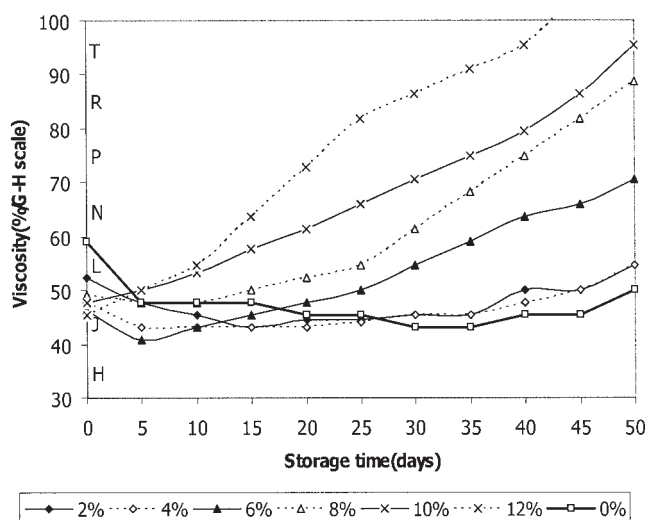


Figure 7 Viscosity changes of UMF resins and control UF resin in storing at room temperature.

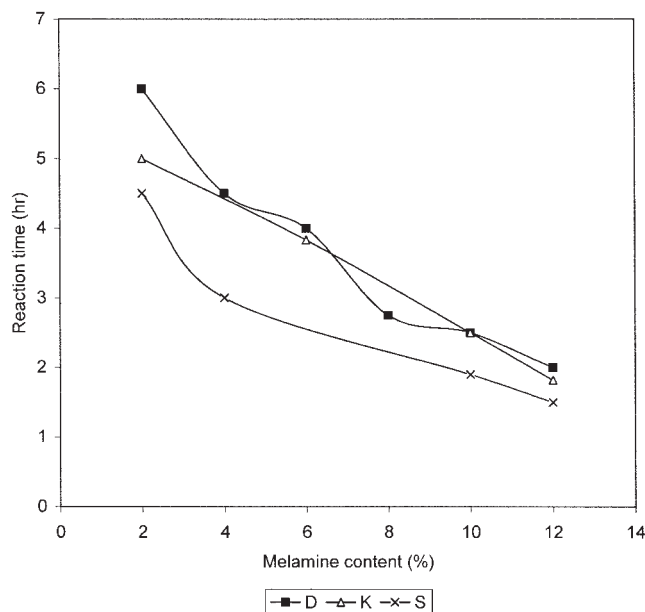


Figure 8 Reaction times taken in syntheses of UMF resins depending on the starting UF base resin viscosity values and melamine levels.

pected. The resin sample taken before the addition of second urea gelled overnight at pH 8.0, indicating that the MF components were low molecular weight, reactive compounds. The ^{13}C -NMR results of Resin UMF12VVU₂, compared with those of typical UF resins²⁴ (Table I), showed that the extent of polymerization attained by the melamine components was very low. The resin remained clear for several days without clouding, and the viscosity of the resin increased the fastest during room-temperature storage (Fig. 7). Thus, MF components in this UMF resin appear to be almost monomeric and remain dissolved and reactive [Fig. 6(c)].

UMF resins made with UF base resins advanced to intermediate extents and at various melamine levels

In these experiments the UF base resin was polymerized at pH 4.6 to D, K, and S viscosities and then reacted at pH 6.3 with 2–12% levels of melamine at $[(F_1 + F_2)/(U_1 + M) = 2.1]$. Resin property data of

selected resins are reported in Table II. The reaction time taken after the melamine addition until the target viscosity of V became shorter as the melamine level was increased, from 5.5 h to 40 min (Fig. 8), indicating that the major reacting components in this stage are the MF components. The reaction time also became slightly shorter as the UF base resin viscosity increased from D to S, as expected. The UF base resin components would have incurred only a small extent of polymerization during the melamine reaction. The cloudiness of UMF resins made with 12% melamine was typical, changing gradually from the opaque to translucent and to clear as the UF base resin viscosity increased from A₂ to V in preadvancement, reflecting the MF components' decreasing extents of polymerization. On the other hand, for a given UF base resin the resultant resins' cloudiness tended to be greater for lower melamine levels because of the higher extents of polymerization incurred. Similarly, the viscosity increases in the room-temperature storage experiment were faster for resins made with more advanced UF base resins (Fig. 7).

General resin properties

The UMF resins generally showed longer gel times than that of the control UF resin with ammonium sulfate catalyst (Table II) and the higher melamine level resins showed longer gel times than those of lower melamine level resins. These gel time trends agree with the generally known fact that MF resins cure slower than UF resins. Detailed differences based on the different synthesis procedures used were not apparent in gel time results. In a companion article,³⁸ the UMF resins were compared for curing properties using the dynamic mechanical analysis (DMA) method at 120–175°C. The DMA curing speeds of resins showed trends similar to those of gel time measurements and also showed differences for different melamine addition points used in resin syntheses. One important question in synthesizing UMF resins will be the efficiency of the MF resin components in curing of resins as adhesives. MF components need to cure cooperatively with UF resin components in the final curing of boards. MF components that are too highly advanced in the resin stage could lose such capacity.

TABLE II
Properties of UF and UMF Resins Synthesized with $F/(U + M) = 1.15$

Resin	pH	Gel time (s)	Specific gravity	Viscosity (G-H scale)	Solids content (%)
UF Control	8.5	88	1.26	N	61.3
UMF6DVU ₂	8.5	135	1.27	JK	62.5
UMF12DVU ₂	8.5	129	1.29	J	64.5
UMF12KVU ₂	8.6	126	1.29	KL	64.4

CONCLUSIONS

UMF resins synthesized with low levels of melamine were shown to have various important resin characteristics that reflected the UF base resin's extent of preadvancement as well as the melamine level. It became apparent that the varying and sometimes inconsistent bonding and formaldehyde emission results of UMF resins reported in previous research would be traced to the advancement imbalances between the UF and MF components in resins. The melamine components need to be reacted at pH 6 or higher and the UF base resin components can be advanced only at pH 4–5 in syntheses of UMF resins. The UF base resin components therefore need to be first advanced to an appropriate extent, followed by the melamine addition and an appropriate further advancement. Furthermore, to have balanced advancements of UF and MF components the extent of advancement of UF base resin components needs to be adjusted to the melamine use levels, less for higher melamine levels, and more for lower melamine levels, to avoid an overpolymerization of the MF components. The storage stability of the cloudy UMF resins made by highly advancing the MF components was generally good and the storage stability of the clear UMF resins made by minimally advancing the MF components was somewhat shorter. Overall, preadvancing the UF base resin components to an appropriate extent was found to be a key parameter in synthesizing various low-level melamine-modified UMF resins.

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