Examination of Selected Synthesis and Room-Temperature Storage Parameters for Wood Adhesive-Type Urea–Formaldehyde Resins by ^{13}C-NMR Spectroscopy. V

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ABSTRACT: The effects of posttreatments of particleboard adhesive-type urea–formaldehyde resins were studied. The resins were synthesized with formaldehyde/first urea (F/U_1) mol ratios of 1.40, 1.60, 1.80, 2.10, and 2.40 and then the second urea was added to give a final formaldehyde/urea ratio of 1.15 in alkaline pH. The resins were posttreated at 60°C for up to 13.5 h and the 2.5-h heat-treated resin samples were stored at room temperature for up to 27 days. Resins sampled during the posttreatments were examined by ^{13}C-NMR and evaluated by bonding particleboards. In the posttreatments, hydroxymethyl groups on the polymeric resin components dissociated to formaldehyde and reacted with the second urea, and methylene and methylene–ether groups were formed from reactions involving the second urea. Methylene–diurea and urea groups bonded to UF polymers were identified. As a result, the viscosity of the resins initially decreased but later increased along with the cloudiness of the resins. Bond-strength and formaldehyde-emission values of particleboard varied with posttreatment variables as well as with the F/U_1 mol ratios used in the resin syntheses. The results would be useful in optimizing resin synthesis and handling parameters. Various reaction mechanisms were considered. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1896–1917, 2003

**Key words:** resins; structure-property relations; thermosets

INTRODUCTION

Urea–formaldehyde (UF) resins[1–8] are the major binders for wood composite boards such as particleboard, medium-density fiberboard, and hardwood plywood.[9] Drawbacks of UF resins are low water resistance and emission of formaldehyde from the wood composite boards.[10–13] The overall formaldehyde/urea (F/U) mol ratio used in the manufacturing of UF resins, currently at a low value of about 1.15 in North America, has been the key parameter used to lower formaldehyde emission. Lower F/U mol ratio resins decrease formaldehyde emission but they also reduce the bond strength and water resistance of boards. Scavengers are also used to reduce formaldehyde emission. Furthermore, the bond-strength and formaldehyde-emission values of boards vary with a given F/U mol ratio of the resins,[14] for which recent research showed several resin synthesis and posttreatment parameters to be responsible.[15–18]

In manufacturing UF resins, as described in previous reports,[15–19] urea is added in two parts: the first urea (U_1) and the second urea (U_2). In the first step, the first urea and formaldehyde are reacted at about 90°C in weak alkaline aqueous media with a formaldehyde/first urea (F/U_1) mol ratio of about 2.10. Mono-, di-, and trihydroxymethylureas are the major reaction products. This hydroxymethylation reaction is slightly reversible: $k = 1.1 \times 10^{-4}$ mol L^{-1} s^{-1} and $k_{-1} = 2.7 \times 10^{-6}$ mol L^{-1} s^{-1} (30°C, pH 8.0),[6] which appears to apply also in weak acidic aqueous media of the second step of resin synthesis and the final curing of resins with acid catalysts. In the second step, the reaction mixture is acidified to pH 4–5 and maintained at about 95°C, where the hydroxymethyl groups of the initial products react with urea amide/imide nitrogens of another molecule to form methylene and some methylene–ether bonds. In this polymerization reaction, some hydroxymethyl groups split off as formaldehyde by the reverse reaction mentioned above due to the decreasing number of amide groups available in the system as the methylene/methylene–ether group content increases. While the theoretical functionality of urea molecules is four, the average value attainable under the typical UF resin synthesis condition is only about 2.5, varying slightly depending on the F/U_1 ratio used. This limitation means expulsion of formaldehyde molecules as the degree of polymerization increases to give rise to free formaldehyde contents in

X = CH₂ and/or CH₂OCH₂

Y = CH₂OH, CH₂OCH₂OH, or H

Z = Y, XNZ(CO)NZZ
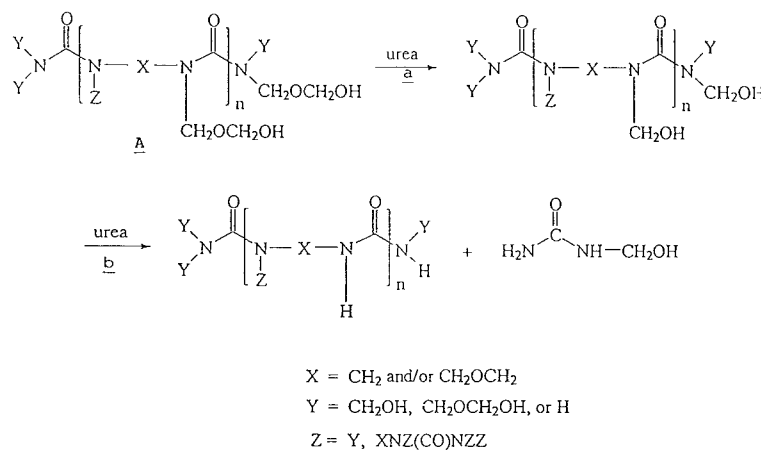
Figure 1 (A) Polymeric UF resin components and migration of (a) hemiformal groups and (b) hydroxymethyl groups from them to monomeric UF resin components.

the reaction mixture of about 0.28 mole per mole of first urea for the typical F/U_1 ratio value of 2.1.

Once the polymerization reaction has progressed to the target value, normally when the reaction mixture's viscosity reaches about "W" by the Gardener–Holdt scale (~32 P) at a resin solids level of 60–65%, the reaction is ended by adjusting the pH back to a weak alkaline value. The resulting products are polymeric methylene/methylene–ether hydroxymethylureas (Fig. 1). In the third step of resin synthesis, cooling is applied, and when the resin mixture reaches about 70°C, the second urea (U_2) is added to give a final formaldehyde/urea [$F/(U_1 + U_2)$] ratio of about 1.15. The second urea cools the batch quickly to about 50°C, but cooling can still take about 2 h to reach room temperature in industry. During this cooling period, part of the second urea reacts with the free formaldehyde present in the reaction mixture to form monomeric hydroxymethylureas. This reaction normally leaves less than 0.5% free formaldehyde and about 25% of all urea used remains as free urea in the finished resins.[18,19] The second urea-derived monomeric components constitute up to 36–52% of the total urea, depending on the F/U_1 mol ratio of between 1.8 and 2.4, and the balance is composed of the first urea-derived polymeric resin components.

In our previous reports,[15–19] the hydroxymethyl groups on the polymeric resin components were found to dissociate to formaldehyde and react with the second urea during the cooling and storage periods (Fig. 1). This migration of hydroxymethyl groups occurring in varying extents at the time of resin use was shown to be partly responsible for the varying bond-strength and formaldehyde-emission values of boards with a given resin as often observed in industry. Initially, the heating/stirring of finished resins at 60°C for up to 2.5 h or the storing at room temperature for up to 2 weeks was shown to cause the migration of hydroxymethyl groups and decreases in the viscosity of the resins. These posttreatments resulted in varying board-strength and formaldehyde-emission values.

The limited functionality of urea at about 2.5 and the reversibility of the hydroxymethylation reactions mentioned above caused the migration of hydroxymethyl groups. In industrial manufacturing of UF resins, the addition of the second urea carried out during the cooling period can affect the migration of hydroxymethyl groups, but the migration extent would vary because of the different cooling rates and varying time lengths between resin manufacture and use.

Other changes occurring in UF resins were also uncovered in the storing of resins at room temperature for up to 50 days. The methylene and methylene–ether group contents increased as well as the viscosity of the resins, and a new phase (white appearance) usually appeared and expanded due to the agglomeration of resin molecules. These increases in degree of polymerization and physical changes occurred with different rates for different F/U_1 mol ratios used in the resin synthesis, with the resin samples taken during the treatments showing varying board-strength and formaldehyde-emission values. In alkaline pH, methylene–ether bonds were generally known to form but methylene bonds do not form. On the surface, these increases in methylene/methylene–ether bond contents were in accord with the fact that UF resins in alkaline pH form weak gels at 100°C in about 40 min or longer. However, it is generally known that UF resins in alkaline pH do not give the type of cured products required as wood adhesives even at elevated temperatures. In this work, therefore, a detailed examination was carried out to study the reactions that occur in alkaline pH and to investigate their effects on the bond strength and formaldehyde emission by extending the stirring/heating treatment of resins at 60°C and storing selected heat-treated resins at room temperature. Thus, the UF resins used in the previous studies were synthesized with F/U_1 ratios of 1.80, 2.10, and 2.40 and cooled to room temperature and the second urea added to F/U ratios of 1.15. These resins were then stirred/heated at 60°C up to 13.5 h depend-

TABLE I
Synthesis Parameters of UF Resins with Preparative Sequences Shown in Parentheses

UF resin	First step	Second step	Third step
2.4b	(1) 5000 g 50% F, 1250 g U_1, pH 7.8, 90°C, 30 min, $F/U_1 = 2.4$	(2) pH 4.1, 95°C, ~ 145 min, viscosity Y	(3) pH 7.8, cool to 4°C, 1359 g U_2, stir 2 h, $F/(U_1 + U_2) = 1.15$
2.1b	(1) 5000 g 50% F, 1428.6 g U_1 pH 7.8, 90°C, 30 min, $F/U_1 = 2.1$	(2) pH 4.5, 95°C, ~ 120 min, viscosity W	(3) pH 7.8, cool to 4°C, 1180.2 g U_2, stir 2 h, $F/(U_1 + U_2) = 1.15$
1.8b	(1) 5000 g 50% F, 1500 g U_{11}, pH 7.8, 90°C, 30 min (3) pH 7.8, 166 g U_{12}, 90°C, 20 min, $F/(U_{11} + U_{12}) = 1.8$	(2)pH 4.7, 95°C, ~ 30 min, viscosity B (4) pH 4.7, 90°C, ~ 30 min, viscosity R	(5) pH 7.8, cool to 4°C, 941 g U_2, stir 2 h, $F/(U_1 + U_2) = 1.15$
1.6b	(1) 1000 g 50% F, 476 g U_{11}, pH 7.8, 90°C, 30 min (3) pH 7.8, 149 g U_{12}, 90°C, 20 min, $F/(U_{11} + U_{12}) = 1.6$	(2) pH 4.7, 95°C, ~ 30 min, viscosity B (4) pH 5.0, 90°C, ~ 30 min, viscosity Q	(5) pH 7.8, cool to 4°C, 245 g, U_2, stir 2 h, $F/(U_1 + U_2) = 1.15$
1.4b	(1) 1000 g 50% F, 476 g U_{11}, pH 7.8, 90°C, 30 min (3) pH 7.8, 238 g U_{12}, 90°C, 20 min, $F/(U_{11} + U_{12}) = 1.4$	(2) pH 4.7, 95°C, ~ 30 min, viscosity B (4) pH 5.0, 90°C, ~ 30 min, viscosity Q	(5) pH 7.8, cool to 4°C, 156 g, U_2, stir 2 h, $F/(U_1 + U_2) = 1.15$

ing on the stability, and the resin samples heated for 2.5 h were allowed to stand at room temperature for up to 27 days to examine the effect of the combined heating/storing treatments. Selected resin samples taken during these posttreatments were analyzed using ^{13}C-NMR and their performance evaluated by bonding particleboards and testing for bond strengths and formaldehyde emission. Also, UF resins normally synthesized with a low F/U_1 mol ratio of 1.40 or 1.60 were not accessible in the past due to short shelf lives, but cooling of the resin mixture prior to the addition of the second urea to ~4°C was found to increase shelf lives. These resins were briefly examined regarding their behavior toward posttreatments.

EXPERIMENTAL

Reagent-grade urea, sulfuric acid, sodium hydroxide, and a fresh industrial-grade 50% formaldehyde solu-

tion, donated by Georgia–Pacific Resins (Louisville, MS) and kept at 60°C in the laboratory, were used. The pH adjustments were made with 4.0% sulfuric acid or an 8.0% sodium hydroxide solution with pH drifts maintained within ±0.2. The synthesis and posttreatment procedures of resins are described below and also summarized for clarity in Tables I and II, respectively.

Resin 2.1b with an F/U_1 ratio of 2.10

For the typical UF resin made, according to the procedure described earlier,[15–19] 3000 g of a 50% formaldehyde solution was added to a stirred reactor, the pH adjusted to 7.8, and then heated to 70°C. The first urea (1428.6 g) was then added over a period of 15 min ($F/U_1 = 2.10$). The temperature of the reaction mixture was maintained at 90°C for 30 min. The reaction mixture was then adjusted to pH 4.5 and reacted at 95°C until a viscosity of "W" was reached (approxi-

TABLE II
Experimental UF Resins Obtained by Heating the Synthesized Resins at 60°C for Given Times (h) and Storing at Room Temperature for 2 Days or Indicated Numbers of Days (d)

UF resin	0.17 h	2.5 h	5.0 h	7.5 h	8.75 h	13.5 h
2.4b	2.4b′	2.4j (7 d) 2.4k (15 d) 2.4l (27 d)	2.4m	2.4n	2.4o	2.4p
2.4b	2.4b′	2.1j (7 d) 2.1k (15d) 2.1l (27 d)	2.1m	2.1n	2.1o	
1.8b	1.8b′	1.8j (7d) 1.8k (15 d) 1.8l (27 d)	1.8m	1.8n		
1.6b	1.6b′					
1.4b	1.4b′					

mately 120 min). The reaction mixture was then made alkaline to pH 7.8 and cooled to 4°C and the second urea added [1180.2 g, $F/(U_1 + U_2) = 1.15$]} and stirred for 2 h without heating to sample resin 2.1b (900 g). The residual resin was stirred and heated to 60°C over a period of 30 min and held for 10 min to sample resin 2.1b′ (900 g). The residual resin was further held at the same temperature for 2.5 h to sample resin 2.1j (900 g), resin 2.1k (900 g), and resin 2.1l (900 g), which were stored for 7, 15, and 27 days, respectively, at room temperature. The residual resin was further held at the same temperature until the total heating time reached 5.0 and 7.5 h, respectively, to give resins 2.1m (900 g) and 2.1n (900 g). Sampled resins were used within 2 days to make boards. The residual resin was heated further until 8.75 h for resin 2.1o (50 g), which was used for ^{13}C-NMR analyses and viscosity measurements.

Resin 2.4b with an F/U$_1$ ratio of 2.40

The procedure described above was used with the first urea reduced to 1250 g ($F/U_1 = 2.40$) and the second step conducted at pH 4.10 to compensate for the slower reaction rate. The polymerization reaction time was lengthened to 145 min to reach a viscosity value of "Y" (Gardner–Holdt). The product was cooled to 4°C and the second urea [1359 g, $F/(U_1 + U_2) = 1.15$] added and then stirred for 2 h without heating to sample resin 2.4b. The residual resin was stirred and heated to 60°C over a period 30 min and kept for 10 min to sample resin 2.4b′ (900 g). The residual resin was further held at the same temperature for 2.5 h to sample resins 2.4j (900 g), 2.4k (900 g), and 2.4l (900 g), which were stored at room temperature for 7, 15, and 27 days, respectively, to make boards. The residual resin was further held at the same temperature until the total heating time reached 5.0, 7.5, 8.75, and 13.5 h, respectively, for resins 2.4m (900 g), 2.4n (900 g), 2.4o (50 g), and 2.4p (50 g). All resins were used within 2 days to make boards except the last two, which were for ^{13}C-NMR analyses and viscosity measurements.

Resin 1.8b with an F/U$_1$ ratio of 1.80

The procedure used above was slightly modified for this low F/U_1 ratio resin. With the same amount of formaldehyde used above, the first urea [1666 g ($F/U_1 = 1.80$)] was divided into two parts to minimize turbidity developing in the polymerization step. Thus, the first part of the first urea (1500 g) was reacted with formaldehyde in alkaline pH as usual and then reacted at pH 4.5 and 95°C for approximately 30 min (10 min after "B" viscosity). Next, the reaction mixture was made alkaline to pH 7.8 and the second part of the first urea (166 g) added and reacted for 20 min at 90°C. The reaction mixture was then acidified to pH 4.70 and reacted at 90°C until an "R" viscosity was reached

(approximately 30 min) and then made alkaline to pH 7.8 and cooled to 4°C. The product showed a light turbidity, much less than when the resin was made without the modification. Then, the second urea [941 g, $F/(U_1 + U_2) = 1.15$] was added and stirred for 2 h without heating to sample resin 1.8b (900 g). The residual resin was stirred and heated to 60°C over a period of 30 min and kept for 10 min to take resin 1.8b′ (900 g). The residual resin was further held at the same temperature for 2.5 h to sample resins 1.8j (900 g), 1.8k (900 g), and 1.8l (900 g), which were stored at room temperature for 7, 15, and 27 days, respectively. The stored resins showed a high level of turbidity. The residual resin was further held at the same temperature for 5.0 and 7.5 h to sample resins 1.80m (900 g) and 1.80n (900 g), respectively, to make boards in 2 days. The residual resin was further heated for viscosity measurements.

Resin 1.6b with a F/U$_1$ ratio of 1.60

The synthesis procedure was similar to that for resin 1.8b. With 1000 g of a 50% formaldehyde solution, the first urea (625 g, $F/U_1 = 1.60$) was divided into two parts. Thus, the first part of the first urea (476 g) was reacted with the formaldehyde in alkaline pH as usual and then reacted at pH 4.5 and 95°C for approximately 30 min (10 min after "B" viscosity). Then, the reaction mixture was made alkaline to pH 7.8 and the second part of the first urea (149 g) was added and reacted for 20 min at 90°C. The reaction mixture was then acidified to pH 5.0, reacted at 90°C until "Q" viscosity was reached (approximately 30 min), and made alkaline to pH 7.8 and cooled to 4°C. The second urea [245 g, $F/(U_1 + U_2) = 1.15$] was then added and stirred for about 2 h without heating to sample resin 1.6b (900 g). Additionally, the residual resin was heated to 60°C over a period of 30 min and held for 10 min and cooled to room temperature to sample resin 1.6b′ to make boards within 2 days. In a preliminary experiment, the stability of this resin and resin 1.4b (see below) was shown to be about 5 days at room temperature. The stability of the resin severely deteriorated in 1 h on heating at 60°C and, therefore, heating and storage experiments were not conducted.

Resin 1.4b with an F/U$_1$ ratio of 1.40

The procedure used was similarly modified as in the synthesis of resin 1.6b. With 1000 g of a 50% formaldehyde solution, the first urea 714 g ($F/U_1 = 1.40$) was divided into two parts. Thus, the first part of the first urea (476 g) was reacted with the formaldehyde in alkaline pH as usual and reacted at pH 4.5 and 95°C for approximately 30 min (10 min after "B" viscosity). Then, the reaction mixture was made alkaline to pH 7.8 and the second part of the first urea (238 g) was added and reacted for 20 min at 90°C. The reaction

mixture was then acidified to pH 5.0, reacted at 90°C until "Q" viscosity was reached (approximately 30 min), and made alkaline to pH 7.8 and cooled to 4°C. The second urea [156 g, $F/(U_1 + U_2) = 1.15$] was then added and stirred for 2 h without heating to sample resin 1.4b (900 g). The residual resin was heated to 60°C over a period of 30 min and held for 10 min and cooled to room temperature to sample resin 1.4b′. Boards were made within 2 days.

Preparation of particleboards

The board manufacturing procedure was the same as those reported earlier.[15–18,20] Single-layer boards were made using dried core–layer wood particles obtained from the Georgia–Pacific Corp. particleboard plant (Louisville, MS). A rotary drum blender, forming box, and automated Diefenbacher hot press were used according to the standard laboratory procedure. Resins were catalyzed with 0.5% ammonium sulfate as a 25% water solution based on the liquid resin weight and resin solids loading levels were 8.0% based on the dry wood weight. No wax was added. Hot pressing was carried out for 3.25 min at 163°C. One panel (860 × 860 × 12.65 mm) was made for each resin with a target density of 801 kg/m^3 (50 lb/ft^3), one of the common particleboard grades used in North America.

Formaldehyde-emission tests

The Small-Scale (SC) Test Chamber Method (ASTM: D6007-96) was used to measure formaldehyde-emission levels of boards at Georgia–Pacific Resins Laboratory (Decatur, GA). Hot-pressed boards were allowed to stand for 24 h in the laboratory and three test specimens (379.5 × 199.2 mm) were cut from each board and the edges were sealed with aluminum adhesive tape to give a total exposed surface area of 0.4536 m^2 per board. The test samples were aired for 7 days at 23.9°C at a relative humidity of 50% and then loaded in the test chamber, which was maintained at a makeup air flow of 8.93 L/min to provide a 1/2 air change per hour. The loading ratio was 0.13 ft^2 of the panel surface area per cubic foot of chamber volume. The formaldehyde level in the exiting air was monitored over time and the steady-state values, *Ceq*, attained in time were reported as the formaldehyde-emission values of the test samples.

The Perforator Extraction (PE) Method (DIN EN120 1992) was also used for selected boards to determine the free formaldehyde contents of boards in this laboratory. Test samples of the boards (2.5 × 2.5 × 1.27 cm) were cut at the same time as were the SC samples and kept in a sealed plastic bag until the test, done within 1 week. Briefly, each test sample was cut into four equal pieces and 110 g was put in a 1-L flask fitted to a condenser and a water trap, and toluene (600 mL) was added and heated to boil to extract the formalde-

hyde. The toluene and formaldehyde vapor rose to the condenser and the liquid mixture collected was forced by gravity to pass through a perforator (fritted glass plate) and then allowed to rise through a column of water (~1 L) for the absorption of formaldehyde. The separated toluene was returned to the boiling flask. This extraction was continued for 2 h and the formaldehyde absorbed in the water measured, in mg per 100 g of the board. Board samples showed little physical degradation from the extraction test.

Internal bond and bending strength tests of boards

Strength tests for the boards were carried out according to ASTM procedure D1037. Test specimens were cut and equilibrated for 3 weeks in a constant humidity room to about 10% moisture content. The internal bond (IB) strength data obtained were normalized with respect to a 50 lb/ft^3 density within each set of the eight test samples tested, where the strength values correlated relatively well with densities, with r^2 values greater than 0.60 in general.

^{13}C-NMR spectra and calculation of carbon group values

Test samples were prepared by mixing 2.0 g of resin with 1.0 g of deuterium oxide. Qualitative spectra were obtained with a Techmag 360-MHz NMR spectrometer using a pulse width of 22 μs (80°) and pulse delay of 10 s (Spectral Dada Services, Inc., Champaign, IL). Decoupling power was kept on during the acquisition and off during the delay to suppress the nuclear Overheuser effect.[21] The ^{13}C-NMR relaxation times, T_1, measured on a typical UF resin by the inversion-recovery method,[22] were 1.4–6.2 s for urea carbonyls, 1.1 s for methanediol, 5.8 s for methanol present as an impurity, and 0.16 s or less for all other methylenic carbons.[15] Normally, about 400 scans were accumulated. Spectra were integrated and urea carbonyls and methylenic carbons separately quantified as percentages. No formaldehyde losses were assumed to occur in resin syntheses for resin composition calculations. Methylenic group percentage values were converted into concentration values by multiplying with F/U ratios. Urea carbonyls were assorted according to the substitution value, that is, free urea, monosubstituted urea, di/trisubstituted urea, and tetrasubstituted urea. The calculation procedures for polymer structures of UF resins derived for differing F/U_1 ratios were described in previous reports.[15–17] To avoid duplications of running similar resin samples, ^{13}C-NMR data of untreated resins 2.4b, 2.1b, and 1.8b were taken from a previous publication.[17]

RESULTS AND DISCUSSION

^{13}C-NMR methods of analyzing UF resins were extensively reported[23–30] and extended in previous publi-

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

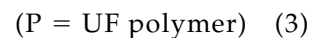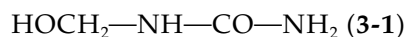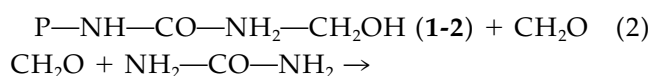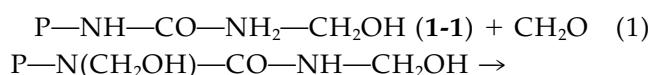| Groups (ppm)	Synthesized, heat-treated, stored UF resin samples with sample nos. as defined in the text												
	2.4b	2.4j	2.4k	2.4l	2.4m	2.4o	2.4p	2.1b	2.1j	2.1k	2.1m	2.1o	1.8b
91.0	0.79	0.69	0.73	0.66	0.60	0.82	0.58	0.52	0.57	0.51	0.67	0.55	0.36
87.0	0.24	0.06	0.16	0.00	0.00	0.00	0.00	0.19	0.00	0.06	0.00	0.00	0.10
83.1	0.28	0.41	0.51	0.50	0.26	0.20	0.27	0.29	0.25	0.18	0.18	0.22	0.28
79.1	2.66	1.95	2.26	2.26	1.82	1.77	1.73	2.22	1.66	1.67	1.36	1.38	2.15
75.1	4.98	4.43	4.12	4.35	3.75	3.54	3.33	4.82	4.32	4.24	4.95	4.59	4.50
69.5	6.79	10.03	10.27	10.90	9.40	11.06	12.15	7.27	9.70	10.46	10.80	11.30	8.92
72.0	17.91	13.88	12.23	12.83	10.47	7.90	5.97	18.52	12.93	11.12	12.32	10.34	15.19
65.2	35.01	30.31	30.24	25.07	36.53	36.79	36.82	29.66	30.91	30.94	27.20	28.11	26.70
60.1	4.62	4.58	4.70	5.20	1.53	1.05	1.15	4.48	3.89	4.60	4.12	4.26	4.29
53.9	21.06	21.17	20.60	20.88	22.32	21.18	20.47	23.79	22.84	21.83	22.98	22.30	25.81
47.4	5.64	12.67	14.18	17.35	13.31	15.69	17.48	8.24	12.88	14.35	15.42	16.95	11.70
164.0	28.01	18.32	14.71	15.30	15.74	12.83	11.17	26.39	18.05	16.51	14.18	12.75	25.08
162.2	23.58	31.42	32.72	34.97	30.81	33.53	35.77	18.44	28.14	30.49	30.35	32.20	15.91
160.7	45.86	47.84	49.60	46.90	51.43	51.50	50.83	54.03	50.70	50.18	53.86	52.93	56.78
158.0	2.55	2.43	2.97	2.83	2.01	2.14	2.22	1.14	3.11	2.81	1.61	2.02	2.23

The carbon group structures for the chemical shift values are shown in Figure 2(a,b).

cations.[15–19] The ^{13}C-NMR data of selected resins obtained in this study are summarized in Table III. The spectrum of resin 2.4o (8.75 h at 60°C) is shown in Figure 2(B) with chemical shifts assignments shown according to the structural groups in Figure 2(A). Spectra of resins 1.6b and 1.4b are shown in Figure 3(A,B), respectively, as these resins were made stable the first time for several days at room temperature. ^{13}C-NMR data were combined with data previously reported for treatments at 60°C for up to 2.5 h (ref. 17) and reported in Figure 4 for hydroxymethyl groups, in Figure 5 for methylene/methylene–ether groups, in Figure 6 for degree of polymerization values, and Figure 7 for urea carbonyl groups. The methylene/methylene–ether group contents of resins were converted into the degree of polymerization values shown in Figure 6 according to the method used earlier.[15] The viscosity changes of resins that occurred in heat treatments are reported in Figure 8.
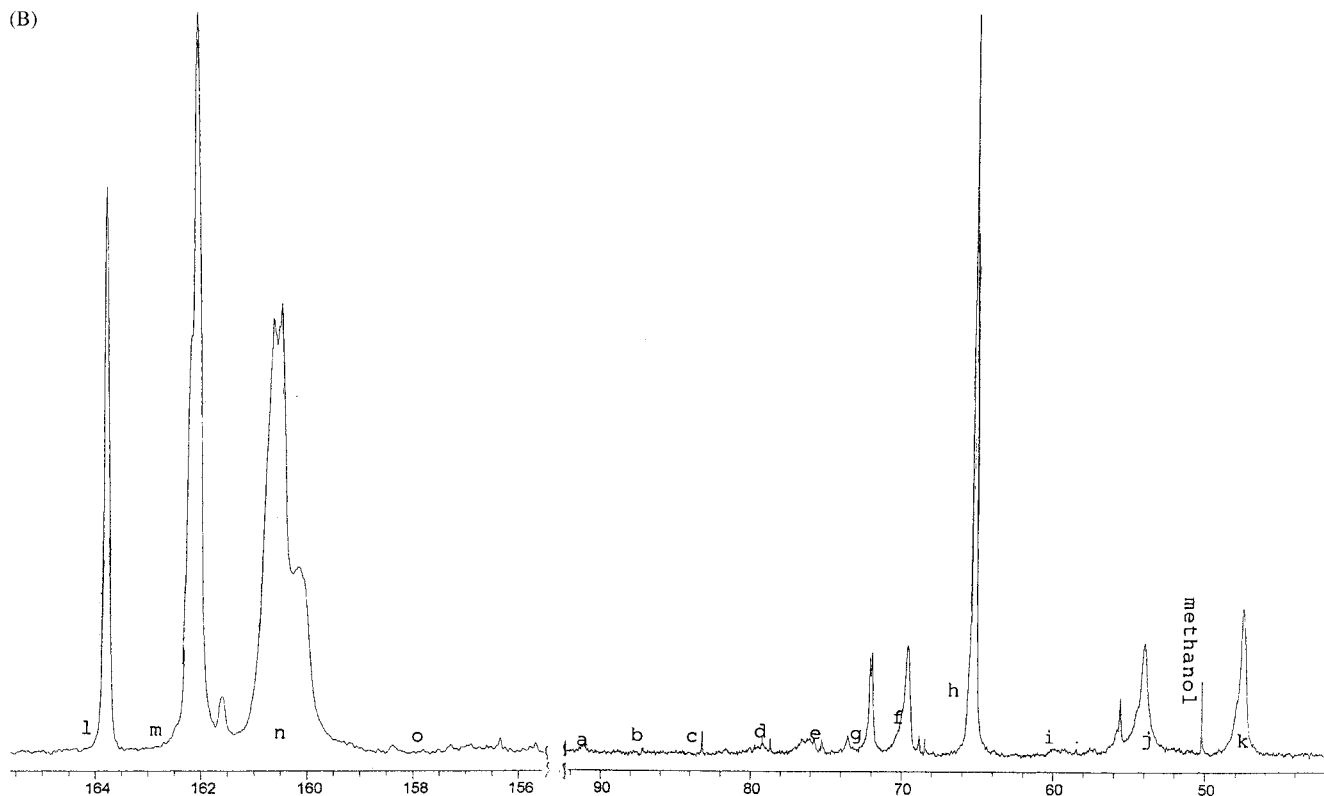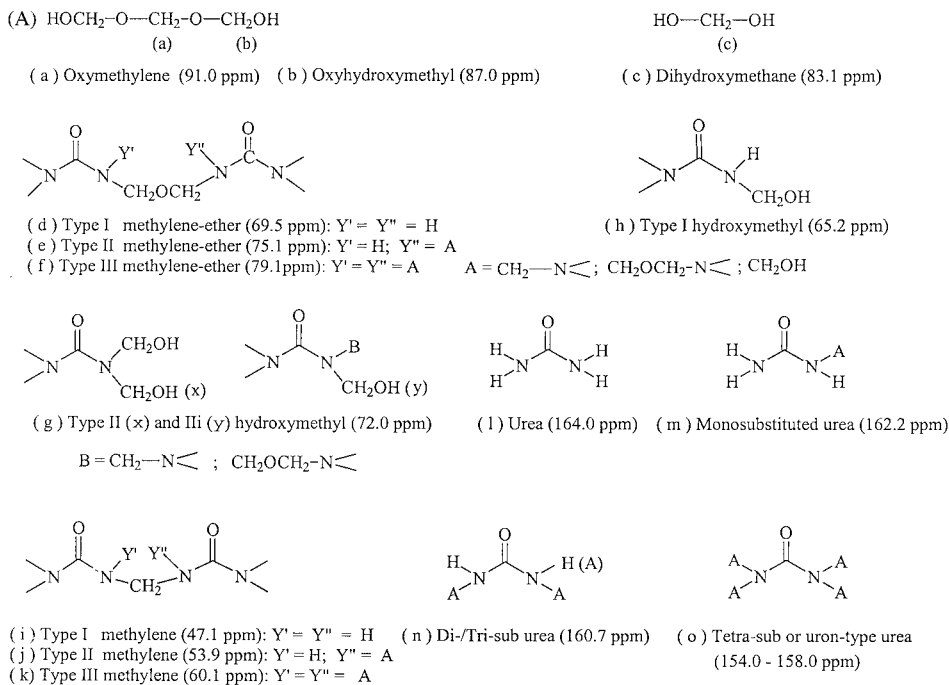
Reexamination of postheat-treatment effects of resins at 60°C for 2.5 h

Data for posttreatments of resins at 60°C to 2.5 h were reported in a previous report.[17] The viscosity of resins decreased and the migration of type II/IIi hydroxymethyl groups from polymeric (U_1) to monomeric (U_2) resin components occurred with minimal increases in the total methylene/methylene–ether group contents (Figs. 4–8). Type I methylene/methylene–ether group contents increased at the expense of types II and III methylene/methylene–ether group contents, reflecting the migration of type IIi hydroxymethyl groups situated in the middle of UF polymer chains. Types II and III methylene/methylene–ether groups that ap-

pear as branched in chemical shift values would decrease and type I groups increase when the hydroxymethyl group bonded to the neighboring nitrogen is type IIi and migrates to the second urea. Similar changes occurred when resins were stored at room temperature for up to about 20 days. Overall, the migration of hydroxymethyl groups resulted in increases in type I hydroxymethyl group contents, decreases in free urea contents, and increases in monosubstituted urea contents. Thus, in this early heat treatment, type II/IIi hydroxymethyl groups on the polymeric resin components break off to form free formaldehyde, which reacts with the second urea to form monohydroxymethylurea (**3-1**) [eqs. (1)–(3)]:

$$P-NH-CO-NH-(CH_2OH)_2 \rightarrow$$

$$P-NH-CO-NH_2-CH_2OH \ (\textbf{1-1}) + CH_2O \quad (1)$$

$$P-N(CH_2OH)-CO-NH-CH_2OH \rightarrow$$

$$P-NH-CO-NH_2-CH_2OH \ (\textbf{1-2}) + CH_2O \quad (2)$$

$$CH_2O + NH_2-CO-NH_2 \rightarrow$$

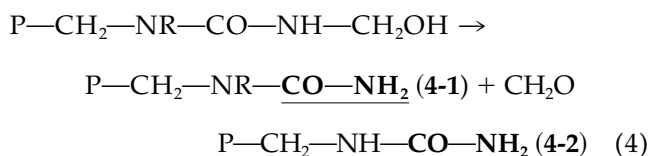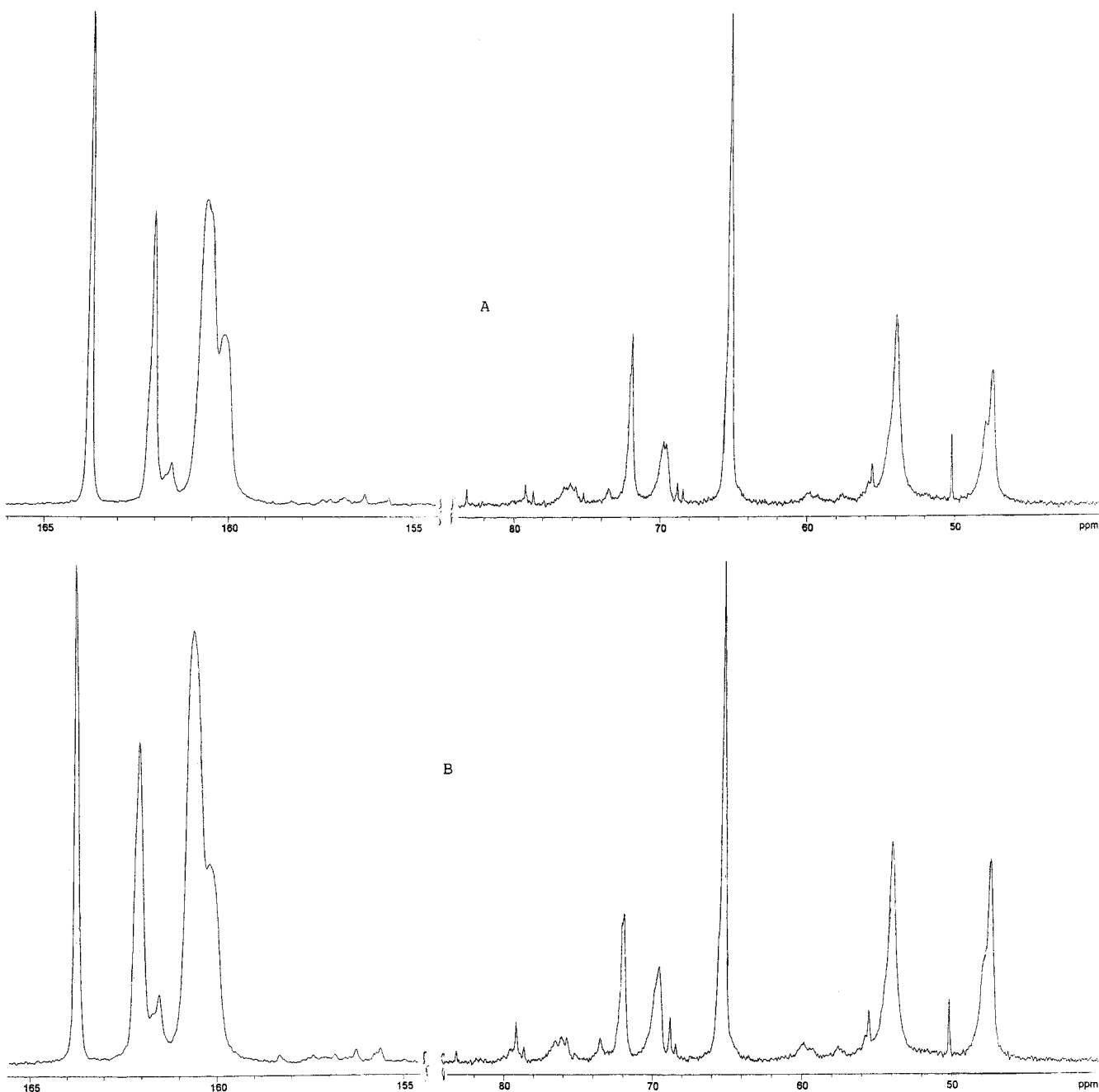$$HOCH_2-NH-CO-NH_2 \ (\textbf{3-1})$$

$$(P = UF \ polymer) \quad (3)$$

Reexamination of the spectral data, however, indicated that other reactions also occurred in this posttreatment (Figs. 4–6). First, the increases in monosubstituted urea carbonyl contents (162.2 ppm) were greater than were the decreases in free urea carbonyl contents (164.0 ppm), and also decreases in di- and trisubstituted urea carbonyl contents were observed. The excess increases in monosubstituted urea carbonyls over the decreases in free urea were about 2.0% for

(A) $HOCH_2-O---CH_2-O-CH_2OH$
 (a)   (b)

HO---CH_2—OH
(c)

(a) Oxymethylene (91.0 ppm)   (b) Oxyhydroxymethyl (87.0 ppm)   (c) Dihydroxymethane (83.1 ppm)

(d) Type I methylene-ether (69.5 ppm): Y' = Y'' = H
(e) Type II methylene-ether (75.1 ppm): Y' = H; Y'' = A
(f) Type III methylene-ether (79.1ppm): Y' = Y'' = A $A = CH_2$—$N\lt$; CH_2OCH_2-$N\lt$; CH_2OH

(h) Type I hydroxymethyl (65.2 ppm)

(g) Type II (x) and IIi (y) hydroxymethyl (72.0 ppm)   (l) Urea (164.0 ppm)   (m) Monosubstituted urea (162.2 ppm)

$B = CH_2$—$N\lt$; CH_2OCH_2-$N\lt$

(i) Type I methylene (47.1 ppm): Y' = Y'' = H   (n) Di-/Tri-sub urea (160.7 ppm)   (o) Tetra-sub or uron-type urea
(j) Type II methylene (53.9 ppm): Y' = H; Y'' = A   (154.0 - 158.0 ppm)
(k) Type III methylene (60.1 ppm): Y' = Y'' = A

(B)

Figure 2   (A) Chemical structures of molecules and carbon groups occurring in polymeric UF resins with the ^{13}C-NMR-shift values identified with small letters from (a) to (o). (B) ^{13}C-NMR spectra of UF resin 2.4o (8.75 h at 60°C) with chemical structures of groups identified with small letters from (a) to (o) with respect to structures shown in (A).

resins 2.4d, 3.9% for resin 2.1d, and 9.4% for resin 1.8d. One explanation for this secondary reaction is the migration of type I hydroxymethyl groups from polymeric resin components to leave behind free amide end groups (4-1) :
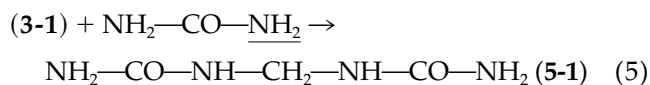
$$P—CH_2—NR—CO—NH—CH_2OH \rightarrow$$

$$P—CH_2—NR—\underline{CO—NH_2}\ (\textbf{4-1}) + CH_2O$$

$$P—CH_2—NH—\underline{CO—NH_2}\ (\textbf{4-2}) \quad (4)$$

Figure 3 ^{13}C-NMR spectra of UF resins (A) 1.6b and (B) 1.4b made with F/U$_1$ mol ratios of 1.6 and 1.4, respectively, and the second urea added to an F/U ratio of 1.15.

In addition, the amide end groups (**4-1**), when the other neighboring nitrogen is bonded to UF polymers only through one methylene group, will be monosubstituted urea groups bonded to UF polymers (**4-2**). This reaction path will increase the monosubstituted urea group contents and decrease the disubstituted urea group contents. Second, increases in type I methylene/methylene–ether group contents were slightly higher than were decreases in type II/III methylene/methylene–ether group contents, indicating that total methylene/methylene–ether group contents began to increase (Fig. 5). A plausible explanation for these

increases is the reaction of monohydroxymethylurea (**3-1**) with free urea to form methylene–diurea (**5-1**) :

$$(\textbf{3-1}) + NH_2\text{---}CO\text{---}\underline{NH_2} \rightarrow$$

$$NH_2\text{---}CO\text{---}NH\text{---}CH_2\text{---}NH\text{---}CO\text{---}NH_2 \ (\textbf{5-1}) \quad (5)$$

Methylene–diurea (**5-1**) is a monosubstituted urea and will increase monosubstituted urea group contents as well as type I methylene group contents. Data presented below indicate that ^{13}C-NMR peaks for monosubstituted urea carbonyls in these resins represent not only mono-
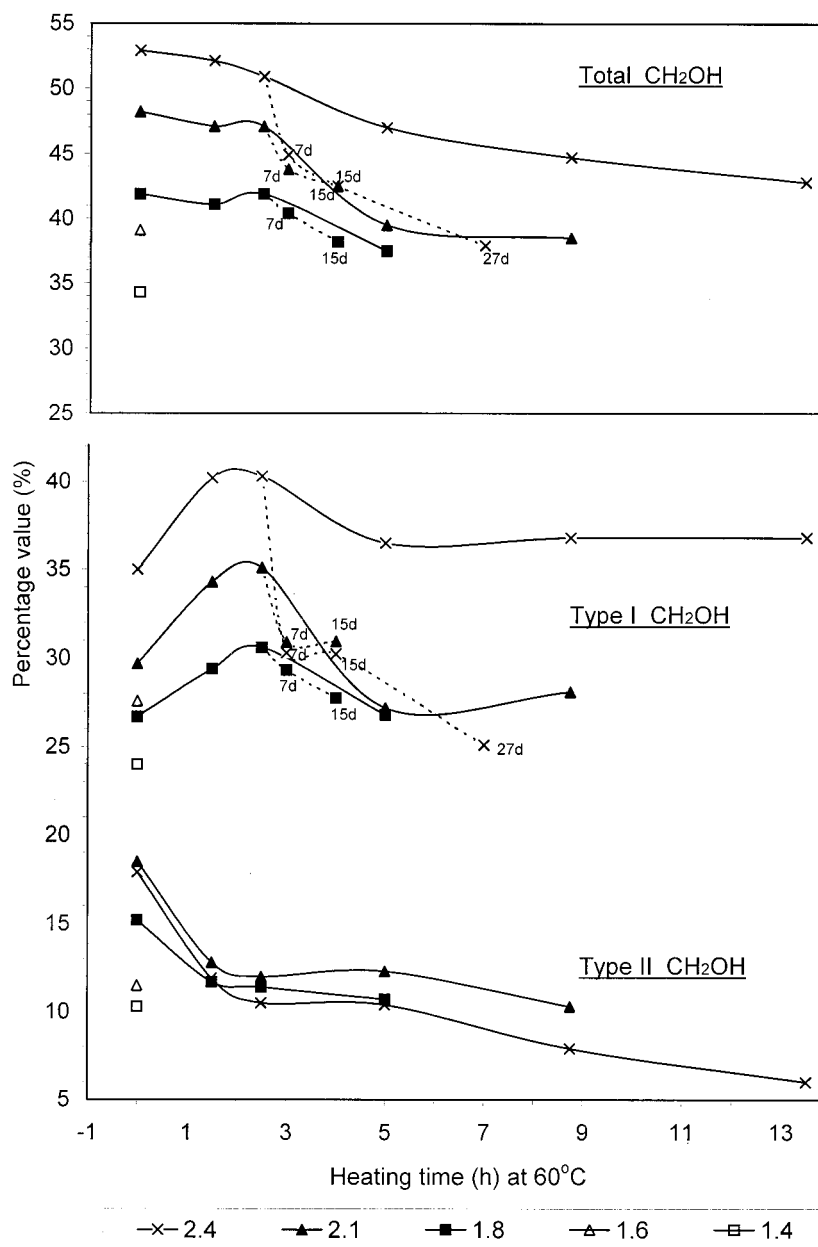
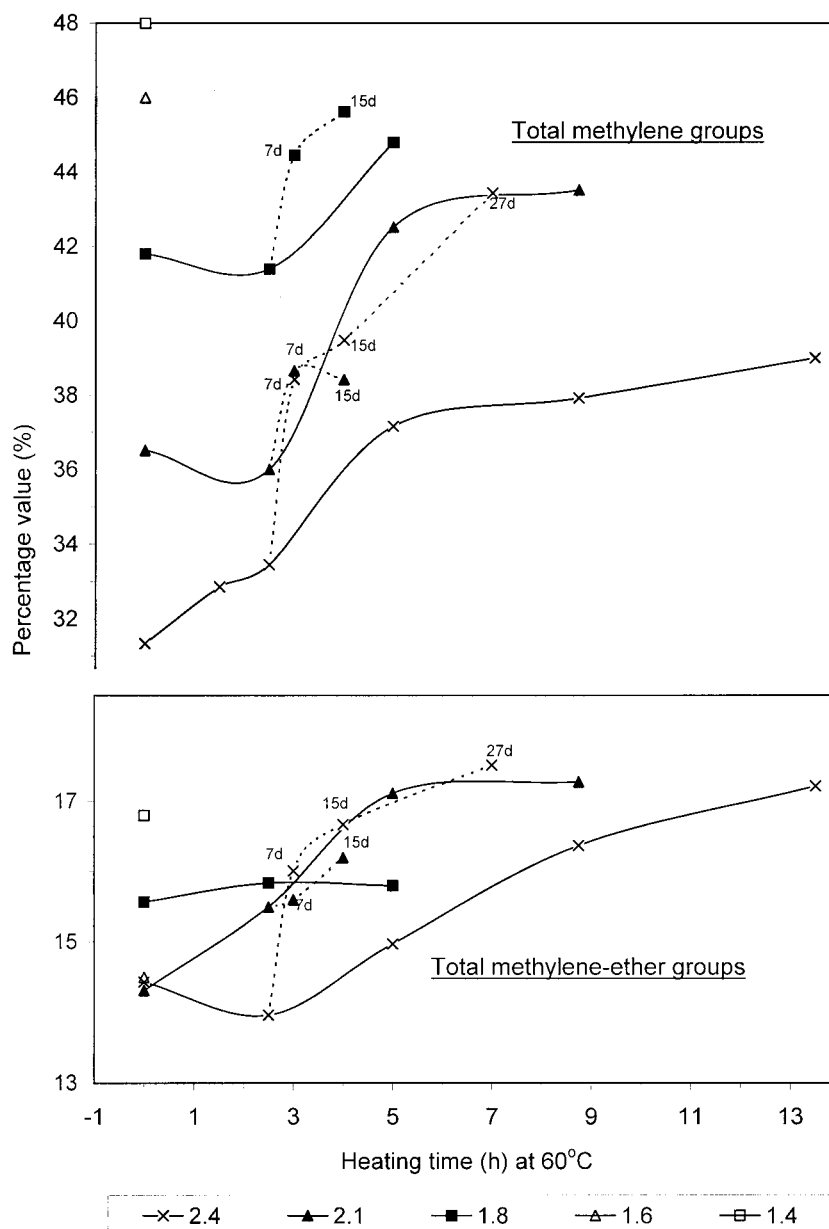**Figure 4** Changes in ^{13}C-NMR values of total and types I and II/IIi hydroxymethyl groups in UF resins 1.4–2.4 (solid line) heated at 60°C for up to 13.5 h and (dotted line) heated at 60°C for 2.5 h and stored at room temperature for 7 and 15 days.

hydroxymethylurea (**3-1**), but also methylene–diurea (**5-1**) and singly bonded urea groups (**4-2**).

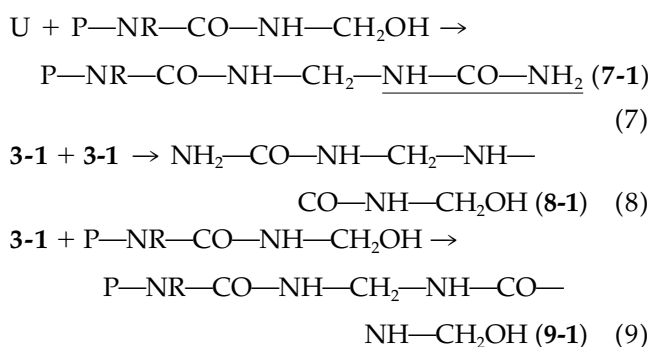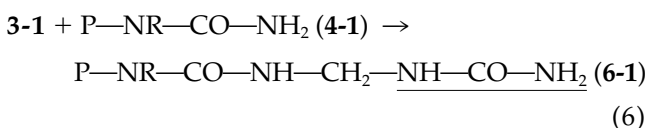### Effects of posttreatments of resins at 60°C for longer than 2.5 h

^{13}C-NMR data of resins posttreated at 60°C for longer than 2.5 h generally indicated the continued migration of hydroxymethyl groups (Table III). This was shown by decreases in both the type II hydroxymethyl group and free urea contents and increases in the monosubstituted urea species content (Figs. 4, 5, and 7). However, the more significant changes were increases in the total and type I methylene/methylene–ether group and disubstituted urea species contents and decreases in type I hy-

droxymethyl group contents. These changes indicated that the resins' degree of polymerization values increased significantly, principally between 2.5 and 5.0 h of heat treatments (Fig. 6). The reactions then slowed down. Similar changes in the resins occurred between 15 and 30 days of storage at room temperature,[18] indicating that the underlying chemical reactions were accelerated by high temperature. Decreases in the free urea content paralleled increases in the disubstituted urea species, and decreases in the hydroxymethyl group contents were about one-half of these amounts. Monosubstituted urea species increased modestly. Normally, peaks for di- and trisubstituted urea carbonyls are only slightly separated, but a close inspection of these peaks indicated that
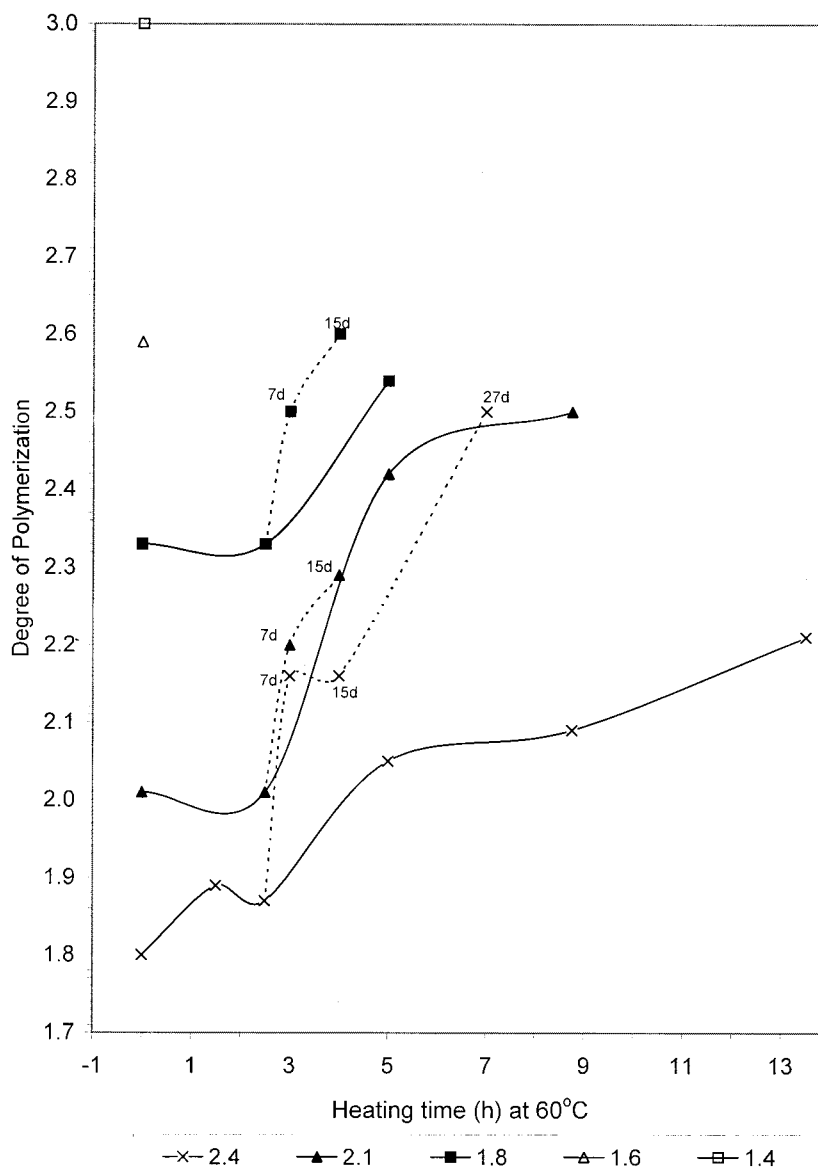
Figure 5 Changes in ^{13}C-NMR values of total methylene and methylene–ether groups in UF resins 1.4–2.4 (solid line) heated at 60°C for up to 13.5 h and (dotted line) heated-treated at 60°C for 2.5 h and stored at room temperature for 7 and 15 days.

most increases were di- rather than trisubstituted urea carbonyls. These functional group changes can be summed up as a result of reactions that occurred between type I hydroxymethyl groups of UF polymers (**1-1**) or monohydroxymethylurea (**3-1**) and free urea or urea groups bonded to UF polymers (**4-1**; **5-1**). The resultant species would be methylene–diurea and UF polymers with singly bonded urea end groups [eqs. (6) and (7)] and their hydroxymethyl group derivatives [eqs. (8) and (9)]:

$$\textbf{3-1} + \text{P—NR—CO—NH}_2 \text{ (4-1)} \rightarrow$$

$$\text{P—NR—CO—NH—CH}_2\underline{\text{—NH—CO—NH}_2} \text{ (6-1)}$$

$$(6)$$

$$\text{U} + \text{P—NR—CO—NH—CH}_2\text{OH} \rightarrow$$

$$\text{P—NR—CO—NH—CH}_2\underline{\text{—NH—CO—NH}_2} \text{ (7-1)}$$

$$(7)$$

$$\textbf{3-1} + \textbf{3-1} \rightarrow \text{NH}_2\text{—CO—NH—CH}_2\text{—NH—}$$

$$\text{CO—NH—CH}_2\text{OH (8-1)} \quad (8)$$

$$\textbf{3-1} + \text{P—NR—CO—NH—CH}_2\text{OH} \rightarrow$$

$$\text{P—NR—CO—NH—CH}_2\text{—NH—CO—}$$

$$\text{NH—CH}_2\text{OH (9-1)} \quad (9)$$

^{13}C-NMR data also indicated that type I methylene and methylene–ether groups were the primary products formed in this posttreatment with negligible in-
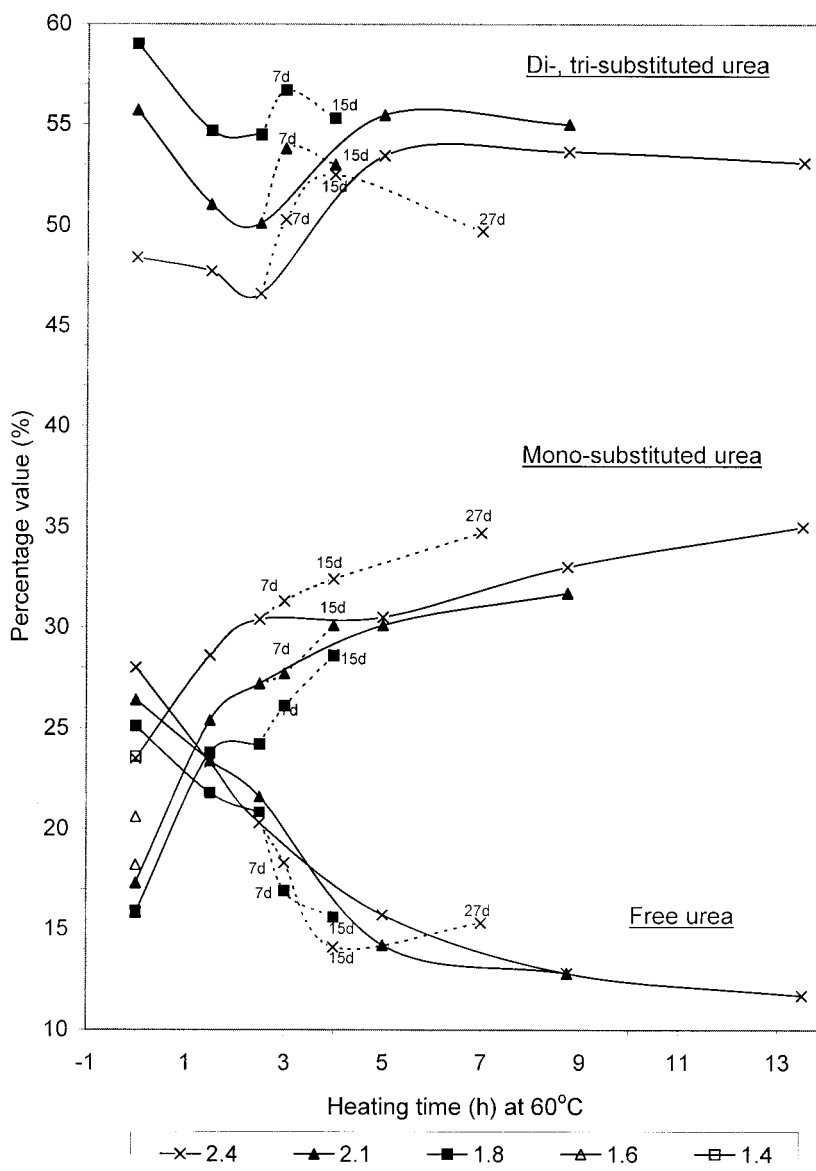
Figure 6 Changes in the degree of polymerization based on all urea of UF resins 1.4–2.4 (solid line) heated at 60°C for up to 13.5 h and (dotted line) heated-treated at 60°C for 2.5 h and stored at room temperature for 7 and 15 days.

creases in type II/III methylene/methylene–ether groups. A limitation in the reaction mechanism is indicated as discussed later.

Details on some of these reactions were directly observed in the ^{13}C-NMR data. The monosubstituted urea carbonyl peak (161.9 ppm) of untreated resins agrees with the reported value for monohydroxymethylurea (**3-1**) when the carbonyl peak of free urea in this work (164.0 ppm) is referenced to the literature value (163.60 ppm).[24] As shown for the urea carbonyl peaks of resin 2.4 series (Fig. 9), the monosubstituted urea carbonyl peak was normally somewhat broad at the base, indicating a hidden peak which did not show up as a separate peak in resins 2.4b (no heat treatment) or 2.4d (2.5-h heat treatment). However, the hidden peak began to show up as a shoulder in resin 2.4o (8.75-h heat treatment) and then as a peak at 162.01

ppm (corrected) in resins 2.4q and 2.4i, separated from the main peak at 161.9 ppm for monohydroxymethylurea. The chemical shift value of 162.01 ppm for the shoulder peak is very close to that of methylene–diurea (**5-1**) reported at 162.1 ppm, measured at 60°C for better solubility.[24] This peak can also be assigned to urea groups singly bonded to UF polymers (**6-1**, **7-1**). Thus, the extended posttreatments of resins gave rise to a peak that is assignable to methylene–diurea and/or singly bonded urea groups shown in eqs. (5)–(7). The combined level of singly bonded urea groups and methylene–diurea in resin 2.4o is approximately 11.1% of the total urea. Since di(and tri)substituted urea species increased by 5.2% in this resin compared to resin 2.4b and this increase can be assigned mostly to the singly bonded urea groups, methylene–diurea amounted to the balance, 5.9%. Overall, these results

Figure 7 Changes in ^{13}C-NMR values of urea carbonyl carbons in UF resins 1.4–2.4 (solid line) heated at 60°C for up to 13.5 h and (dotted line) heated-treated at 60°C for 2.5 h and stored at room temperature for 7 and 15 days.

indicated that free urea reacted with monohydroxymethylurea to form methylene–diurea and also with UF polymers to become incorporated as singly bonded urea groups between 2.5 and 8.75 h of heat treatment.

As an illustration of UF resins attainable by post-treatments, the composition of resin 2.4o was calculated to consist of free urea (12.8%), monohydroxymethylurea (22.4%), methylene–diurea (5.9%), and polymeric UF components (58.1%). The polymeric UF components of resin 2.4o including methylene–diurea showed a number-average degree of polymerization of about 12 and each molecule has about 2.4 type I hydroxymethyl groups, 1.1 type II hydroxymethyl groups, and a 0.6 singly bonded urea group, for a total of 3.6 end groups. All type II/IIi hydroxymethyl groups were assumed to be type II.

Another polymer end group possible in UF resins is the gem-disubstituted urea group located in the middle of polymer chains:

$$P—N—CO—NH_2 \ (\mathbf{10}—\mathbf{1})$$
$$|$$
$$P—NR—CO—NH—CH_2$$
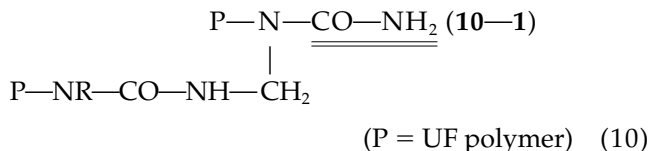
$$(P = UF \ polymer) \quad (10)$$

An approximate value can be calculated from values of types I, II, and III methylene/methylene–ether groups for a UF polymer,[17] and calculation showed that the polymeric resin components of resin 2.4o would have 5.7 polymer end groups. Therefore, there should be about 2.1 gem-disubstituted urea end groups (**10-1**). A schematic structure of this UF polymer thus obtained is shown in Figure 10.
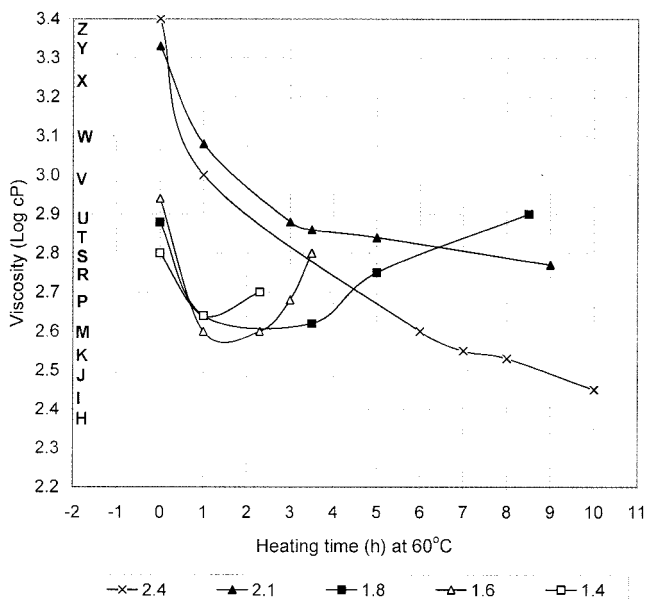
Figure 8 Changes in viscosity of UF resins 1.4–2.4 heated at 60°C for up to 10.0 h.

## Posttreatments of resins at 60°C for 2.5 h and storing at room temperature

Methylene/methylene–ether groups in resins heated for 2.5 h increased rapidly in 7 days of storage time and then slowly afterward until 27 days (for simplicity, overlaid with dotted lines in Figs. 5 and 6). Similar changes occurred between 2.5 and 5.0 h in continuous heat treatments or between 15 and 30 days of storage at room temperature without a prior heat treatment.[17,18] Although the 2.5-h heat treatments expedited group changes occurring afterward, as expected, the question was whether the reaction products from storage treatments would be similar to those observed with continuous heating/stirring treatments. Two major differences were observed in storage treatments: monosubstituted urea carbonyl species, that is, methylene–diurea and singly bonded urea groups, increased significantly while di/trisubstituted urea species only minimally increased. This result suggests that free urea reacted mainly with monohydroxymethylurea to form methylene–diurea and only minimally with polymeric resin components to form urea groups singly bonded to UF polymers in the storage experiments. Resin 2.4 showed this effect more prominently due to the larger amount of free urea available. Thus, resin 2.4q (2.5 h at 60°C and 27 days at room temperature) and resin 2.4i (50 days at room temperature) reported earlier showed this trend clearly with the two equally strong peaks for monosubstituted urea species (Fig. 9). Resin 2.4q was estimated to have about 35.0% of total urea as monosubstituted and half of that, 17.5%, as methylene–diurea and singly bonded urea groups. However, since di- and trisubstituted urea species, which represent singly bonded

urea groups, increased only by about 1.3–3.7%, the methylene–diurea amounts to the difference, 13.8–16.2%. This value is high compared with the 5.9% for resin 2.4o (8.75 h at 60°C) discussed above. Thus, the formation of methylene–diurea was favored over that of urea groups singly bonded to UF polymers [eqs. (6) and (7)] in storage treatments. Stirring of resins during reactions ensures a more uniform reaction among the various monomeric and polymeric resin components. Storing of reactive resins without stirring thus appears to favor monomeric or low molecular weight components, such as monohydroxymethylurea and urea, to react among them rather than reacting with polymeric UF molecules. Thus, methylene–diurea was expected to be the major product. The different resin compositions could make significant curing differences of resins.
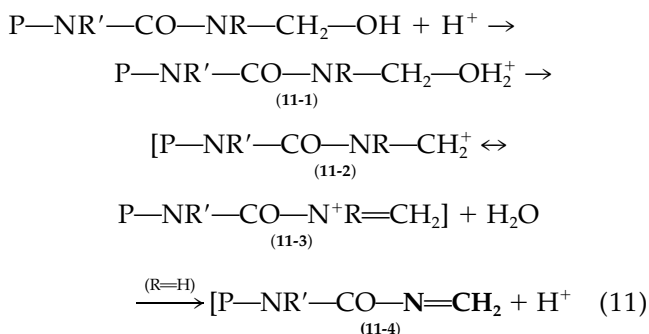
Reaction mechanisms of methylene/methylene–ether group-forming reactions

The methylene/methylene–ether group-forming reactions in alkaline pH were observed to be slower than were similar reactions occurring in acidic pH during resin syntheses or curing of the resins. It is known that UF resins in alkaline pH can transform into a solid mass when stored for a long period time at room temperature or heated at elevated temperatures, but the solidified resins did not show the kind of cure required as wood adhesives. In similar melamine–formaldehyde resins, the methylene/methylene–ether bond-forming reactions in neutral or mild alkaline pH proceeds more readily during resin synthesis, but the final cure of resins is achieved similarly with relatively strong acid catalysts.[31] The transformation of UF resins into solids in alkaline pH would entail the formation of methylene/methylene–ether groups with physical agglomeration of the resin molecules amplifying the process as the resin molecular weights increase. In a previous report,[18] the methylene/methylene–ether group-forming reactions in alkaline pH were reported by the authors and suggested to entail a general acid catalysis mechanism. General acids, such as water, a resin's hydroxymethyl groups, and undissociated acid species present in the weak alkaline resin system would be the catalyst for the activation of hydroxymethyl groups.

In weak acidic aqueous media of UF resins and similar melamine– or phenol–formaldehyde resins, the facile methylene/methylene–ether bond-forming reactions were formulated as the hydrogen ions' (H^+) activation of hydroxymethyl groups in the form of a hydrogen ion complex (**11-1**),[31–36] which then breaks into the cationic methylene intermediate (**11-2**) by expelling a water molecule in the rate-determining step:
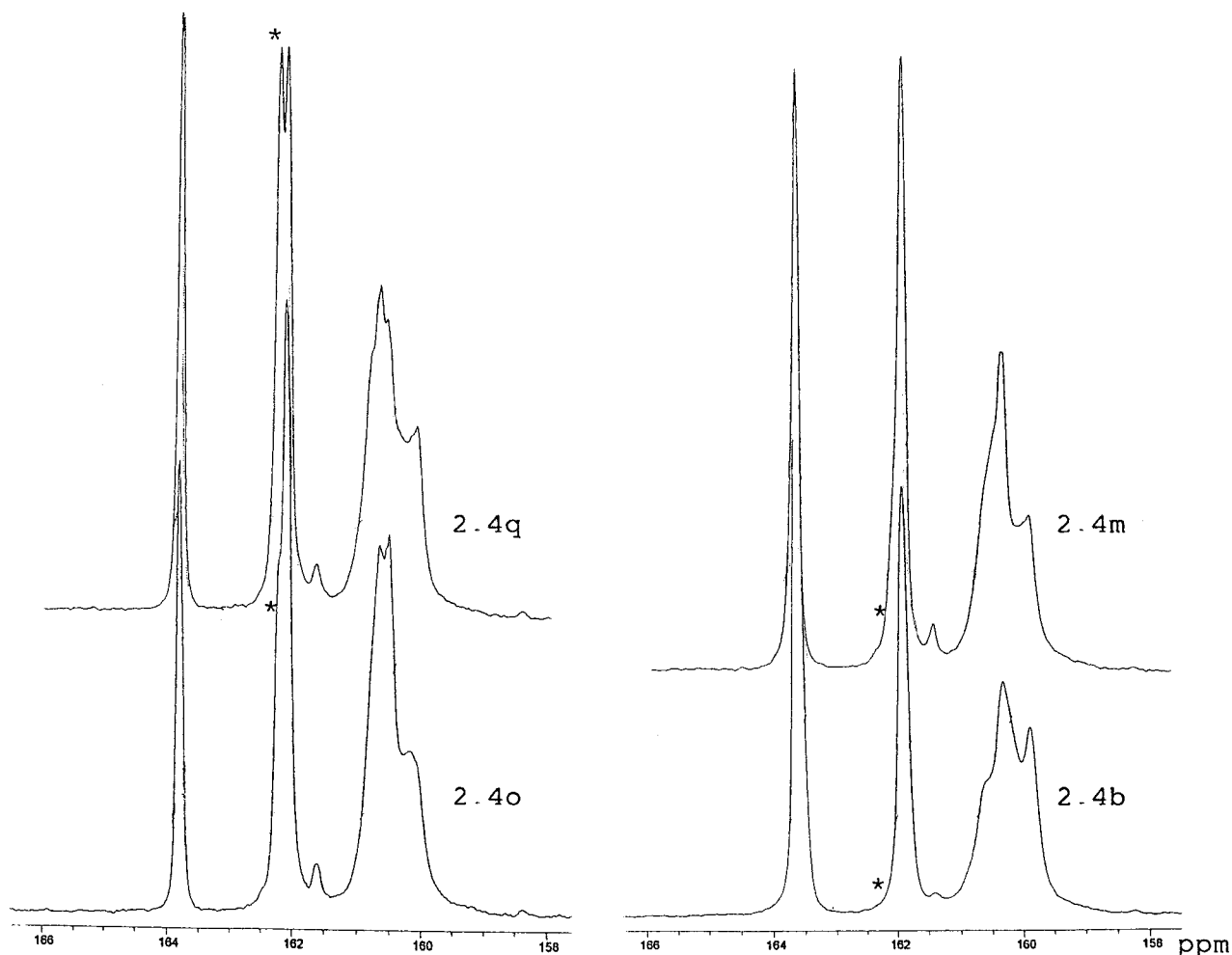
Figure 9 ^{13}C-NMR spectra of urea carbonyl carbons of resins 2.4b, 2.4m (5.0 h at 60°C), 2.4o (7.75 h at 60°C), and 2.4q (2.5 h at 60°C; 25 days at room temperature) showing (*) the growth of the monosubstituted urea species peak at ~162.1 ppm.

P—NR′—CO—NR—CH$_2$—OH + H$^+$ →

P—NR′—CO—NR—CH$_2$—OH$_2^+$ →
(11-1)

[P—NR′—CO—NR—CH$_2^+$ ↔
(11-2)

P—NR′—CO—N$^+$R=CH$_2$] + H$_2$O
(11-3)

$\xrightarrow{\text{(R=H)}}$ [P—NR′—CO—N=**CH$_2$** + H$^+$ (11)
(11-4)

The cationic methylene intermediate is resonance-stabilized with the methylene imidinium ion (**11-3**), making the activation process occur at a lower energy level. Thus, the higher the hydrogen ion concentration, the greater the polymerization/curing rates of the resins. These reactions go readily at a mild acidity of pH 4–5 at room or elevated temperatures as observed in resin syntheses or potlife studies of UF resins. The cationic methylene intermediate, a strong electrophile, would react with the amide nitrogen and hydroxyl nucleophiles to form methylene/methylene–ether bonds. When the activated hydroxymethyl group is type I, the cationic methylene imidinium ion (**11-3, R=H**) may equilibrate with the methylene imine (**11-4**) to further lower the reaction energy barrier. On the other hand, for type II hydroxymethyl groups which create branched or crosslinked polymer structures in resin synthesis or curing, the formation of imidinium ions (**11-3, R=—CH$_2$—**) is a quaternization reaction of nitrogen, which has normally a higher reaction barrier. The first reaction would go faster than would the second reaction in curing. Particleboard binder-type UF resins have F/U mol ratios of 1.15 or higher and, therefore, would harbor significant levels of type II hydroxymethyl groups. That these UF resins give well-cured, crosslinked wood adhesives in the presence of an acid catalyst indicates that both reactions readily occur in acidic aqueous media.

In weak alkaline aqueous media, on the other hand, the cationic methylene intermediate[31–36] would arise from the general acid catalysis mecha-
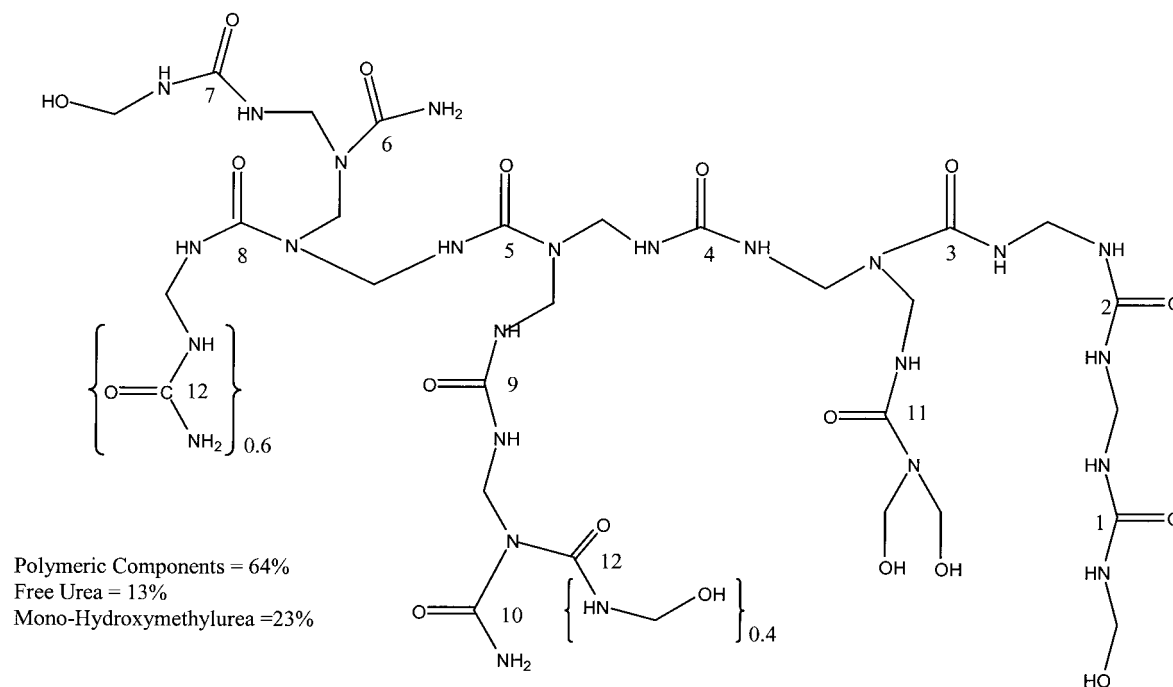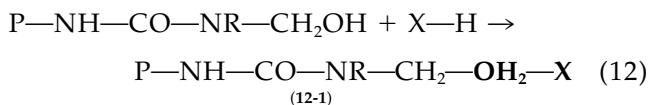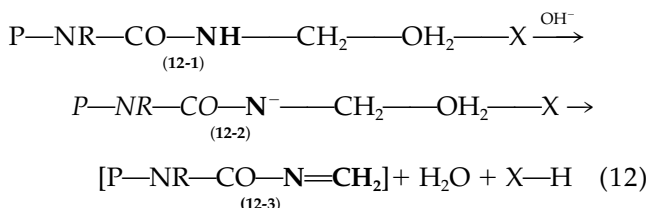
Figure 10 Schematic polymer structure for the polymeric components of resin 2.4o.

nism,[37] where un-dissociated acid species (X—H) available in the resin system form an acid complex with the hydroxymethyl group (**12-1**):

$$P—NH—CO—NR—CH_2OH + X—H \rightarrow$$
$$P—NH—CO—NR—CH_2—\mathbf{OH_2—X} \quad (12)$$
$$\text{(12-1)}$$

The general acid complex would not be as strong as that formed by hydrogen ions in an acidic media and, therefore, expelling a water molecule to form the cationic methylene intermediate would be relatively difficult. The slow advancement of UF resins in weak alkaline pH demonstrated in this work may be due to this weaker acid complex. On the other hand, a mechanism of activation appears available for type I hydroxymethyl groups through the abstraction of the weakly acidic hydrogen on amide nitrogen by a hydroxide ion (OH⁻). Initially, the amide anion (**12-2**) will be formed and then transformed into the methylene imine (**12-3**) by eliminating a water molecule:

$$P—NR—CO—\mathbf{NH}——CH_2——OH_2——X \xrightarrow{OH^-}$$
$$\text{(12-1)}$$
$$P—NR—CO—\mathbf{N^-}——CH_2——OH_2——X \rightarrow$$
$$\text{(12-2)}$$
$$[P—NR—CO—\mathbf{N{=}CH_2}] + H_2O + X—H \quad (12)$$
$$\text{(12-3)}$$

The methylene imine, a cationic methylene equivalent, would then react with nitrogens or hydroxyl nucleophiles to form methylene/methylene–ether bonds.

The formation of the methylene/methylene–ether groups in alkaline pH normally does not increase with pH increases. Therefore, the amide anion-forming step should not be the rate-determining step. This mechanism would not apply for type II hydroxymethyl groups since the corresponding amide anion (**12-2**) could not be formed due to the lack of a hydrogen for abstraction by hydroxide ions. This reaction mechanism is a speculation but conveniently agrees with the fact that type II/III methylene/methylene–ether groups do not form in the posttreatment experiments discussed above as well as that the polymerization reactions in alkaline pH normally do not give completely cured products. UF polymers would grow through the activation of type I hydroxymethyl groups with ensuing molecular entanglement and agglomeration, but the relatively high level of type II hydroxymethyl groups in UF resins will brake the resin system to an incomplete resin cure. Overall, it appears certain that the polymerization reactions discussed do occur in alkaline pH and are not the result of a faulty analytical method. Since these reactions have not been well recognized until now, little has been mentioned on modifying UF resins through posttreatments except the ill-defined ripening times often mentioned in industry.

One puzzling question regarding the reactions occurring in alkaline pH is the observation that the free urea levels and type II hydroxymethyl group contents are relatively high in the longest heat-treatment samples or 50-day stored resin samples. For example, the free urea level is about 11% and the type II hydroxy-

methyl group level about 6.0% in resin 2.4o, indicating that the migration of hydroxymethyl groups from polymeric resin components to free urea came to a standstill. Similarly, the formation of methylene/methylene–ether groups significantly slowed down after the initial rapid pickup during heating/storing treatments even though the type I hydroxymethyl group and free urea contents are relatively high. It is not clear why these reactions slow down. It may be that UF polymers in posttreatments at a given temperature attain certain molecular structures of a tertiary nature, or agglomerate, with strong intramolecular hydrogen bonding interactions. These resin molecules would make themselves less available to polymerization reactions. As the treatment temperature is increased, this barrier would be steadily overcome and the methylene/methylene–ether group contents increase to eventually reach the gelation stage as observed in gel tests carried out at 100°C, usually occurring in about 40 min or longer. Overall, the formation of methylene/methylene–ether groups appear to be the underlying reactions for the gelation and hardening changes of UF resins in alkaline pH although the mechanistic limitation would prevent the resin system from reaching a fully cured state. Unfortunately, ^{13}C-NMR tends to give less reliable results for resins in this later stage of treatment due to the molecular agglomeration and solidlike materials formed in the resins.

Viscosity and phase changes of UF resins during heating/storage treatments

The initial viscosity decreases in resins observed on heating at 60°C in the first 2.5 h were reported earlier. In the extended heating treatments of resins carried out in this study, similarly decreasing trends were observed, although the viscosity decrease was less for lower F/U_1 ratio resins (Fig. 8). Thus, the viscosity of resin 2.4 decreased the most and that of resin 2.10 decreased modestly until 7.5 h and they remained stable until 13.5 h of heat treatment. ^{13}C-NMR data showed, as in the room-temperature storage, the gradual migration of hydroxymethyl groups from polymeric to monomeric resin components in this heat-treatment period. Loss of hydroxymethyl groups for polymeric resin components would mean lowered molecular weights and the freed amide end groups at low levels would favor polymeric resin molecules to interact with the water media rather than with other polymeric resin molecules to result in lower associative effects and viscosity. However, both resins 2.4 and 2.1 became slightly turbid at the end of the heating periods, indicating that some molecules' associative tendency increased to cause agglomeration of molecules to form a second solidlike phase. The increased associative tendency of molecules would increase the viscosity of resins as well as with the methylene/methylene–ether group contents increases. These ef-

fects did not reverse the viscosity decreasing trends for higher F/U_1 mol ratio resins in the heating-treatment periods studied.

On the other hand, resin 1.80, slightly turbid as made, showed a slight decrease in viscosity in the 2.5-h heat treatment and then the viscosity continuously increased until 7.5 h of heat treatment, with the turbidity also increasing. The viscosity increasing effect, due to increased molecular association and increased methylene/methylene–ether group contents, appears to outweigh the viscosity decreasing effect of the hydroxymethyl group migrations. Furthermore, resins 1.6 and 1.4 were already somewhat turbid as made, although the starting viscosity values were comparable or lower relative to higher F/U_1 mol ratio resins. These resins, made by adding the second urea at about 4°C, were stable for about 5 days at room temperature and their ^{13}C-NMR spectra were obtained for the first time in this laboratory [Fig. 3(A,B)]. Using the traditional method of adding the second urea at 70°C would result in resins that solidify within a few hours. When heated at 60°C, the latter two resins increased in viscosity and turned into a semisolid mass in about 1.0 h for resin 1.6 and in 0.5 h for resin 1.4. For these lower F/U_1 mol ratio resins, the amount of second urea was lower and the proportion of polymeric resin components and the average degree of polymerization were higher. All these factors and the lower levels of hydroxymethyl groups would have contributed to the short lifetimes in the heating/storage treatments.

However, the increased molecular association/agglomeration tendency of lower F/U_1 mol ratio resins also appeared to have played a larger role in the rapid viscosity increases. For example, the methylene/methylene–ether group contents of resins 1.6b or 1.4b with no heat treatment were comparable with those of resin 2.4o with 8.75-h heat treatment at 60°C. But resin 2.4o remained at the low viscosity attained by heat treatment for several weeks, while resins 1.6b and 1.4b gelled within about 5 days at room temperature. It was also observed that the viscosity increases of resins generally lagged behind the methylene/methylene–ether group increases. Thus, although the viscosity increases would be helped by increases in the degree of polymerization or the methylene–diurea content, the agglomeration tendency of resin molecules appears to be playing a major role. It was suggested in the previous report that the lower extents of polymer chain branching for these lower F/U_1 mol ratio resins would make resin molecules agglomerate more easily to effect faster viscosity increases.[17,18]

F/U_1 mol ratio and posttreatment effects on resin polymer compositions

As discussed above, the F/U_1 mol ratio and posttreatment parameters that effected resins to advance to

have unique polymer compositions. First, the methylene/methylene–ether group content, or the average degree of polymerization, for untreated resins were in the order of resins 1.4 > 1.6b > 1.8b > 2.1b > 2.4b (Fig. 6). These differences in degree of polymerization would make resins cure differently, possibly affecting the bond strengths of the boards. Therefore, a direct comparison of bond results for these resins should not be emphasized and each resin system should be examined for various behaviors. The major reason for these differences was the extent of polymerization, that is, the different target viscosity values employed in the second step of resin syntheses were not accurately controlled with respect to different F/U_1 mol ratios used. If the target viscosity values were lowered further for lower F/U_1 ratio resins, resins with longer lifetimes would be obtained, although their agglomeration tendency might remain in the same order.

Furthermore, resins with higher F/U_1 mol ratios have greater amounts of free urea and advance in posttreatments mostly by forming type I methylene/methylene–ether groups. For example, resins 2.4 and 2.1 increased in the degree of polymerization to higher levels in both types of posttreatments and resulted in resins having unique compositions from the F/U_1 mol ratio used. Type I methylene/methylene–ether groups in lower F/U_1 mol ratio resins are mostly part of the polymeric components, while those in higher F/U_1 resins after posttreatments are those of methylene–diurea and newly formed urea groups singly bonded to UF polymers. Additionally, the methylene–diurea contents would be higher in resins obtained from nonstirring storage treatments in comparison with continuous heat treatments, as discussed above.

One interesting future research indicated by this study is that the posttreatment approach would offer ways to use F/U_1 mol ratios higher than 2.6 for synthesizing wood adhesive-type UF resins. Resin syntheses using F/U_1 mol ratios at these high levels requires a pH of about 1 to carry out the polymerization reaction[38,39] and result in resins with polymer structures having some intramolecular ether bonds, that is, uron rings. The resins need larger amounts of second urea to lower the overall F/U ratio to about 1.15, and because of this, if posttreatments are not used, the resins would be of limited utility as particleboard binders. The heating/storage treatments in alkaline pH would improve this deficiency by advancing the degree of polymerization for the resins incorporating the second urea. The resultant resins would have polymer structures and compositions that have increased amounts of the reaction products from the posttreatments discussed above. The resins would perform reasonably well as particleboard binders although their bonding and formaldehyde-emission performances might differ. One limitation in this approach would be the time-consuming nature of the posttreatments to be used by industry standards. Also, the
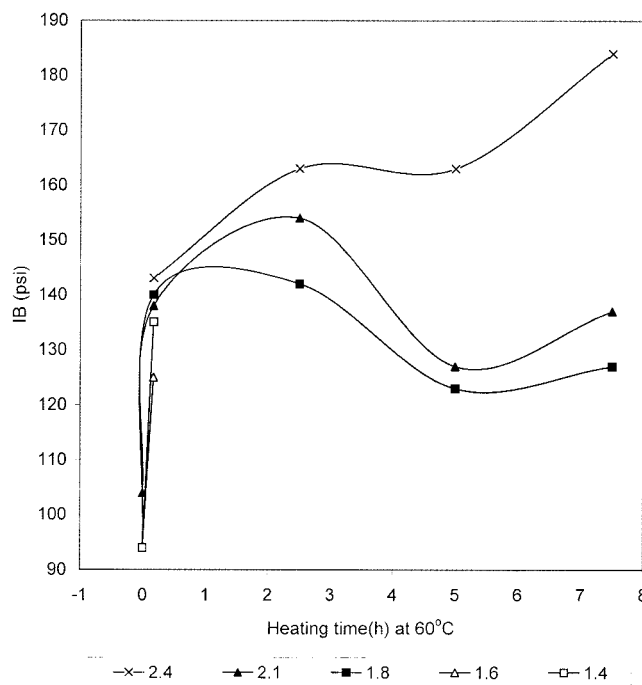
Figure 11 IB strength values of particleboards bonded with UF resins 1.4–2.4 heat-treated at 60°C for 0.0, 0.17, 2.5, 5.0, and 7.5 h.

slowdown of the methylene/methylene–ether group-forming reactions after the initial buildup discussed above may limit the scope of this approach. Further research is needed but a solution to these problems may come from carrying out the posttreatment procedures at lower pH and/or higher temperatures. Overall, the F/U_1 mol ratio and posttreatment parameters were shown to affect various polymer structures and compositions in resins that are difficult to derive from ordinary resin synthesis procedures and thus the scope of the UF resin system was expanded.

Heat-treatment effects of resins on particleboard strengths and formaldehyde emission

Industrial particleboards manufactured with densities close to the value used in this study are the highest-grade materials and normally show IB strengths of 100–160 psi, bending modulus of elasticity (MOE) values of 300–600 kpsi, and bending modulus of rupture (MOR) values of 1800–3000 psi.[40] The resin samples used in bonding particleboards were those treated at 60°C for 0.0, 0.17, 2.5, 5.0, and 7.5 h, which were slightly different treatment times than for samples used in the ^{13}C-NMR analyses. The IB, MOE, and MOR values of particleboards obtained were in the normal ranges and showed the differentiating effects of posttreatment and F/U_1 mol ratio parameters (Figs. 11–14).

First, all board-strength values of untreated resin samples were unusually low for all F/U_1 mol ratios of
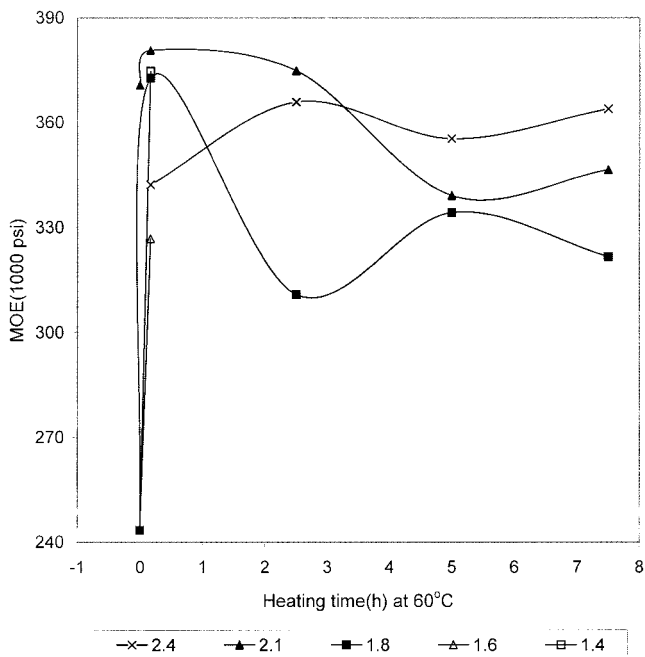
Figure 12 MOE values of particleboards bonded with UF resins 1.4–2.4 heated at 60°C for 0.0, 0.17, 2.5, 5.0, and 7.5 h.

resins compared with treated resins. The migration of hydroxymethyl groups did not occur in these resins and, therefore, the poor performance could be traced to the second urea components that are deficient of functional groups in curing. A 10-min heat treatment resulted in improved strength values improved for all resins. The extent of hydroxymethyl group migration that occurred in 10-min heat treatments would be
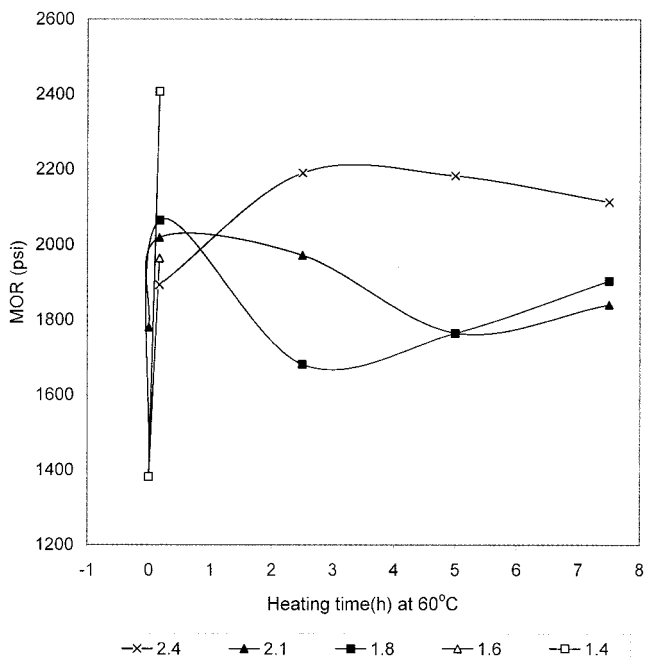

Figure 13 MOR values of particleboards bonded with UF resins 1.4–2.4 heated at 60°C for 0.0, 0.17, 2.5, 5.0 , and 7.5 h.
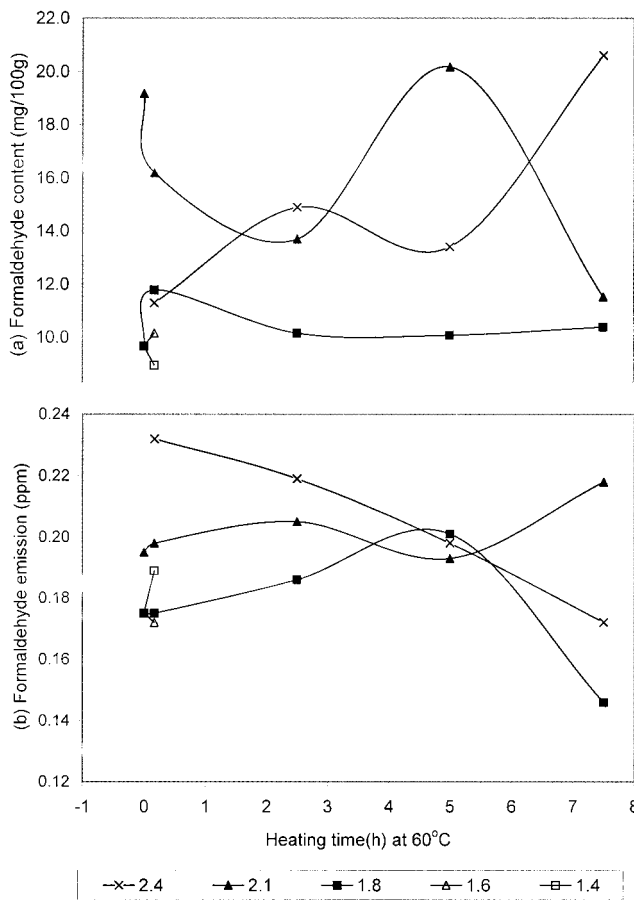

Figure 14 (a) PE and (b) SC formaldehyde values of particleboards bonded with UF resins 1.4–2.4 heated at 60°C for 0.0, 0.17, 2.5, 5.0, and 7.5 h.

relatively small but appeared to have sufficiently increased the functionality for the second urea components. In the curing of UF resins to form crosslinked polymers, the greater the distribution of methylenic functional groups on urea molecules within the resin system, the better the overall efficiency of the curing reactions. Furthermore, a low extent of hydroxymethyl group migration would lead to localized excesses of functional groups with respect to the availability of amide groups. This appears to be the cause of higher formaldehyde-emission values of boards bonded with these resins, especially for resin 2.4b (Fig. 14). Therefore, the extent of hydroxymethyl group migrations in UF resins could be a useful industrial parameter which has been vaguely known, up to now, only as the ripening times of resins. This parameter has been roughly met in most cases in industry because of the relatively long cooling time being taken in resin manufacture and transportation/storage times.

Boards bonded with resin 1.8, in general, particularly with resins 1.4b and 1.6b, performed somewhat poorly. The latter two resins, evaluated only at the 10-min heat-treatment stage due to their limited stability, showed IB values lower than those of the other resins although MOE and MOR values were compa-

rable or slightly higher. IB values of the boards reflect mostly the strength of the core layers and low values often indicate an undercure of the resin in the core layers. MOE and MOR values of the boards reflect mostly the strength of surface layers, and low values often indicate overcure of the resins, and high values, a good resistance to the overcure tendency. In addition to these curing-rate parameters of resins, past experience indicates that thermosetting resins like UF or phenol–formaldehyde resins cure poorly when some resin components have a limited miscibility and so remain in the vitrification stage. It appears that the uniformity of resin matrices was perturbed and resulted in an incomplete curing and low bond strength. Similarly, the higher tendency to agglomerate for resin molecules in low F/U_1 mol ratio resins would likely cause poor IB values of the boards. It appears that the temperature of the core layers (~127°C) was too low to unscramble the agglomerated resin molecules during curing, while the higher temperature in the surface layers (~160°C) adequately assimilated the agglomerated resin fractions.

At the 2.5-h heat-treatment stage, all resins showed increased IB strength values in the order of resin 2.4 > 2.1 > 1.8. Thus, the migration of hydroxymethyl groups in this heat-treatment period made all three resins cure faster or better in the core layer. The MOR/MOE values of the boards improved for resin 2.4, remained the same for resin 2.1, and decreased for resin 1.8. Resin 1.8 appears to be adversely affected by the extended migration of hydroxymethyl groups and increased agglomeration of resin molecules even in the surface layers.

At the 5.0- and 7.5-h heat-treatment stages, the IB strength of the boards increased with resin 2.4 but decreased with resins 2.1 and 1.8, with similar trends observed for MOE/MOR values (Fig. 11–13). The increased IB strength with resin 2.4 was interesting and indicates that the increase in methylene/methylene–ether group contents with the formation of methylene–diurea and urea groups bonded to UF polymers during these heat treatments made resin 2.4 a better binder in the core layers. Thus, the optimum resin composition of UF resins for particleboard core-layer binders appears to be a high F/U_1 mol ratio. Resins made with higher F/U_1 mol ratios would, in general, provide wider parameter ranges for posttreatments. On the other hand, boards bonded with resins 2.1 and 1.8 showed decreased strength values. However, since these lower bond-strength values appear to be due to the increased agglomeration tendency of resin molecules from increased molecular weights, optimum UF resins would be obtained by optimizing the polymerization end point according to the F/U_1 mol ratio. Resins other than resins 2.4 made in this study, if made with lowered polymerization end points, would have wider posttreatment parameter ranges and may
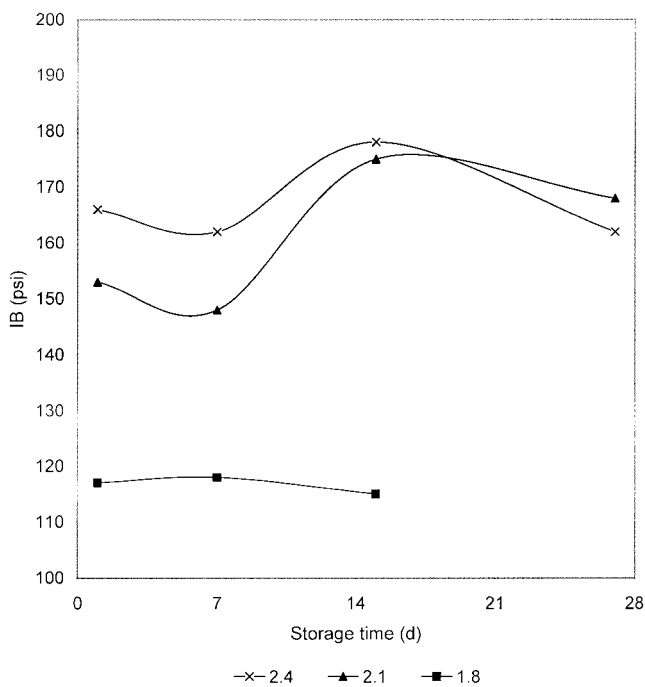
exhibit optimum bond performances specific to certain board-manufacturing conditions.

Formaldehyde-emission values of boards bonded with heat-treated resins (Fig. 14) showed also the effects of the F/U_1 mol ratio and heat-treatment times. The PE values, or residual formaldehyde values in boards, were, in general, lower for resin 1.8 over the entire 7.5-h heat-treatment period [Fig. 14(a)]. The formaldehyde values of resins 2.4 and 2.1 were higher and affected differently by the heat-treatment times. Resin 2.1 showed high values at zero and 5.0 h of heat treatment and resin 2.4 a high value at 7.5 h of heat treatment. The residual free formaldehyde contents of boards would primarily depend on the amount of hydroxymethyl groups that break off as formaldehyde during curing and also the free formaldehyde content of resins. However, formaldehyde values of 10–20 mg per 100 g of board are equivalent to 0.13–0.26% of the formaldehyde used in the resin syntheses. Although some free formaldehyde gas escapes from boards during hot pressing, the residual formaldehyde values are relatively small and comparable with the free formaldehyde contents commonly measured in UF resins. Therefore, the sources of residual formaldehyde in boards have been difficult to correlate with specific polymer structures or compositions of uncured resins. However, it appears that the low values of resin 1.8 are traced to reduced hydroxymethyl group contents, assuming that the amount of hydroxymethyl groups that break off to free formaldehyde during curing are proportional to the total amount of hydroxymethyl groups in the resins. The question remains whether the poorer bond performance of low F/U_1 mol ratio resins can be improved without increasing the residual formaldehyde values. Furthermore, the changing PE formaldehyde content values for the resins 2.4 and 2.1 series indicate that posttreatments of resins play important roles.

SC formaldehyde-emission values measured after airing for 8 days for the same boards used in PE formaldehyde tests also showed the varying effects of F/U_1 mol ratios and heat treatments [Fig. 14(b)]. The emission values of boards showed little change between 2.5- and 5.0-h heat-treated resins where most of the degree of polymerization increase occurred. These formaldehyde emissions may represent the typical industrial particleboard values considering the heat-treatment history of common industrial UF resins and that the SC method is the preferred formaldehyde-emission measurement in industry. The high formaldehyde-emission value of resins 2.4 at 10-min heat treatment is indicative of the high proportion of hydroxymethyl groups in the high molecular weight components. However, the heat treatments continuously decreased the emission value for resin 2.4. Resin 2.1 showed small changes until 5.0-h treatments but an increase at 7.5-h treatment opposite to the low PE formaldehyde value. Resin 1.8 showed slight increases

initially but gave a low value at the 7.5-h treatment, agreeing with the low PE formaldehyde values. Both PE and SC formaldehyde-emission results are somewhat different from the results obtained from the 50-day storage experiments reported earlier.[18]

SC formaldehyde-emission values can be considered products of the residual formaldehyde content and porosity of boards and, therefore, SC values would follow PE values when the boards' porosity characteristics are similar. However, the SC and PE formaldehyde values showed several conflicting values, indicating that the porosity characteristics would be somewhat different for those boards. Porosity of boards is related to the density and density profiles of the boards. The density and density profiles of all boards showed the usual varying densities higher in the surface layers than in the core layer but similar, as expected, from using the same press closing speed and the same target board density value. In this case, the porosity of boards for formaldehyde diffusion would be differentiated by the quality of adhesive layers in the boards. Resins that flow well in curing would result in better bonding and better continuity in adhesive layers and lower SC formaldehyde values. These trends are not well identified except perhaps for resin 2.4, which resulted in board-strength values that generally increased while SC formaldehyde values decreased as the heat treatment time was extended. Overall, both PE and SC formaldehyde values obtained were in the normal range for laboratory particleboards and suggest further studies to lower formaldehyde emissions.
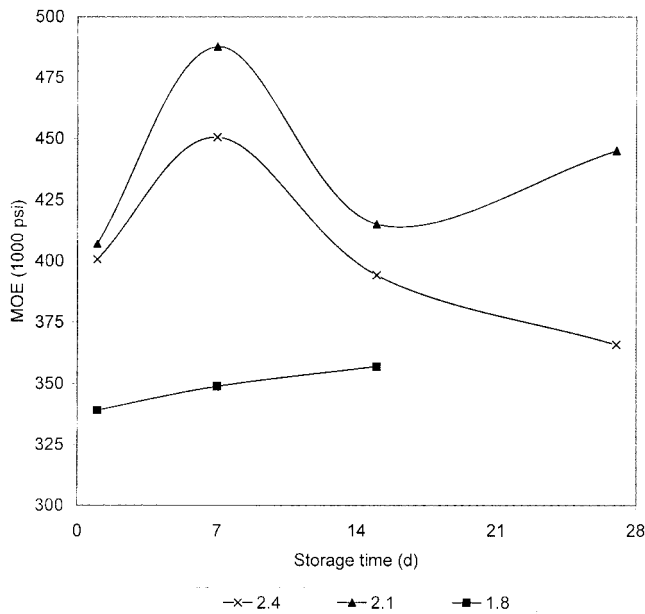
Figure 16 MOE values of particleboards bonded with UF resins 1.8–2.4 heated at 60°C for 2.5 h and stored at room temperature for up to 27 days.

Effects of heat-treatments for 2.5 h at 60°C and storing of resins at room temperature on particleboard strengths and formaldehyde emission

These boards were made at an earlier time than were the boards discussed above. In these posttreatments, most methylene/methylene–ether groups were formed within 7 days of storage time. In general, boards bonded with resin 1.80 performed poorly in comparison to those bonded with resins 2.4 and 2.1 for all heat-treatment/storage days (Figs. 15–17), similar to the continuous heat treatments discussed above. In comparison with boards made with 10-min heat-treated resins, boards bonded with 7-day stored resins 2.4 and 2.1 showed little changes in the IB but their MOE and MOR values significantly increased and also showed decreased SC formaldehyde-emission values, indicating a higher bond quality (Fig. 18). This trend was different from that observed in the continuous heat treatments. These board-performance improvements coincided with the formation of methylene/methylene–ether groups, which involved formation of more methylene–diurea and fewer increases in molecular weights for polymeric resin components in comparison with changes incurred from the continuous heat treatments.

Boards bonded with 14- and 27-day stored resins 2.4 and 2.1 showed some increases in IB strength, some decreases in MOE and MOR values, and increases in the SC formaldehyde-emission value compared with boards made with 7-day stored resins. The increased levels of methylene–diurea in resins increased the IB values but adversely affected the surface layers and lowered the MOE/MOR and SC formaldehyde-emis-

Figure 15 IB strength values of particleboards bonded with UF resins 1.8–2.4 heated at 60°C for 2.5 h and stored at room temperature for up to 27 days.
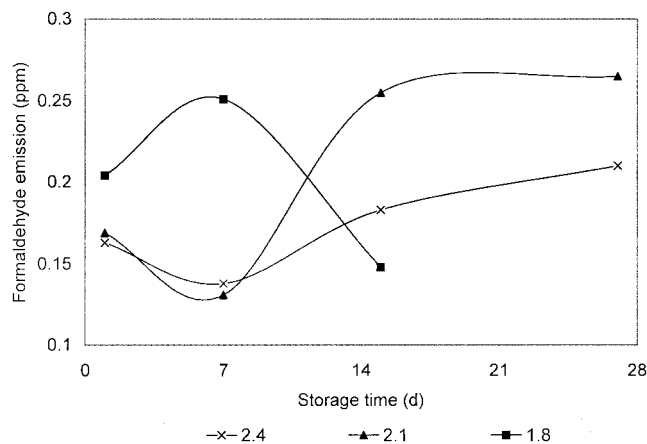
sion values. The long-term storage parameters appear to have some merit to control resin compositions especially as core-layer binders. More detailed study would be needed for these long-term storage parameters with respect to the control for the polymerization end point discussed above.

CONCLUSIONS

Two posttreatments methods were investigated for particleboard adhesive-type UF resins synthesized with F/U_1 mol ratios of 1.40, 1.60, 1.80, 2.10, and 2.40 and the second urea added to give an overall F/U ratio of 1.15 in alkaline pH. In 2.5-h heating/stirring treatments at 60°C, some hydroxymethyl groups were shown to migrate from the polymeric resin components to the second urea and form monohydroxymethylurea by the reversibility of the reaction, and the viscosity of the resins decreased more prominently for higher F/U_1 mol ratio resins. In 2.5- and 5.0-h heating/stirring treatments at 60°C, or 7 days of storage at room temperature after 2.5-h heat treatments at 60°C, some type I methylene/methylene–ether groups were formed from reactions involving the second urea. The methylene/methylene–ether-forming reactions in alkaline pH progressed slowly to form methylene–diurea and urea groups bonded to UF polymers, resulting in increases in the degree of polymerization of the resins. Methylene–diurea was formed prominently in resins stored longer than 7 days due to a lack of stirring. The reaction mechanism for these reactions was proposed to be by the amide anion and methylene imine intermediates formed from type I hydroxy-
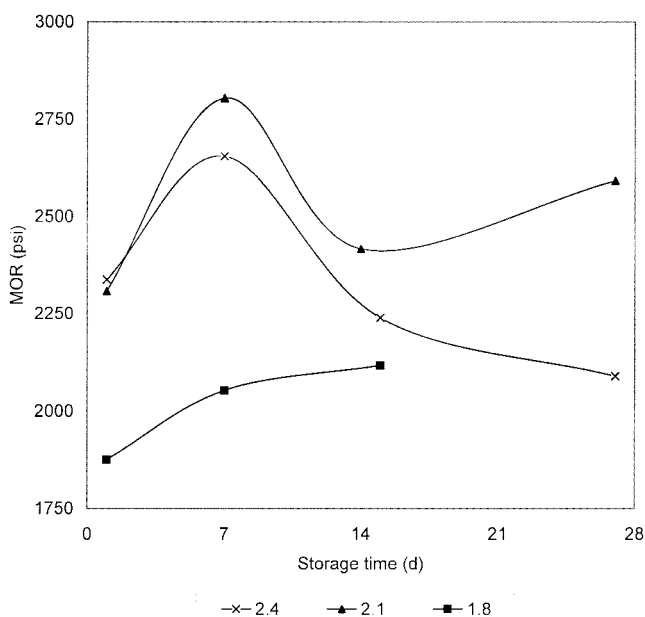
Figure 18 SC formaldehyde values of particleboards bonded with UF resins 1.8–2.4 heated at 60°C for 2.5 h and stored at room temperature for up to 27 days.

methyl groups but not from type II hydroxymethyl groups.

Agglomeration of resin molecules appeared to occur in the later stages of heating/storing treatments as shown by the viscosity and turbidity of resins increasing with minimal increases in the degree of polymerization. The agglomeration tendency was minimal for resins 2.4 and 2.1 but significantly higher for resins 1.8, 1.6, and 1.4 due to the resins' lower extents of polymer chain branching and higher degrees of polymerization. Use of lower degrees of polymerization in resin syntheses would lead to less agglomeration tendency for low F/U_1 mol ratio resins. The bond-strength and formaldehyde-emission values of particleboard bonded with the posttreated resins varied to reflect the resin composition and physical changes that occurred in the resins. Resin 2.4, in terms of the internal bond strength of boards, appeared to be optimum if posttreatments were included as part of the resin manufacture, although other lower F/U_1 mol ratio resins would behave similarly if the extent of polymerization end points were lowered in resin syntheses. In conclusion, this investigation elucidated the major polymer structures and compositions of UF resins affected by various posttreatments and F/U_1 mol ratio values used in resin synthesis which were unavailable or poorly understood until now. The scope of the UF resin system was significantly expanded to suggest future improvement directions toward solving various bonding problems.

Figure 17 MOR values of particleboards bonded with UF resins 1.8–2.4 heated at 60°C for 2.5 h and stored at room temperature for up to 27days.

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