

# Examination of Selected Synthesis Parameters for Typical Wood Adhesive-Type Urea–Formaldehyde Resins by $^{13}\text{C}$ -NMR Spectroscopy. II

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**ABSTRACT:** A particleboard adhesive-type urea–formaldehyde (UF) resin was made at a formaldehyde ratio of 2.10 and added with a second urea at low temperature to the typical final formaldehyde/urea ratio of 1.15. Time samples taken during heat treatments of the resin sample up to 70°C over a period of 250 min showed decreases in Type II/III hydroxymethyl group content, accompanied with decreases in resin sample viscosity and increases in formaldehyde emission of bonded particleboards. The results indicate that various hydroxymethyl groups of polymeric UF resin components migrate to the second urea to form Type I hydroxymethyl groups. Time samples taken during the room-temperature storage of the resin sample over a period of 1 month behaved similarly initially, but in the later stage, some polymerization progressed, shown by increases in viscosity and methylene and methylene–ether group contents. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1243–1254, 2000

**Key words:** urea–formaldehyde adhesive resins; viscosity; hydroxymethyl groups

## INTRODUCTION

In previous publications, some details on reaction pathways occurring during and after the synthesis of wood adhesive-type urea–formaldehyde (UF) resins were reported based on  $^{13}\text{C}$ -NMR data.<sup>1,2</sup> UF resins have been known for many decades<sup>3–11</sup> and are currently used worldwide as thermosetting wood adhesives in manufacturing particleboard (PB) and medium-density fiberboard.<sup>12</sup> Drawbacks of UF resins are low water resistance and tendency to emit formaldehyde from bonded wood composite boards.<sup>13–16</sup> The overall formaldehyde/urea (F/U) mol ratio currently used in manufacturing UF resins is about 1.15, a value

too low for good crosslinking but needed in complying with the regulated low formaldehyde emission levels. These resins also resulted in lowering the wood composite boards' water resistance in comparison to the higher F/U mol ratio resins used earlier. A further reduction of the F/U mol ratio has been proved very difficult due to performance property degradation, and scavengers are being used to keep the formaldehyde emission levels low.<sup>17</sup>

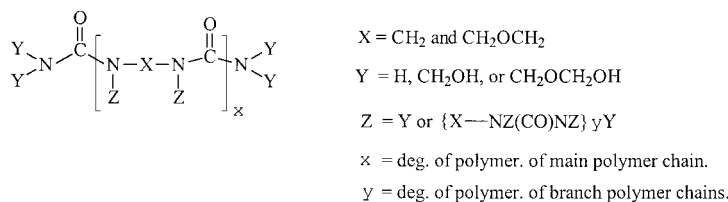
In typical synthesis of UF resins (Fig. 1), urea is added to formaldehyde in two parts, described here as the first urea ( $\text{U}_1$ ) and the second urea ( $\text{U}_2$ ). In the first step, the first urea is reacted at about 90°C with aqueous formaldehyde in a weak alkaline pH at an F/ $\text{U}_1$  ratio of about 2.10. Major reaction products are mono-, di-, and trihydroxymethylureas and secondary products containing methylene–ether bonds are formed, presumably methylene–ethers of hydroxymethylureas.<sup>1</sup> The

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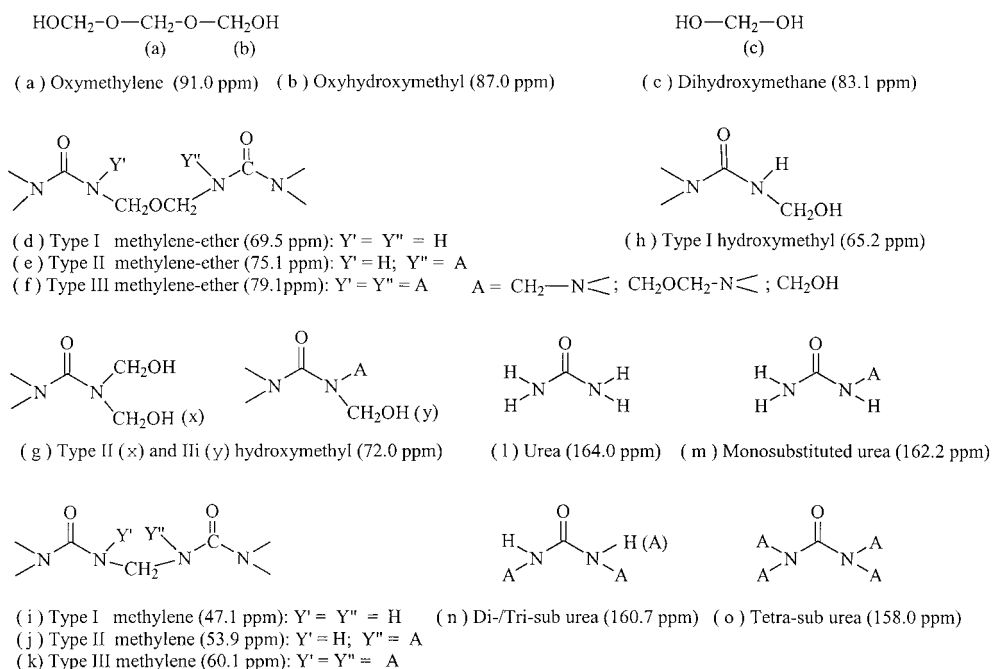


**Figure 1** Schematic representation of UF-resin polymer molecules with group Z's representing possible polymer-chain branches that also form polymer-chain branches themselves.

hydroxymethylation reactions occurring between urea and formaldehyde are slightly reversible with the forward reaction about 100 times faster than the backward reaction.<sup>6</sup> In the second step, the reaction mixture is adjusted to an acidic pH between 4 and 5 and reacted at 90–95°C to form methylene bonds between the urea units, resulting in polymeric UF resin molecules and splitting off of some of the formaldehyde. The polymerization reaction is normally carried out until a viscosity of about *W* by the Gardener–Holdt (G–H) scale (32 P) is reached at resin solids levels between 60 and 65%. Neutralizing the reaction mixture to a weak alkaline pH ends the polymerization reaction. Since most of the methylene–ether groups formed in the first step remain unchanged, the

reaction products are (oligomeric) UF polymer molecules of methylene–methylene–ether hydroxymethylureas and contain some free formaldehyde (Fig. 1).

In the third step of resin syntheses, while cooling the weak alkaline polymer mixture, the second urea is added to a combined formaldehyde/urea [ $F/(U_1 + U_2)$ ] ratio of about 1.15. In the subsequent mixing and cooling period, the second urea reacts with free formaldehyde present in the reaction mixture to form various monomeric hydroxymethylureas. Also, a significant amount of Type II/III hydroxymethyl groups of the polymeric UF resin molecules cleaves and the freed formaldehyde similarly reacts with the second urea in this period (Fig. 2).<sup>2</sup> This migration of hydroxy-



**Figure 2** Chemical structures of carbon groups and molecules occurring in polymeric UF resins with their chemical shift values, identified as from (a) to (o) in <sup>13</sup>C-NMR spectra in Figure 4(A6).

methyl groups appeared to depend on the temperature used at the time of the second urea addition and the time taken in cooling the reaction mixture, occurring as a result of the reverse hydroxymethylation reaction. Type I hydroxymethyl groups would similarly migrate to the second urea although not being measurable by  $^{13}\text{C}$ -NMR because of the chemical-shift overlap of Type I hydroxymethyl groups bonded to the monomeric and polymeric UF resin components. The resultant concentration distribution of hydroxymethyl groups between the monomeric and polymeric components could result in varying the bonding performance and formaldehyde emission levels of the bonded wood composite boards. In this work, therefore, this hydroxymethyl group migration was examined in detail by  $^{13}\text{C}$ -NMR and by making PBs and determining the formaldehyde emission levels. A typical UF resin was made with the second urea added at low temperature and one sample was subjected to a heat-treatment schedule and the other to a 1-month room-temperature storage schedule, and the time samples taken were examined. The heat-treatment schedule would simulate the time-temperature effects of the second urea addition operation in industrial resin manufacture, and the room-temperature storage schedule, the effects of transportation and storage of UF resins until use.

Because of the limited solubility of UF resins in water and in many other solvents and the labile nature of hydroxymethyl functional groups,  $^{13}\text{C}$ -NMR spectroscopy has been used as a uniquely suited method for their molecular-structure characterizations.<sup>1,2,18-22</sup> The migration of Type II/III hydroxymethyl groups to the second urea, which depends on the samples' history as discussed above, causes spectral changes on the neighboring methylene and methylene-ether carbons in the lifetime of UF resins. This phenomenon was used advantageously to derive approximate polymer-chain structures of UF resins.<sup>2</sup> Those spectral changes are sometimes difficult to be differentiated from the intrinsically variable  $^{13}\text{C}$ -NMR results in quantifying the functional groups of UF resins due to changes in their  $^{13}\text{C}$ -NMR relaxation parameters, although the variability appears to be minimal and controllable by using optimum experimental parameters except when UF resins become highly turbid and partially insoluble due to solidlike particles formed during manufacturing or storage.

## EXPERIMENTAL

Reagent-grade urea, sulfuric acid, sodium hydroxide, and a fresh 50% formaldehyde solution obtained from a Georgia-Pacific Corp. (Louisville, MS) plant, kept at 60°C, were used. Minor pH adjustments were made using 4.0% sulfuric acid and 4.0% sodium hydroxide solutions and drifts of indicated pH values were maintained within a  $\pm 0.1$  unit in most cases. Viscosities were measured at 25°C using the Gardener-Holdt method and the values were converted into cP units when necessary.

### Synthesis of a Typical UF Resin and Heat Treatments

A typical wood adhesive-type UF resin was synthesized and samples from A1 to A6 were taken as follows: A 3150-g aliquot of 50% formaldehyde solution was charged into a stirred reactor, its pH adjusted to 7.8, heated to 70°C, and the first urea (1,500 g) added over a period of 15 min (F/U = 2.10). The temperature of the reaction mixture was then allowed to increase to and then maintained at 90°C for 30 min by applying an intermittent external cooling. Then, the pH of the reaction mixture was lowered to 4.5, and the temperature was increased to and maintained at 90°C until the reaction mixture reached a viscosity of *W* (approximately 125 min). The reaction mixture was then immediately neutralized to pH 7.8 to stop the polymerization reaction and cooled with an ice-water bath. With the stirring maintained, the following sampling procedure was carried out:

*Sample A1*—When the reaction mixture was cooled to about 10°C, Sample A1 (2.0 g) for NMR was taken, a water-clear syrup having a viscosity of *W* and an F/U ratio of 2.10. The second urea (1239 g) was then added to the reaction mixture to attain an F/U ratio of 1.15, resulting in cooling the reaction mixture to about 4°C, at which it was held for 90 min. *Sample A2*—Then, the resin mixture was stirred and allowed to warm up to 20°C over a period of 15 min, and sample A2 (800 g) was taken, having a viscosity of *S*. *Sample A3*—The temperature was then increased to 40°C over a period of 5 min and held at that temperature for 25 min, and sample A3 (800 g) was taken, having a viscosity of *RS*. Afterward, the resin mixture was heated further at the same temperature for 45 min, at the end of which the viscosity remained

unchanged at *RS*. *Sample A4*—The temperature was then increased to 50°C over a period of 15 min and held at the temperature for another 15 min, and Sample 4 (800 g) was taken, having a slightly decreased viscosity of *QR*. Afterward, the resin was further heated at 50°C for 30 min, at the end of which the viscosity remained unchanged at *QR*. *Sample A5*—The temperature was then increased to 60°C over a period of 10 min and kept at 60°C for 30 min and Sample 5 (800 g) was taken, having a decreased viscosity of *P*. *Sample A6*—The resin mixture was further heated at 60°C for 30 min, at the end of which the viscosity decreased to *N*. Then, the temperature was increased to 70°C and held for 30 min, and sample A6 (800 g) was taken, having a decreased viscosity of *K* with a very light turbidity appearing in the sample. A continued heating of the resin at 70°C for another 30 min resulted in increased turbidity and lower viscosity, but samples were not taken. The pH value of the resin samples was maintained between 7.7 and 8.0 during the heat treatments. All resin samples were stored at 4°C in a refrigerator for 1 week and sent overnight for NMR analysis and used for PB manufacturing after briefly warming up to room temperature and adding 0.3% ammonium sulfate as a catalyst.

#### Room-temperature Storage Treatment of UF Resin Samples

The UF resin synthesis procedure used above was repeated until the Sample A1 stage was completed ( $F/U = 2.10$ ), resulting in *Sample B1* having a viscosity of *V*. The resin batch was then divided into six equal portions (~ 785 g each) and stored in a refrigerator at about 4°C. To each of the resin samples, the second urea (207 g) was stirred in to a complete dissolution, at varying dates based on the date of the PB preparation, to attain an  $F/U$  ratio of 1.15. The resulting resin samples were then stood at room temperature (~ 23°C) and checked for viscosity as follows: *Sample B6 (30-day storage)*—The viscosity gradually decreased from *P* to *K* in 12 days and then started to slowly increase to reach *N* on the last day. A light turbidity arose in the sample at about the 20th day. *Sample B5 (22-day storage)*—The viscosity behaved similarly to reach *M* with a light turbidity occurring in the resin. *Sample B5c*—A small sample of B5 was stored at 4°C for 22 days for NMR analysis as a comparison. The sample remained water-clear with little change in

viscosity. *Sample B4 (16-day storage)*—The viscosity behaved similarly to reach *L*. *Sample B3 (7-day storage)*—The viscosity was reduced from *P* to reach *L*. *Sample B2 (1-day storage)*—The viscosity was reduced from *P* to *OP*. NMR samples (2.0 g) were taken from all the resin samples at the end of storage period and stored at 4°C until being sent overnight for analysis. All resin samples were used directly in PB manufacture on the 30th day of storage for Sample B1. This resin sampling sequence was based on a reasonable assumption that Sample B1 ( $F/U = 2.10$ ) would change little on storing at 4°C, at which temperature it actually increased in viscosity a little, from *V* to *W*, while it reached *YZ* when stored at room temperature. The sampling sequence was also designed to minimize synthesis duplication errors expected when different resin batches are made at different times. The pH values of the resin samples did not change much during the storage periods.

#### Procedures for $^{13}\text{C}$ -NMR Spectra and Calculation of Carbon Group Values

NMR samples were prepared by mixing 2.0 g of resin and 1.0 g of  $\text{D}_2\text{O}$ , resulting in samples having viscosities in the range of 60–90 cP. Carbon spectra were obtained on a Techmag 360 MHz NMR spectrometer using a 22- $\mu\text{s}$  pulse width (80°) and 10-s pulse delay, by Spectral Data Services, Inc., Champaign, IL. The decoupling power was kept on during the acquisition and off during the delay to suppress the nuclear Overhauser effect.<sup>23</sup> Under this condition, the  $^{13}\text{C}$  relaxation times,  $T_1$ , measured on a sample similar to Sample A1 using the inversion-recovery method,<sup>24</sup> were 1.4–6.2 s for urea carbonyls, 1.1 s for methanediol, 5.8 s for methanol present as impurity, and 0.16 s or less for all other methylenic carbons. About 400 scans were accumulated for all samples. The chemical-shift values reported were based on methanol present at 50.7 ppm. Peak integration values of methylenic carbons and urea carbonyls were separately summed and percentage values were calculated for various carbon groups. Then, using the materials' charge values, assuming minimal losses occurred in formaldehyde and other methylenic species, the carbon group percentage values were multiplied with the synthesis  $F/U$  mol ratio (2.10) to obtain the group concentration values based on 1 mol of the first urea. The group concentration values were used to derive the polymer structures of polymeric UF



resin components, apart from those of monomeric UF components derived from the second urea.

### Preparation and Testing of Laboratory PBs

Resin samples from A2 to A6 and from B2 to B6 were used to bond the PBs. Dried core-layer wood particles were obtained from the Georgia-Pacific Corp. PB plant in Louisville, MS. Standard, 801 kg/m<sup>3</sup> density (50 lb/ft<sup>3</sup>), single-layer PBs were made using a rotary drum blender, a forming box, and a 557 × 607-mm platen Williams-White hot press according to the standard laboratory procedure. Two PB panels were made for each resin sample and one panel was used for testing. For the formaldehyde emission test, the manufactured PBs were first stood for 24 h in the laboratory and eight test pieces (69.6 × 126.5 mm) were cut from each board, wrapped in a plastic bag, and sent to the Composite Panel Association's testing laboratory (Gaithersville, MD). The standard 2-h desiccator method<sup>25</sup> used for this test includes an airing of board samples for 24 h and measuring the amount of formaldehyde emitted over a period of 2 h at 75°F. All test pieces were sealed on the edges with molten wax to have a total exposed board surface area of 0.141 m<sup>2</sup> and placed in a desiccator along with a shallow beaker containing 25 mL water, which absorbed the emitting formaldehyde. The test results are reported in μg formaldehyde per mL water. The results of internal bond and bending strength tests, carried out after equilibrating for 3 weeks in a constant humidity chamber to about 10% moisture content and in accordance with the American Society for Testing and Materials Procedure D 1037, were in the normal range (details to be reported later).

## RESULTS AND DISCUSSION

### Polymer Structures of UF Resin Samples from <sup>13</sup>C-NMR Data

The optimization of the <sup>13</sup>C-NMR measurement condition as used in this study and the overall chemical and polymer structures of the UF resin components in terms of polymeric methylene-methylene-ether hydroxymethylureas were discussed in a previous publication.<sup>2</sup> In general, the amide nitrogens of urea units in polymeric UF resin molecules are singly and doubly bonded to methylene and methylene-ether groups, forming

branched polymer-chain structures as shown Figure 1. Various chemical structures occurring in UF resin polymer molecules and chemical-shift assignments are shown in Figure 2 and 3. Type I and Type II hydroxymethyls are bonded to urea nitrogens of polymer-chain ends, and Type Iii hydroxymethyls, to internal urea nitrogens. Types II and Iii hydroxymethyls overlap in <sup>13</sup>C-NMR, preventing the calculation of the number of polymer-chain ends from the hydroxymethyl group values. In <sup>13</sup>C-NMR spectra of the UF resin samples obtained prior to the addition of the second urea (Sample A1 types), the hemiformal groups present exert β-substituent effects on the hydroxymethyl groups to which they are bonded, making the latter overlap with methylene-ether groups. This complication mostly disappears after the second urea addition, making the spectra simpler to explain (Fig. 4). Also, as discussed above, the level of Types II/Iii hydroxymethyl groups formed on polymeric UF molecules decreases, that is, they migrate to the second urea to form Type I hydroxymethyls. A similar migration of Type I hydroxymethyl groups would occur, although not measurable in <sup>13</sup>C-NMR. Type Iii hydroxymethyl groups present in varying extents on polymeric UF resin molecules exert β-substituent effects on the neighboring methylenes and methylene-ethers, making these bond groups appear as higher-type groups, preventing the calculation of polymer-chain branching extents based on the number of methylene and methylene-ether bonds. Approximate measures of Type Iii hydroxymethyl groups on polymeric UF resin molecules can be obtained from the changes in methylene and methylene-ether values often occurring due to the group's migration to the second urea, which is expedited at elevated temperatures. Under a mild heat-treatment condition, Type II/Iii hydroxymethyl group content can be seen to decrease and often reaches a minimum value in a relatively short period time, and the changes that occurred in the various methylene and methylene-ether values can be obtained.

### Heat-treatment Effects in Samples A1-A6

<sup>13</sup>C-NMR data in Table I indicate that Types II/Iii hydroxymethyl groups decreased gradually from Sample A2 to A5 and then rapidly in Sample A6 (also shown in Figs 3 and 4). The viscosity of the resin sample also decreased continuously during the heat treatment ascribable to the shedding of hydroxymethyl groups, that is, decreases in mo-



**Table I Percentage Values of Various Methylenic Carbons and Carbonyls of UF Resin Samples A1–A6 Determined by <sup>13</sup>C-NMR, Sample Viscosity, and 2-h Desiccator Formaldehyde Emission Values of PBs Bonded with the Resin Samples**

Groups (ppm)	A1	A2	(A2–A1)	A3	A4	A5	A6	(A5–A2)
91.0	1.42	0.72	(–0.70)	0.70	0.82	0.40	0.59	(–0.32)
87.0	5.40	0.00	(–5.40)	0.00	0.00	0.00	0.00	(0.00)
83.1	5.88	0.67	(–5.21)	0.00	0.37	0.00	0.33	(–0.67)
79.1	2.30	2.30	(0.00)	2.15	2.03	2.01	1.91	(–0.29)
75.1	7.28	5.40	(–1.88)	5.61	5.17	4.55	4.40	(–0.85)
69.5	9.56	8.31	(–1.25)	8.31	8.61	8.69	10.68	(+0.38)
72.0	19.80	17.06	(–2.74)	18.60	15.95	13.72	7.70	(–3.34)
65.2	15.36	31.81	(+16.45)	31.03	31.91	37.50	39.06	(+5.69)
60.1	5.50	3.42	(–2.08)	3.21	3.00	2.28	2.57	(–1.14)
53.9	20.96	22.21	(+1.25)	22.55	23.11	22.27	19.70	(–0.06)
47.4	6.53	8.13	(+1.60)	7.84	9.03	10.37	13.06	(+2.19)
164.0	00.0	32.91	—	33.97	31.42	28.07	21.73	(–11.80)
162.2	4.50	20.86	—	20.01	21.46	24.80	31.24	(+3.94)
160.7 <sup>a</sup>	95.50	46.22	—	46.02	46.96	47.12	47.03	(+0.90)
CH <sub>2</sub> O <sup>b</sup>	ND	0.70	—	0.73	0.84	0.82	0.94	—
Vis. <sup>c</sup>	W	S	—	RS	QR	P	N	—

Sample numbers are defined in the text. The values in parentheses are differences between the samples. Chemical structures for chemical-shift values (ppm) are defined in Figure 2.

<sup>a</sup> The group value includes approximately 2–3% of tetra-substituted urea carbonyls.

<sup>b</sup> Formaldehyde emission values of PBs in  $\mu\text{g/mL}$ .

<sup>c</sup> Viscosity of resin sample by Gardener–Holdt method.

content remaining in Sample A6, 7.70%, is similar to the previously reported value. Then, the Type III group content, if assumed to be about one-half of 7.70%, is relatively small and can be ignored as an approximation to calculate an approximate polymer-chain structure based on methylene and methylene–ether bond contents. The data in Table I indicate that Sample 6 would have an UF polymer-chain structure consisting of 81% methylenes and 19% methylene–ether bonds, and to construct a typical representation of the polymer-chain structure, combining methylenes with methylene–ethers ( $\times 0.5$ ) by bond types results in the following bond-type values per mole of the first urea used: Type I, 0.386 bond ( $18.4\% \times 2.1$ ), Type II, 0.460 bond ( $21.9\% \times 2.1$ ), and Type III, 0.074 bond ( $3.5\% \times 2.1$ ), with a total of a 0.920 bond group. These group values indicate a number-averaged 12.5-mer  $\{n = 1/(1 - 0.92)\}^{26}$  which possesses a total of 5.81 urea-chain branches ( $2 + 0.46 \times 12.5 \times 0.5 + 0.074 \times 12.5 \times 1$ ) for the polymeric UF resin molecules of Sample A6.

Since UF resin polymer-chain structures based on methylene and methylene–ether bonds would change little by mild heat treatments carried out in weak alkaline pH, it is useful to compare the number of urea-chain branches, or of terminal urea nitrogens, obtained (5.81) with the number of Type I and II hydroxymethyl terminal groups for Sample A1 where few of them have migrated to the second urea. The number of Type I hydroxymethyl groups  $\{(0.154 + 0.013) \times 2.1 \times 12.5 = 4.36\}$  and that of one-half of Type II hydroxymethyl groups  $\{(0.198 + 0.019)/2 \times 2.1 \times 12.5/2 = 1.42\}$ , assuming that Type II hydroxymethyl groups constitute about one-half of the Type II/III peaks, amount to 5.78, which compares well with the number of urea-chain branches obtained. Some free amide nitrogens were indicated to be present for Sample A1-type resins studied earlier,<sup>2</sup> but the Sample A1 used in this work contains very few free-amide terminal groups. Uncertainty exists in the 1 : 1 proportioning of Type II/III hydroxymethyl groups used as well as in the unknown level of Type III hydroxymethyl groups

remaining in Sample A6. For the latter, if it is assumed to be one-half of the residual Type II/III hydroxymethyls (3.85%), the total number of polymer branches obtained based on methylene and methylene–ether bonds needs to be revised down by 0.51. This would lead to a further refinement of the polymer-chain structure. Overall, the polymer structure of Sample A1 obtained here appears to be the closest one obtainable currently and it appears to be in accord with the general concept of resol-like structures long held in the UF resin industry. Thus, Sample A1 can be represented as a 12.5-mer having 5.81 polymer-chain branches capped with Type I or II hydroxymethyl groups and Type III hydroxymethyl groups are present bonded to some internal urea nitrogens in polymer chains. The overall reacted F/U ratio is of approximately 1.70 with an average functionality of 2.39 for (first) urea. The amounts of Type II/III hydroxymethyl groups formed on the second urea during the heat-treatment period appear to be small. For Sample A6, for example, the total formaldehyde that migrated to the second urea amounts to 0.365 mol per mol of the second urea, at which the mol ratio the Types II/III hydroxymethyl groups formed on the second urea will be negligible.

#### Resin Effects of Hydroxymethyl Group Migrations to Second Urea

$^{13}\text{C}$ -NMR data (Table I) indicate no significant changes in the amounts of methylenes or methylene–ethers during the heat treatments used. Therefore, the UF resin samples can be viewed as a mixture of monomeric urea and hydroxymethyl-ureas derived from the second urea (44%) and polymeric UF molecules derived from the first urea (56%). This is shown also by the urea carbonyl values in that the monomeric UF resin components consist of large amounts of unreacted and monomeric urea even for Sample 6. In Samples A2 and A3, it is seen that most free formaldehyde and hemiformals present in Sample A1 have reacted. Samples A2 and A3 are very similar in NMR and viscosity value and this indicates that the heat treatment used to obtain Sample A3 (25 min at 40°C) had only a minor effect: 3.02–4.80% decrease in Type II/III hydroxymethyl groups. Furthermore, the viscosity of Sample A3 did not change for the next 45 min of heating at 40°C, indicating that the hydroxymethyl group-transfer rate is relatively slow even at this increased temperature. This 40°C heat treatment would be a

rather severe one if it is compared with the temperatures encountered in the storage and transportation of industrial UF resins. In industry, wood PB adhesive-type UF resins are transported and stored at cold temperatures and normally used within 1 week. In Sample A4, obtained at the end of the next heating period, 50°C for 30 min including the heating-up time, a slightly reduced viscosity of *QR* was obtained and the cumulative decrease of Type II/III hydroxymethyl groups reached 6.25%. The viscosity of the resin sample remained unchanged for the next 30 min of heating at 50°C, indicating a similarly good stability at this temperature. Therefore, the overall results indicate that the migration of hydroxymethyl groups occurring during transportation and storage of UF resins in industrial practice would be relatively slow.

In Sample A5, obtained at the end of the heating at 60°C for 40 min including the heat-up time, the viscosity was reduced to *P* and Type II/III hydroxymethyl groups decreased by 9.99%. When the heat treatment at 60°C was continued for the next 30 min, the viscosity decreased relatively fast to *N*, and increasing the temperature to 70°C and holding it for 30 min resulted in a rapid decrease in viscosity to *K* for Sample A6.  $^{13}\text{C}$ -NMR of Sample A6 indicated a decrease in Type II/III hydroxymethyl group content by 15.37% in comparison with the value of Sample A1 with a light turbidity arising in the resin sample. Sample A6 also showed a slight increase in the methylene–ether content as expected in the alkaline pH used. The viscosity reduction and turbidity increase became relatively faster when the resin sample was heated beyond Sample A6. The somewhat stepwise, gradual decreases in viscosity and Types II/III hydroxymethyl groups observed appear to indicate that some barriers to the dehydroxymethylation reaction are present. Overall, these results can be compared with the resin-manufacturing practice in the industry, where the addition of a second urea is commonly carried out during the cooling period of the resin batch. It starts at 60–70°C with the subsequent cooling operation extended over a period of 2 h or more due to the slow heat transfer of viscous resin. Therefore, the extent of migration of hydroxymethyl groups in industrial UF resins will decrease as the batch temperature at the time of the second-urea addition decreases or the resin batch is cooled faster. Once the resin batch is cooled to room temperature, the hydroxymethyl groups would migrate to the second urea only very



**Table II Percentage Values of Various Methylenic Carbons and Carbonyls of Resin Samples B1-B6 Determined by  $^{13}\text{C}$ -NMR, Viscosity, Number of Days of Storage, and 2-h Desiccator Formaldehyde Emission Values of PBs Bonded with the Resin Samples**

Groups (ppm)	B1	B2	(B2-B1)	B3	B4	B5	B6	(B5-B2)
91.0	1.14	0.55	(-0.59)	0.65	0.58	0.66	0.54	(+0.11)
87.0	5.55	0.00	(-5.55)	0.11	0.00	0.00	0.00	(0.00)
83.1	6.77	0.17	(-5.60)	0.20	0.19	0.31	0.23	(+0.14)
79.1	1.41	1.05	(-0.40)	0.76	1.00	1.12	1.26	(+0.07)
75.1	7.18	4.73	(-2.45)	4.64	5.21	4.95	4.94	(+0.22)
69.5	8.66	7.20	(-1.46)	8.00	9.35	9.89	11.34	(+2.69)
72.0	19.71	20.65	(+0.95)	17.02	14.73	13.94	12.93	(-6.71)
65.2	14.76	30.41	(+15.65)	30.76	29.52	28.86	22.82	(-1.55)
60.1	6.54	5.18	(-1.36)	4.22	5.33	5.32	6.02	(+0.14)
53.9	20.84	22.71	(+1.87)	24.43	22.62	22.41	22.20	(-0.30)
47.4	7.44	7.35	(-0.09)	9.22	11.25	12.52	17.72	(+5.17)
164.0	00.0	26.73	—	22.75	18.60	16.88	12.71	(-9.85)
162.2	4.83	17.83	—	23.31	27.31	29.97	33.15	(+12.14)
160.7 <sup>a</sup>	94.17	55.44	—	53.94	54.08	53.15	54.15	(-1.29)
CH <sub>2</sub> O <sup>b</sup>	ND	1.20	—	1.23	1.36	1.50	1.26	—
D <sup>c</sup>	0	1	—	7	16	22	30	—
Vis. <sup>d</sup>	V	P	—	L	L	M	N	—

See first footnote to Table I.

<sup>a</sup> See footnote a to Table I.

<sup>b</sup> See footnote b to Table I.

<sup>c</sup> Number of days of storage at room temperature.

<sup>d</sup> See footnote c to Table I.

slowly, but some variability in the hydroxymethyl-group distribution between polymeric and monomeric UF resin components is expected in industrial UF resins.

The somewhat stepwise manner of viscosity decreases observed during the heat-treatment period is an interesting phenomenon. Type I and II hydroxymethyl groups constitute the polymer chain ends while Type III hydroxymethyl groups are bonded to urea imide nitrogens in the middle of polymer chains. Almost all hydroxymethyl groups in A1-type UF resins are likely to belong to trisubstituted urea units and their migration to the second urea entails a dehydroxymethylation reaction, which would be responsible for the stepwise manner of viscosity decreases observed. Although it is unclear at this time, the cause would probably be that hydroxymethyl groups bonded to disubstituted urea units, once formed during the heat treatments, are slower to dissociate than are those bonded to trisubstituted urea units. Also, hydroxymethyl groups are stabilizing groups for

polymeric UF resin molecules responsible for the resins' stability, that is, they help keep them swollen and suspended in the aqueous medium. Loss of hydroxymethyl groups would result in agglomeration of polymeric UF resin molecules to form solidlike particles and cause the turbidity seen in Sample A6 and beyond.

#### Room-temperature Storage of UF Resins

$^{13}\text{C}$ -NMR results of the Sample B series (Table II) reflect the migration of Type II/III hydroxymethyl groups occurring at room temperature, in the absence of stirring, over a period of 1 month. Sample B1, made using the same procedure and formula of Sample A1, turned out to be slightly lower in viscosity and slightly different in structure: increased substitution on urea units as seen by higher values of Type II/III hydroxymethyl and Type III methylene groups. These differences are probably due to some synthesis parameters inadequately noted or attended, but, overall, they are

very similar. In the initial period of the room-temperature storage, the migration of Type II/III hydroxymethyl groups to the second urea occurred and the viscosity of the resin decreased similarly as in the heat treatments. The viscosity decreased from *P*, reaching to *L* on the 5th day, remained at *L* until the 7th day (Sample B3), and decreased to *K* on the 12th day. The  $^{13}\text{C}$ -NMR data and viscosity changes indicate that the 7–12-day storage samples are comparable to Sample A4 obtained by heat treatments up to 15 min at 50°C. The viscosity change and migration of Type II/III hydroxymethyl groups was negligible at 4°C for 22 days for Sample B5c (NMR data not reported).

However, some unexpected behaviors were observed in the later period of the room-temperature storage experiments. After about the 12th day, the viscosity of the resin sample started to gradually increase, a phenomenon not observed in the heat-treatment experiments. The turbidity of the resin sample arose between the 7th and 14th day (Samples B4–B6) and increased gradually further, although it was still relatively light even for Sample B6. Reasons for the viscosity increase observed were not clear initially, but  $^{13}\text{C}$ -NMR results indicated that, although the migration of Type II/III hydroxymethyl groups continued, some increases in methylenes and methylene–ethers had occurred in Sample A6. Methylene–ether groups would be formed to some extent in the alkaline pH used, but the significant increases in Type I methylenes in Samples B5 and B6 were not expected. The increases were accompanied by decreases in hydroxymethyl groups and there were no apparent decreases in Type II or III methylene groups. This result indicates that a significant amount of Type I methylene groups are actually formed during the later part of the room-temperature storage. In contrast, the smaller increase in Type I methylene groups that occurred in the heat-treated Sample A6 was accompanied by a decrease in Type II methylenes, allowing it to be ascribable to the migration of Type III hydroxymethyl groups.

Methylene groups have been known to form only in the acidic pH within the common time regimes used in the manufacturing of UF resins.<sup>1,3–11</sup> In addition, the turbidity of Samples B5 and B6 cast some uncertainty on the accuracy of  $^{13}\text{C}$ -NMR results, but it was very light and appears to be too minimal to increase the Type I methylene-group content by preferentially suppressing other carbon groups. The increases in

Type I methylene groups in Sample B5 and B6 are corroborated by the significant decreases in the overall hydroxymethyl-group content as well as decreases in the free urea content observed in the  $^{13}\text{C}$ -NMR carbonyl-group data. The author earlier observed a similar increase in Type I methylene-group content for UF-resin samples stored for a long period time (6 months or more) at about 4°C. In industry, UF resins in weak alkaline pH are observed to turn into flimsy gels in about 30 min at 100°C, and upon storage for a long period time at room temperature, they increase in viscosity and turbidity and eventually form water-in-oil-type gels. Therefore, opposed to the traditional view, certain polymerization reactions appear to be progressing in UF resins in the weak alkaline pH, especially in standing for a long period of time. In this regard a suggestion was made earlier that methylene bonds would form in UF resins even in the weak alkaline pH if an ample amount of free amide groups is available.<sup>27</sup> Also, a trace amount of methylene groups was observed to be present in the reaction products sampled just after the first weak alkaline condensation step of UF-resin synthesis (30 min at 90°C), although it was assumed to be insignificant and unexplained.<sup>1</sup> Overall, the standing of UF resins having a high free urea content for a long period of time appears to allow Type I methylene groups to form even in the weak alkaline pH. The formation of methylene bonds in the alkaline pH is likely due to the general acid-catalysis by unionized acidic components present. Overall, the results indicate that an extended resin storage time would increase the extent of hydroxymethyl-group migration as well as promote the formation of methylene and methylene–ether groups. The room-temperature storage method may provide a way to increase the Type I methylene-group content of UF resins.

#### Formaldehyde Emission Test Results of PBs

The internal-bond and bending-strength values of boards obtained were in the range of values for typical laboratory-made PBs (details to be reported later), indicating that the board-manufacturing parameters used were adequate enough to allow the comparison of the formaldehyde emission values. The 2-h desiccator method<sup>25</sup> used in this study provides a relative measure of the amount of free formaldehyde generated and entrapped in boards during the hot pressing of the boards. The test results for Sample A series (Ta-

ble I) indicate that the formaldehyde emission was the lowest in Sample A1 and increased gradually until Sample A6, from 0.70 to 0.94  $\mu\text{g}/\text{mL}$ . Thus, the formaldehyde emission showed increases as the amount of hydroxymethyl groups migrated from the polymeric-to-monomeric UF-resin components increased. The reason behind this phenomenon is unclear. One possible explanation is that in the initial phase of resin curing the hydroxymethyl groups would react mostly with the free amide groups of the second urea to form methylene groups, and this would result in segregating out those second-urea components that have already acquired migrated hydroxymethyl groups. Thus, segregated domains of hydroxymethylureas, in the final stage of curing, could reach an F/U ratio that is greater than the average value and emit an increased amount of formaldehyde. The level of such segregated domains would increase as the amount of migrated hydroxymethyl groups increases from Sample A2 to A6. The formaldehyde emission increase from Sample A1 to A6 observed, of up to 35%, appears to be large enough to deserve a detailed study for feasibility of using in practice. Overall, the lower the temperature of the second-urea addition and the faster the subsequent cooling rate, the lower the formaldehyde emission level of PBs when the resin is used within 1 week or so.

For Sample B series (Table II), the formaldehyde emission level increased gradually from 1.20  $\mu\text{g}/\text{mL}$  for Sample B2 to 1.50  $\mu\text{g}/\text{mL}$  for Sample B5 and then decreased to 1.26  $\mu\text{g}/\text{mL}$  for Sample B6. First, the overall formaldehyde emission level is appreciably higher than those of the Sample A series, which is apparently due to some differences in the board-manufacturing procedure including the season of the year and wood raw material used. Nevertheless, the increasing trend of the formaldehyde emission level with respect to the extent of the hydroxymethyl-group migration up to Sample B5 is very similar to the trend observed in the Sample A series. The results indicate that shorter storage times would show less formaldehyde emissions for UF resins made by adding the second urea at low temperatures. About 1 week's resin storage time at room temperature hardly increases the formaldehyde emission. The lowered formaldehyde emission of Sample B6 is interesting, coinciding with, and may trace to, the increase in the Type I methylene content and decrease in the hydroxymethyl-group content discussed above. Overall, the results indicate that typical industrial UF resins manufac-

tured by adding the second urea at 60–70°C and thus having a considerable amount of hydroxymethyl groups migrated to the second urea at the end of resin manufacture would show, initially, a high formaldehyde emission value, which may decline when the resin storage time is lengthened. This observation thus appears to be in accord with the optimum aging time concept used for UF resins in industry, although little detail has been documented. Further studies would clarify these causes and effects and possibly uncover a room-temperature aging method that provides an additional way of reducing the formaldehyde emission of UF resin-bonded wood composite boards.

## CONCLUSIONS

Hydroxymethyl groups of the polymeric UF-resin components in UF resins, in weak alkaline pH, migrate to the second urea to form monomeric hydroxymethylureas. The migration is relatively slow at low temperatures occurring over a period of 1 month or more at room temperature and becomes relatively fast above 50°C. In general, the hydroxymethyl-group migration decreases the viscosity of the resin and increases the formaldehyde emission of PBs bonded to the resin. The results indicate the varying performance properties possible in industrial UF resins depending on the time/temperature parameters used in the second-urea addition and subsequent cooling period in resin manufacture. When UF resins are stored at room temperature for an extended period time, some polymerization reactions appear to occur, by forming methylene and methylene-ether bonds involving the second urea, resulting in affecting the resin properties and formaldehyde emission of bonded PBs.

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