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

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ABSTRACT: Typical particleboard wood-adhesive urea–formaldehyde (UF) resins, synthesized with formaldehyde/first urea (F/U$_1$) mol ratios of 1.80, 2.10, and 2.40 and the second urea added to an overall F/U ratio of 1.15, in weak alkaline pH, were allowed to stand at room temperature over a period of 50 days. ^{13}C-NMR of time samples taken over the storage period showed gradual migration of hydroxymethyl groups from the polymeric first-urea components to the monomeric second-urea components and also an advancing degree of polymerization of resins by forming methylene and methylene ether groups involving the second urea. These phenomena that varied with the F/U$_1$ mol ratios used in the resin syntheses due to the varying polymer branching structures resulted in the first step of resin synthesis. Varying viscosity decreases and increases of the resins also occurred. Due to these chemical and physical changes, the particleboards that bonded with the sampled resins showed varying bond strength and formaldehyde-emission values, indicating process optimizations possible to improve bonding and formaldehyde-emission performances. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1155–1169, 2001

Key words: wood adhesive; urea–formaldehyde resins; UF resin chemistry; particleboard bonding; formaldehyde emission of particleboards

INTRODUCTION

Urea–formaldehyde (UF) resins have been known for many decades and currently are used as thermosetting wood-adhesive binders in manufacturing interior-use wood-composite boards, such as particleboard (PB) and medium-density fiber-

board.[1–9] The drawbacks of UF resins are the low water resistance and high formaldehyde-emission levels of wood-composite boards,[10–13] which have been the industry's concern in recent years. The overall formaldehyde/urea (F/U) mol ratio used in the manufacturing of UF resins, which currently runs at a low value of about 1.15, has been the key parameter used in controlling the formaldehyde-emission level. Use of higher F/U mol ratios in resins improves the wood-composite boards' physical performance but it also increases the formaldehyde-emission level. Scavengers are often used to keep the formaldehyde-emission levels in check. Furthermore, even with a given UF resin,

X = CH$_2$ and CH$_2$OCH$_2$

Y = H, CH$_2$OH, or CH$_2$OCH$_2$OH

Z = Y or {X—NZ(CO)NZ} yY

x = deg. of polymer. of main polymer chain.

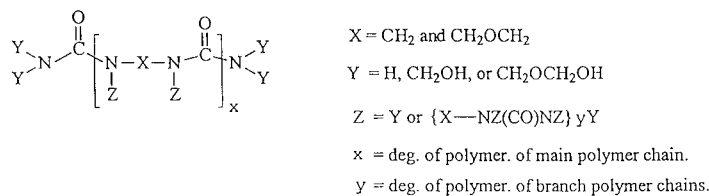y = deg. of polymer. of branch polymer chains.

Figure 1   A schematic representation of UF resin polymer molecules with group Z's representing possible polymer chain branches that can also form polymer chain branches themselves.

the formaldehyde-emission level and bond performance of wood-composite boards vary significantly because of the varying mat-forming and hot-pressing conditions in the board-manufacturing process.[14] Recent research reports on UF resins obtained using ^{13}C-NMR[15–17] revealed several resin synthesis and handling parameters that affect the formaldehyde-emission and bonding performance of PBs, as discussed briefly below.

In manufacturing wood-adhesive UF resins, as described in previous reports,[15–19] urea is employed in two parts: first urea (U_1) and second urea (U_2). In the first step, the first urea is reacted with formaldehyde at about 90°C at a formaldehyde/urea (F/U_1) ratio of about 2.10 in a weak alkaline aqueous medium. Mono-, di-, and trihydroxymethylureas and minor amounts of their reaction products containing methylene–ether bonds are formed (Fig. 1). This hydroxymethylation reaction between formaldehyde and urea 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},[6] and this reversibility of the reaction appears to be operative throughout the life of UF resins while in weak alkaline pH. In the second step of resin synthesis, the reaction mixture is acidified to a pH between 4 and 5 and maintained at about 95°C, where the hydroxymethyl groups attack urea amide nitrogens to form methylene groups, resulting in UF resin polymers. In this polymerization reaction, some hydroxymethyl groups split off as formaldehyde due to the reverse hydroxymethylation reaction that is effective also at acidic pH and due to the decreasing number of amide groups available in the resin system caused by the increasing methylene bond content. While the theoretical functionality of a urea molecule is 4, 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. These limitations mean the expulsion of formaldehyde molecules, especially from more-substituted urea, as a result of forming UF resin

polymers even when the F/U_1 ratio used is a typical value between about 2.1 and 1.80.

Once the target polymerization extent is attained in the resin synthesis, that is, reaching a viscosity value of about "W" by the Gardener–Holdt scale ($\sim$32 P), with the solids levels at between 60 and 65%, the polymerization reaction is ended by adjusting the pH to a weak alkaline value. The resulting products are polymeric methylene and methylene ether hydroxymethylureas (Fig. 1). In the third step of the resin synthesis, while the reaction mixture is being cooled to room temperature with the weak alkaline value pH being maintained, the second urea (U_2) is added and thoroughly mixed, resulting in a combined F/U [F/($U_1 + U_2$)] ratio of about 1.15. In the subsequent cooling and storage and transportation period, the second urea reacts with free formaldehyde present in the reaction mixture to form various monomeric hydroxymethylureas. It was also shown that some hydroxymethyl groups of polymeric UF resin molecules cleave, due to the reversibility of the hydroxymethyl group-forming reaction, and the freed formaldehyde reacts with the second urea (Fig. 2). This hydroxymethyl group migration from the polymeric to monomeric UF resin components also proceeds appreciably at room temperature and increases at higher temperatures and is accompanied by a reduction in the viscosity of the resins. In the resin-manufacturing industry, the temperature of the resin mixture at the time of the second urea addition and the batch cooling rate vary as do the subsequent storage and transportation time and conditions. This results in varying distributions of hydroxymethyl groups among the first urea polymeric and the second urea monomeric resin components. This variability affects the PB bonding and formaldehyde-emission performances.[15–17]

In a previous publication,[17] we reported on the polymer structural changes and varying resin viscosity behaviors occurring due to different F/U_1 mol ratios of 1.80, 2.10, and 2.40 used in the first

$X = CH_2$ and/or CH_2OCH_2

$Y = CH_2OH$, CH_2OCH_2OH, or H
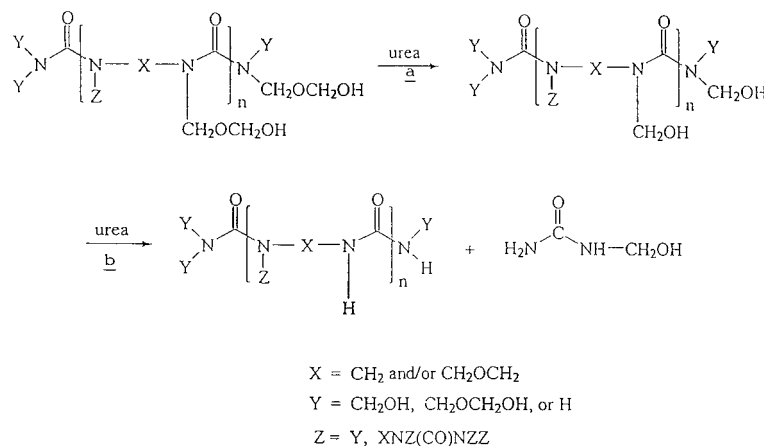
$Z = Y$, $XNZ(CO)NZZ$

Figure 2 Migration of (a) hemiformal groups and (b) hydroxymethyl groups from polymeric to monomeric UF resin components.

step of resin synthesis. Higher F/U_1 values slow the rate of viscosity advancement and polymerization and increase the number of side branches in the resultant polymers, while lower F/U_1 values increase the rate of viscosity advancement and polymerization and decrease the number of side branches. F/U_1 values lower than about 1.80 result in resins having an increasingly higher turbidity and greater non-Newtonian viscosity behavior as well as an altered wood-bonding efficiency.[18] On the other hand, since the overall F/U ratio and final viscosity of UF resins are relatively in fixed ranges of about 1.15 and 300–500 cP, respectively, in industry, use of higher F/U_1 ratios results in higher molecular weights in the polymerization step and greater amounts of the second urea needed in resin manufacturing. These variations in molecular structures and molecular weights and relative amounts of monomeric/polymeric components resulted in varying viscosity behaviors of the resins on heat treatment or room-temperature storage.

The room-temperature storage experiment of the three different F/U_1 mol ratio resins in the previous study[17] resulted in an unexpected result. In this experiment, the second urea was added to the resin synthesis mixture after cooling to ~4°C to suppress the migration of hydroxymethyl groups, and then the resulting resin was allowed to stand at room temperature for 50 days. A viscosity reduction was observed in the first 20 days in which hydroxymethyl groups were shown to gradually migrate from the polymeric UF resin components to the second urea, with almost no increase in the methylene or methylene ether group content. This result is similar to what was

observed when resins were treated at 60°C for 2 h in the study. However, the viscosity of the room-temperature-stored resin samples began to increase after the 20-day storage time, with the rate of increase being the highest with the 1.80 F/U_1 ratio resin and the slowest with the 2.40 F/U_1 ratio resin. The reason behind this phenomenon was unclear. In the PB industry, also, the adhesive bonding and formaldehyde-emission performances of UF resins have been known to vary over a storage period of time, but the underlying chemical mechanisms are obscure. In this study, therefore, more detailed work was carried out to examine the resin samples taken in the 50-day room-temperature storage experiment. UF resins were synthesized with initial F/U ratios of 1.80, 2.10, and 2.40 and the second urea added to F/U ratios of 1.15, and time samples were taken over a storage period of 50 days at room temperature and examined using ^{13}C-NMR and also by bonding PBs and measuring the strength properties and formaldehyde-emission levels.

EXPERIMENTAL

Reagent-grade urea, sulfuric acid, sodium hydroxide, and a fresh industrial-grade 50% formaldehyde solution kept at 60°C in the laboratory were used. pH adjustments were made with a 4.0% sulfuric acid or an 8.0% sodium hydroxide solution, with pH drifts maintained within ±0.10. Although the resin synthesis procedures were exactly the same as those reported in the previous publication,[17] the plan of making and remaking

resins and storing them over the 50-day period to allow PBs be made on the same day at the end of storage presented a materials and procedure variability problem. This was circumvented by making a large batch of resin for each F/U_1 mol ratio, cooled to room temperature, and, without adding the second urea, divided into six equal portions and stored at 4°C. One of resin samples was taken out on the scheduled day for a desired number of storage days and the second urea added and stirred at room temperature, and room-temperature storage was commenced.

Resin Sample 2.10 Series with F/U_1 Ratio of 2.10

For this typical resin, according to the procedure described earlier,[16–19] 3150 g of a 50% formaldehyde solution was charged into a stirred reactor and the pH adjusted to 7.8 and then was heated to 90°C, and 1500 g of first urea 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 with intermittent external heating and cooling applied as needed. The reaction mixture was then adjusted to pH 4.5 and reacted at 95°C until a viscosity of "X" was reached (approximately 120 min). Then, the reaction mixture was made alkaline to pH 7.8 and cooled to room temperature. The resin product was divided into six equal portions (6 × 775 g) and numbered as Resin 2.10b, 2.10e, 2.10f, 2.10g, 2.10h, and 2.10i and stored at 4°C. The amount of the second urea to be added to each portion to attain an $F/(U_1 + U_2)$ ratio of 1.15 was 206.2 g.

Resin Sample 2.40 Series with F/U_1 Ratio of 2.40

The procedure was the same as the one used above except that the amount of the first urea was reduced to 1313 g ($F/U_1 \times 2.40$). To compensate for the slower reaction rate at this higher F/U ratio, the acidic polymerization reaction was conducted at pH 4.10. The polymerization reaction time was still lengthened to 145 min. The product was divided into six equal portions (6 × 744 g) and numbered as Resins 2.40b, 2.40e, 2.40f, 2.40g, 2.40h, and 2.40i and stored at 4°C. The amount of the second urea to be added to each portion to attain an $F/(U_1 + U_2)$ ratio of 1.15 was 237.7 g.

Resin Sample 1.80 Series with F/U_1 Ratio of 1.80

The procedure used above was slightly modified for these low F/U_1 ratio resins. With the same amount of formaldehyde used above, the amount of the first urea, 1750 g ($F/U_1 = 1.80$), was divided into two parts to minimize the turbidity developing in the reaction mixture during the polymerization step. Thus, the first part of the first urea (1500 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 (250 g) was added and reacted for 20 min at 90°C. The reaction mixture was then acidified to pH 4.50 and reacted at 90°C until a viscosity of "W" was reached (approximately 30 min), which was then made alkaline to pH 7.8 and cooled to room temperature. The resin product showed a very light hazy appearance, which was much less turbid than that of resins made without the modification. The resin product was divided into six equal portions (6 × 816.7 g) and numbered as Resins 1.80b, 1.80e, 1.80f, 1.80g, 11.80h, and 1.80i and stored at 4°C in a cold-storage room. The amount of the second urea to be added to each portion for an $F/(U_1 + U_2)$ ratio of 1.15 was 164.8 g.

Room-temperature Storage and Viscosity Measurement

On the first day, samples of Resins 2.10i, 2.40i, and 1.80i were taken from the cold-storage room and the required amounts of the second urea were added to attain an overall F/U ratio of 1.15. The resin samples were gently stirred for 3 h at room temperature, resulting in dissolving of the second urea in, and warming up of, the resin mixture to room temperature. These resin samples were allowed to stand on a bench in an air-conditioned laboratory and the viscosity was checked periodically over a period of 50 days. A similar addition of the second urea and storage treatments with the subsequent resin samples carried out on scheduled days resulted in the following resin samples: 2-day-stored sample, -b series; 7-day-stored sample, -e series; 15-day-stored sample, -f series; 30-day-stored sample, -g series; 45-day-stored sample, -h series; and 50-day-stored, sample -i series. Most of these samples were analyzed using ^{13}C-NMR and also used in bonding laboratory PBs. This storage experiment was carried out from December to early January. The same storage experiment was repeated from April to May.

Particleboard Preparation Procedure

PB manufacturing and testing procedures were the same as those reported earlier.[15–17,19] Briefly, single-layer PBs were made using dried core-layer wood particles obtained from the Georgia-Pacific Corp. PB plant in Louisville, MS. A rotary drum blender, forming box, and Williams–White hot press were used according to the standard laboratory procedure. The resin loading level was 8.0% based on an oven-dry wood weight, the mat moisture content was about 9.0%, and the hot-pressing time was 3.25 min at 163°C. No wax was added. Two panels (506 × 506 × 12.65 mm) were made with a target board density of 801 kg/m^3 (50 lb/ft^3) for each resin sample.

Formaldehyde-emission Tests

In the 2-h desiccator formaldehyde-emission tests,[20] hot-pressed PBs were first allowed to equilibrate 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 (Gaithersburg, MD). The formaldehyde-emission test consists of airing test pieces for 24 h in a laboratory room and then measuring the amount of formaldehyde emitted over a period of 2 h at 75°F. Test pieces were edge-sealed with molten wax and provided a total exposed board surface area of 0.141 m^2 per resin sample. The test consists of placing test pieces in a closed desiccator along with 25 mL water in a shallow beaker, which absorbs the formaldehyde emitted. The water is titrated to give the formaldehyde concentration in g/mL water.

The small-scale test chamber method (ASTM D 6007-96) was also used to evaluate the formaldehyde-emission levels of boards, where a longer preconditioning time than in the 2-h desiccator method is prescribed. Thus, hot-pressed PBs were allowed to equilibrate for 24 h in the laboratory, and three samples (379.5.5 × 199.2 mm) were cut and edge-sealed with aluminum adhesive tape to give a total exposed surface area of 0.454 m^2 per resin sample. Test samples were aired for 7 days at 23.9°C at a relative humidity of 50%. A set of test samples was loaded in the test chamber (15 × 24 × 7 7/8 in.) maintained at a make-up air flow of 8.93 L/min to provide a 1/2 air change per hour. The loading ratio was 0.13 ft^2 panel surface area per cubic foot of chamber volume. The formaldehyde level in the exiting air was monitored over time and the steady-state value, C_{eq}, attained in time was obtained as the formaldehyde-emission value of the test samples.

Mechanical Tests of Boards

Internal bond (IB) and bending strength values of the boards were measured after equilibrating test specimens for 3 weeks in a constant humidity room to about 10% moisture content in accordance with the American Society for Testing and Materials Procedure D 1037. IB strength data obtained were normalized with respect to a 50 lb/ft^3 density within each set of eight test samples. The IB strength values correlated relatively well, with r^2 values greater than 0.60 in general.

Procedure for ^{13}C-NMR Spectra and Calculation of Carbon-group Values

Test samples were prepared by mixing 2.0 g of resin and 1.0 g of deuterium oxide. 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 Data 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 Sample 4B 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 methylene carbons.[15] Normally, about 400 scans were accumulated. Spectral peaks were integrated and urea carbonyls and methylenes quantified as percentages, assuming no formaldehyde losses were incurred during the resin syntheses. The methylenic group percentage values were converted into concentration values by multiplying with F/U$_1$ ratios to obtain group values of polymeric UF resin components apart from those of the monomeric UF components derived from the second urea. Urea carbonyls were converted to percentages according to the substitution values, that is, urea, monosubstituted urea, disubstituted urea, trisubstituted urea, and tetrasubstituted urea. The calculation procedure and results for the polymer structures of UF resins made with differing F/U$_1$ ratios were described in previous reports.[15–17]

Table I Percentage Values for Various Methylenic and Carbonyl Carbons of UF Resin Samples Determined Using ^{13}C-NMR Spectroscopic Method

Groups (ppm)	Synthesized/Room-temperature-stored UF Resin Samples												
	2.4b	2.4g	2.4h	2.4i	2.1b	2.1e	2.1f	2.1g	2.1h	2.1i	1.8b	1.8g	1.8h
91.0	0.79	0.00	0.00	0.00	0.52	0.31	0.25	0.00	0.00	0.00	0.36	0.00	0.00
87.0	0.24	0.00	0.00	0.00	0.19	0.06	0.05	0.00	0.00	0.00	0.10	0.00	0.00
83.1	0.28	0.18	0.14	0.18	0.29	0.10	0.10	0.22	0.12	0.14	0.28	0.23	0.08
79.1	2.66	2.12	2.17	2.13	2.22	2.12	2.10	1.86	1.64	1.37	2.15	2.07	1.78
75.1	4.98	4.51	4.79	4.38	4.82	4.80	4.83	4.82	4.52	4.14	4.50	4.31	4.33
69.5	6.79	11.60	12.12	12.70	7.27	7.38	8.63	11.52	12.06	12.51	8.92	11.24	10.36
72.0	17.91	11.34	10.63	9.13	18.52	17.82	15.65	11.69	10.59	9.19	15.19	9.46	10.92
65.2	35.01	26.19	25.55	26.50	29.66	29.76	29.42	24.40	24.55	26.17	26.70	27.46	27.62
60.1	4.62	3.20	3.09	3.13	4.48	4.43	4.15	3.25	2.99	2.77	4.29	3.10	3.12
53.9	21.06	22.63	22.56	22.29	23.79	23.90	23.62	24.03	23.71	22.71	25.81	23.86	25.27
47.4	5.64	18.24	18.96	19.55	8.24	9.32	11.20	18.22	19.81	20.98	11.70	18.27	16.51
164.0	28.01	13.56	12.68	11.76	26.39	22.76	19.10	14.32	11.76	11.50	25.08	12.65	15.62
162.2	23.58	37.37	38.42	38.47	18.44	23.39	28.10	35.81	35.90	37.69	15.91	34.34	30.36
160.7	45.86	47.32	47.17	47.32	54.03	52.50	51.33	48.21	50.31	49.38	56.78	51.33	52.65
158.0	2.55	1.75	1.73	2.45	1.14	1.35	1.47	1.75	2.03	1.42	2.23	1.68	1.37

Sample numbers are as defined in the text: numbers 2.4, 2.1, and 1.8 indicate resin synthesis F/U1 mol ratios and -b, -e, -f, -g, -h, and -i indicate, respectively, 2, 7, 15, 30, 45, and 50 days of room-temperature storage times. Chemical structures and chemical shifts are shown in Figure 3(a,b).

RESULTS AND DISCUSSION

Effects of F/U$_1$ Mol Ratios on the Resin Formation and Polymer Structures

^{13}C-NMR analysis methods of UF resins have been well documented.[18,23–26] ^{13}C-NMR data of selected resin samples are summarized in Table I and spectra of the Resins 2.10-series are shown in Figure 3 with chemical-shift assignments for major structural groups. ^{13}C-NMR analysis results of Resins 1.80b, 2.10b, and 2.40b, aged for 2 days at room temperature, were discussed in the previous report.[17] Briefly, the degree of condensation (n) of polymeric UF resin products before the addition of the second urea, on the basis of the total methylene and methylene–ether bond contents per mol of the first urea, was 37.0 for Resin 2.40, 12.4 for Resin 2.10, and 8.0 for Resin 1.80. These differences are a result of the similar extent of reaction attained in the resin syntheses by using the reaction mixture's viscosity as the measure, between $V - X$. Using a 50% formaldehyde solution and 100% urea without adding compensating water resulted in more dilute systems for resins having higher formulated F/U$_1$ mol ratios and this resulted in higher advancements.

Another major difference arising from the different F/U$_1$ mol ratios used in the resin synthesis

was the extent of branching of the polymeric UF resin components based on methylene and methylene–ether bonds. Based on 1 mol of the first urea, the number of side-chain branches was 0.388 for Resin 2.40b, 0.355 for Resin 2.10b, and 0.310 for Resin 1.80b. The maximum possible value is 1.0 for a polymer chain with every urea unit having one branch, and the minimum possible value is zero for no branch. The linear UF polymer chain was suggested to be the major structure of UF resin polymers in the early period of development.[28] In other words, the ^{13}C-NMR results indicated that the extent of branching is about one for every 2.6 to 3.2 urea units for polymeric UF resin components. The number of terminal hydroxymethyl groups per mol of the first urea was 0.401 for Resin 2.40b, 0.449 for Resin 2.10b, and 0.443 for Resin 1.80b, the increasing trend of which is due mainly to the decreasing degree of polymerization. It was also indicated that the terminal free amide group content on polymeric UF resin molecules would increase as the F/U$_1$ mol ratio decreases. On the other hand, the second urea added in the third step of the resin synthesis reacts with formaldehyde to form hydroxymethylureas that remain monomeric, but it reduces the viscosity of the resin mixtures and the reduction is greater, with higher F/U$_1$ ratio

resins evening out the molecular weight difference effects to some extent. Thus, the degree of polymerization (n) calculated based on the combined amount of the first and second urea was <u>1.80</u> for Resin 2.40b, <u>2.01</u> for Resin 2.10b, and <u>2.33</u> for Resin 1.80b.

Polymer Structural Changes Occurring During Room-temperature Storage

^{13}C-NMR data of samples stored over the 50-day period (Table I) showed continuous decreases in the Type II hydroxymethyl group and free urea contents (Fig. 4). The beginning part of the decreases would be due to the migration of the hydroxymethyl groups from the polymeric to monomeric UF resin components as observed in the heat treatments of UF resins.[15–17] In the end, the methylene and methylene ether group contents increased significantly for all resin samples, and the Type I hydroxymethyl group content decreased for Resins 2.40 and 2.10, but not for Resin 1.80 (Figs. 4 and 5). These bond-content changes increased the degree of polymerization values of the resins, calculated based on all urea (Fig. 6). The resins' degrees of polymerization remained stable for about 15 days but increased at a fast rate until 30 days and then remained relatively constant for the last 20 days. Between the 15 and 30 days of storage time, the Type I hydroxymethyl group content decreased significantly for Resins 2.40 and 2.10 and the free (second) urea content of all three resins also decreased similarly (Figs. 4 and 5). These latter changes indicate that the polymerization reactions have occurred involving the second urea and Type I hydroxymethyl groups.
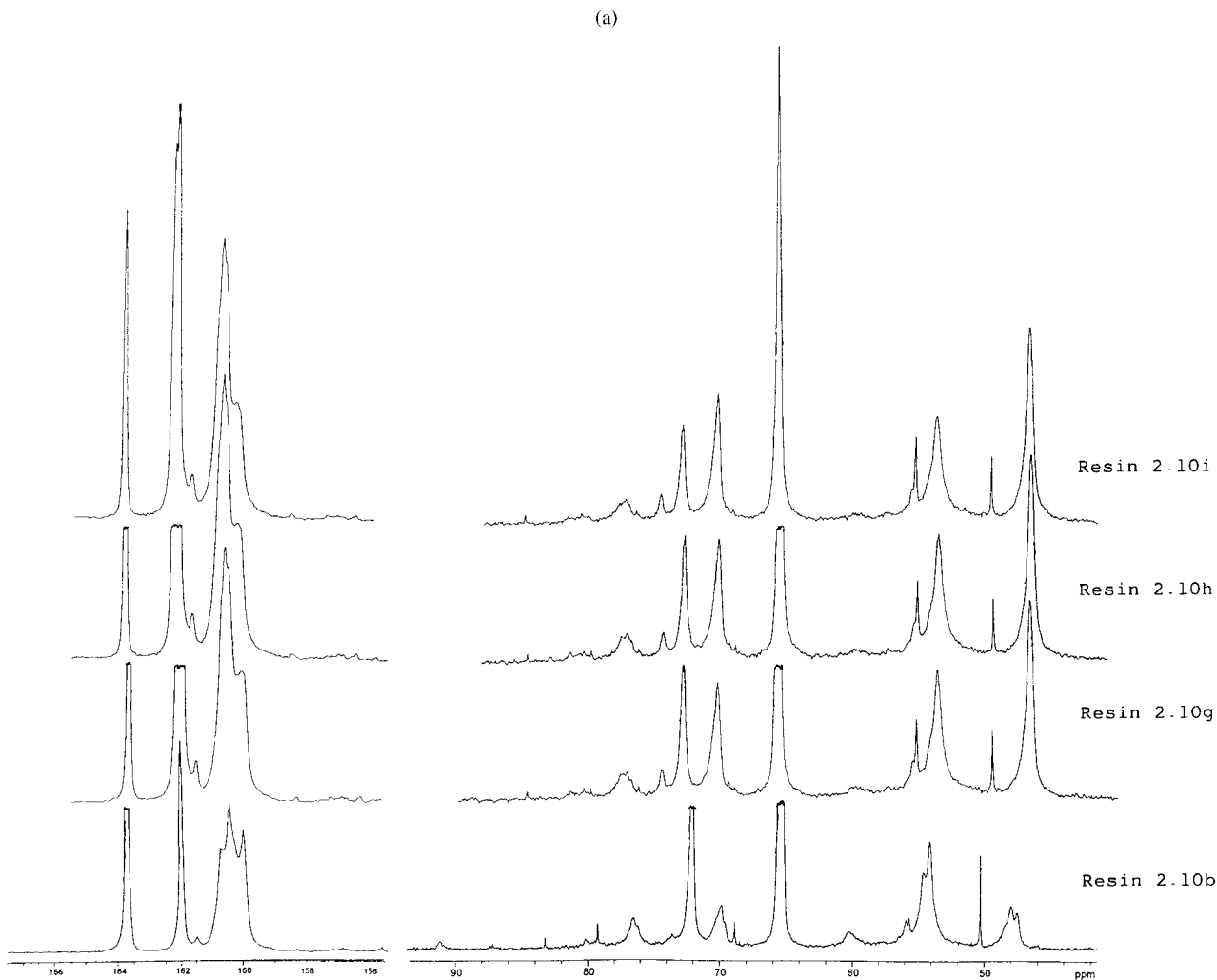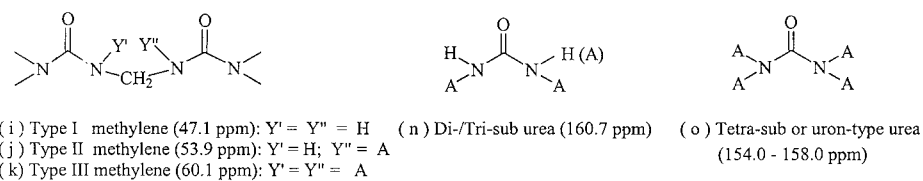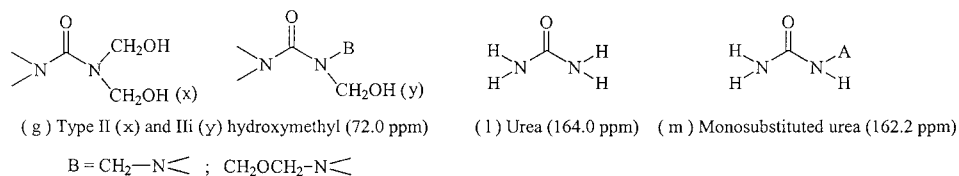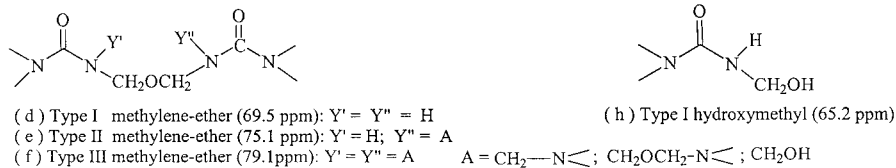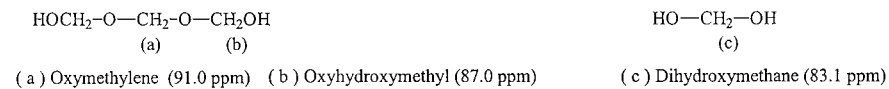
The formation of methylene bonds in UF resins in alkaline pH and the resultant increases in the degree of polymerization observed here have not been reported before, although they are in line with the general fact that most UF resins maintained in the weak alkaline pH, on storing for a long-term period, become highly viscous and finally turn into an immobile mass. UF resins in weak alkaline pH also turn into gels in about 30 min when they are heated at 100°C with minimal stirring and minimal evaporation of the content water. It has been known that UF resins do not satisfactorily cure in the hot pressing of wood-composite boards unless an appropriate amount of acidic catalysts is added or wood itself provides it. It has been also known that few methylene bonds are formed, or the viscosity of a reaction mixture increases, in the alkaline condensation step of the normal UF resin manufacturing. Apparently, this methylene bond-forming reaction occurring in the alkaline pH cannot be made to progress in the hot pressing of wood-composite boards, and the reaction mechanism is therefore puzzling, although such a possibility was suggested earlier.[28]

Resin Viscosity Changes in Room-temperature Storage

The viscosity increases of the resin samples over the 50-day storage period, reported earlier,[18] are shown in Figure 7. The viscosity values of the resins, in the order of Resin 2,40b > Resin 2.10b > Resin 1.80 in the beginning, decreased initially to some lower values, with the extent of change being the highest for Resin 2.40b and the lowest for Resin 1.80b. These viscosity decreases are ascribable to the migration of hydroxymethyl groups from the polymeric to monomeric UF resin components as in the heat/stirring experiments. The viscosity values attained between 7 and 20 days of storage were in the order of Resin 1.80 > Resin 2.10 > Resin 2.40, in line with the degree of polymerization values (n) based on the combined urea. The viscosity values of the resin samples then began to increase at about the 20th day and they continued to increase to some high values at 50 days of storage. Resins 2.40b and 2.10b behaved similarly with moderate rates of increase, but Sample 1.80 increased more rapidly and Resin 1.80i (50-day storage) was barely mobile and Resin 1.80h (45 days) gelled, preventing the board preparation. In general, these increasing viscosities or gelation of resin samples are in accord with the increases in the methylene and methylene ether group contents discussed above with ^{13}C-NMR spectral data.

On the other hand, ^{13}C-NMR data indicated very little increase in the degree of polymerization from about 30 days while the viscosity values kept increasing. UF resin molecules in aqueous media and high resin solids regimes are strongly associative due to ample hydrogen bonds. Therefore, it appears that bigger polymer clusters are increasingly forming as the molecular weights increase. The rapid rise in viscosity from about 30 days suggests that the molecular weight increases attained in the previous storage period has enhanced the associative power of the UF resin molecules. According to the dynamics theory of associative polymer systems,[29–32] molecular weight increases of polymers push the resin

HOCH₂—O—CH₂—O—CH₂OH
(a)   (b)

HO—CH₂—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 = CH₂—N< ; CH₂OCH₂-N< ; CH₂OH

(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 = CH₂—N< ; CH₂OCH₂-N<

(i) Type I   methylene (47.1 ppm): Y' = Y" = H
(j) Type II methylene (53.9 ppm): Y' = H; Y" = A   (n) Di-/Tri-sub urea (160.7 ppm)
(k) Type III methylene (60.1 ppm): Y' = Y" = A

(o) Tetra-sub or uron-type urea
(154.0 - 158.0 ppm)

(a)

Resin 2.10i

Resin 2.10h

Resin 2.10g

Resin 2.10b

(b)

system from the dynamic cluster regime to the bond-breaking regime and then to the sticky-motion regime. The UF resin samples appear to go through these cluster regime stages on storing without stirring at room temperature in which the process is helped by the increases in molecular weight of UF resin polymers occurring. Furthermore, the number of polymer side-chain branches discussed above, Resin 2.40b > Resin 2.10b > Resin 1.80b, appears to affect the relative stability of the resins against the polymer cluster associations, that is, the rapid increase in viscosity and the gelation of Resin 1.80 appears to be due to the least extent of side-chain branching of its polymers.

The rapid increases in viscosity with little increase in the degree of polymerization of the resin samples in ^{13}C-NMR over the 30–50-day storage period is somewhat puzzling, although it is likely that the formation of methylene and methylene–ether bonds had slowed down due to the increased viscosity or reduced molecular mobility. The rate of polymer cluster–cluster interactions would increase as the cluster size increases and it appears that the viscosity increases are due mainly to the increased polymer cluster interactions. On the other hand, the formation of methylene and methylene–ether bonds may have continued, but some parts of the polymer clusters in resins can attain the solidlike structures and the reduced molecular mobility would cause decreases in the ^{13}C-NMR detection of methylene and methylene–ether bonds. It needs to be further investigated. Overall, these analysis results indicate that the formation of methylene and methylene–ether bonds and attendant viscosity increases occurring in the room-temperature storage of resins would result in significant changes in the resins' thermosetting, wood-bond-forming kinetics and affect the strength and formaldehyde-emission properties of wood-composite boards.

Internal Bond and Bending Strengths of Boards

Both the resin storage time and the F/U_1 ratio of resin synthesis significantly affected the bond-strength values of the boards. Industrial PBs
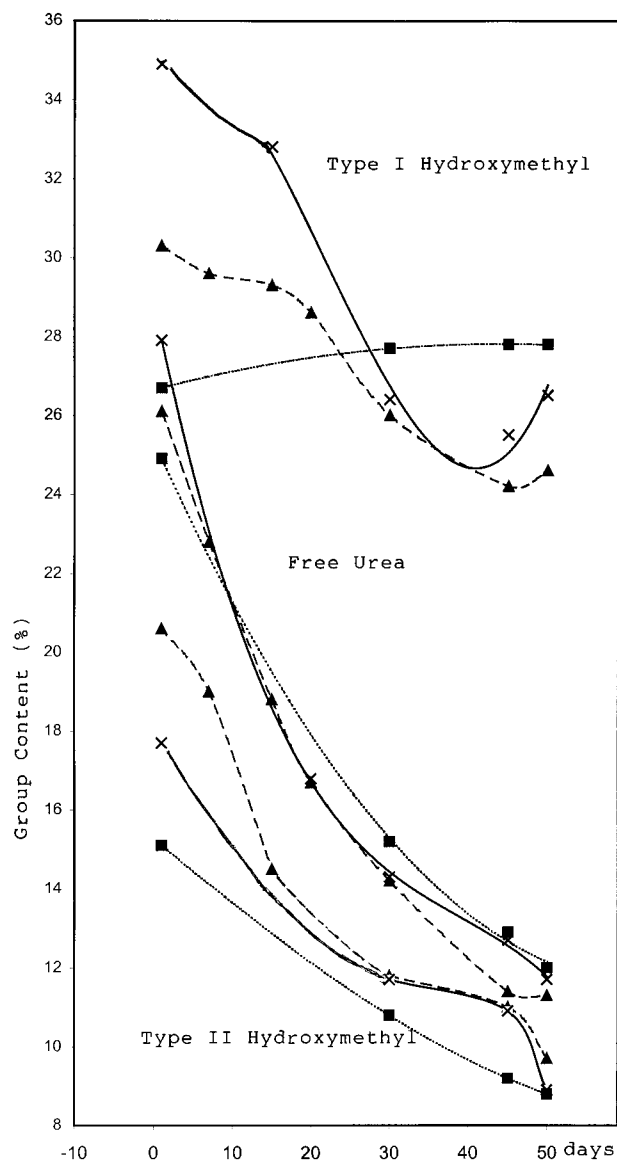

Figure 4 Changes in ^{13}C-NMR values of total Type I and II/IIi hydroxymethyl groups and free urea contents in UF Resins (· · · ■ · · ·) 1.80, (–▲–) 2.10, and (—✕–) 2.40 stored at room temperature for 50 days.

manufactured with density values close to the value used in this study normally show IB strengths of 100–160 psi, a bending modulus of elasticity (MOE) value of 300–600 kpsi, and a

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Figure 3 (a) Chemical structures of molecules and carbon groups occurring in polymeric UF resins with their ^{13}C-NMR shifts identified with small letters from (a) to (o). (b) ^{13}C-NMR spectra of UF Resins 2.10b, 2.10g, 2.10h, and 2.10i with chemical structures of groups in UF resin molecules identified with small letters (a) to (o) with respect to structures shown in (a).

bending modulus of rupture (MOR) values of 1800–3000 psi.[33] IB strength values normally reflect the strength of the core layer in boards, while MOE and MOR strength values reflect more the strengths of the surface layers. Board-strength data (Figs. 8–10) indicate that at 2-day storage Resin 1.80 showed relatively good IB, MOE, and MOR values, while Resins 2.10 and 2.40, in that order, showed significantly lower values. This order in performance is in accord with the average degree of polymerization of the polymers. At the 15-day storage time, however, Resin 1.80 showed significantly decreased strength values, while Resins 2.10 and 2.40 showed appreciably increased strength values. The ^{13}C-NMR data indicated that this storage period involves the migration of hydroxymethyl groups from the polymeric to monomeric UF resin components to result in a more uniform distribution of functional groups on
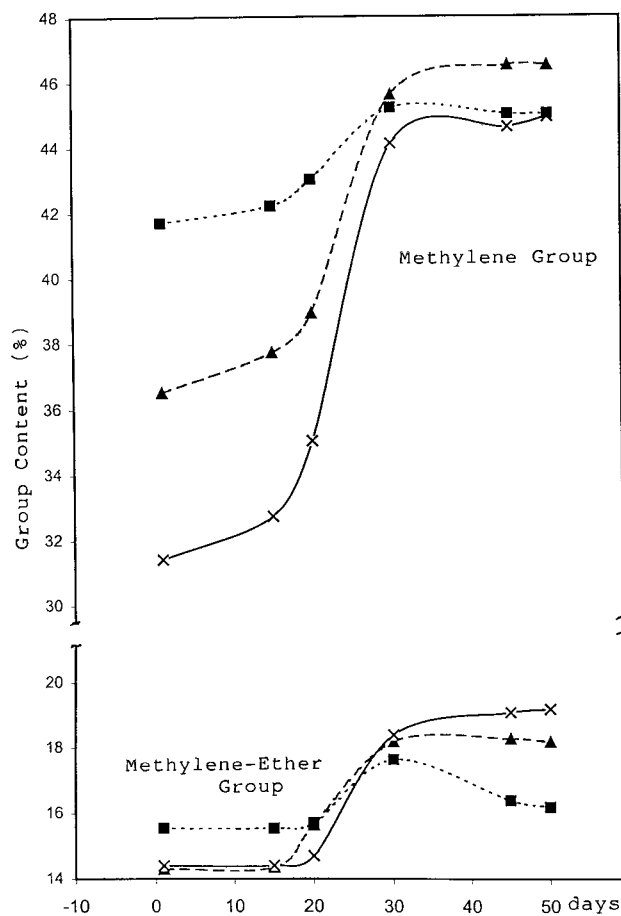
Figure 5 Changes in ^{13}C-NMR values of total methylene and methylene ether groups in UF Resins (· · · ■ · · ·) 1.80, (–▲–) 2.10, and (—✗–) 2.40 stored at room temperature for 50 days.
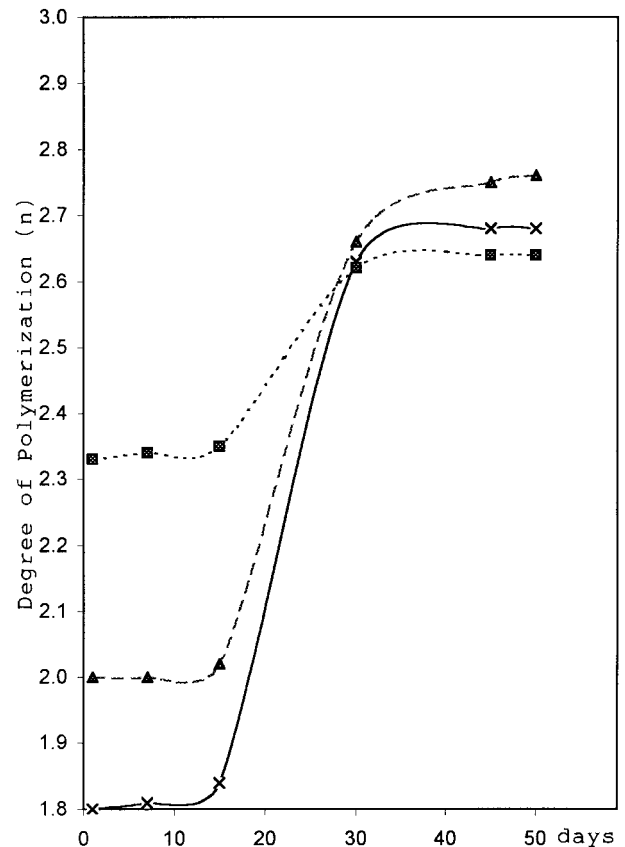

Figure 6 Changes in the degree of polymerization based on all urea of UF Resins (· · · ■ · · ·) 180, (–▲–) 2.10, and (—✗–) 2.40 during room-temperature storage for 50 days.

all urea molecules. This migration of functional groups, improving Resins 2.10 and 2.40 while deteriorating Resin 1.80 in board-strength performance, appears to be the reason behind the so-called ripening times used in the UF resin industry. The deteriorating performance of Resin 1.80 is puzzling but appears to be due to an increased precuring tendency of the resin on wood in the board-preparation step. The IB value of Resin 2.10 was appreciably higher than that of Resin 2.40, while the MOE and MOR values of Resin 2.40 were higher than were those of Resin 2.10, indicating that Resin 2.10 resulted in a faster curing speed, making it more suitable as a core-layer binder, while Resin 2.40 is more suitable as a surface-layer binder in the normal industrial three-layer board mat construction. The higher polymer chain-branching extent of Resin 2.40 in comparison with Resin 2.10 may have contributed to this difference in curing speed.

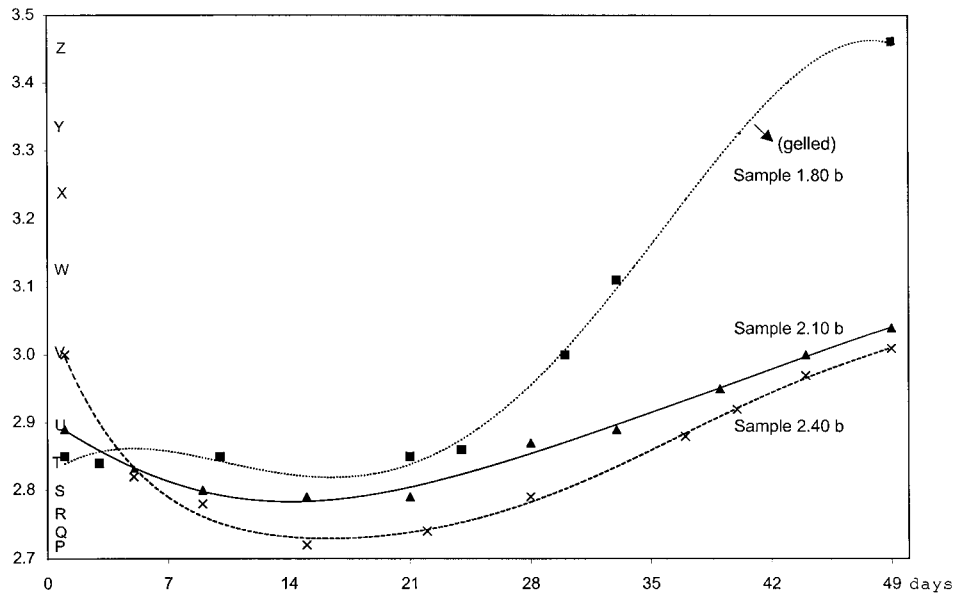At the 30-day storage time, although the degree of polymerization increased to about 2.65 for

Figure 7 Changes in viscosity of UF Resins (· · ·■■· · ·) 1.80, (–▲–) 2.10, and (—×–) 2.40 during the room-temperature storage for 50 days.

all three resins and the viscosity values increased due to increased polymer associations, only some minor changes in the IB, MOR, and MOE values were obtained in comparison with the 15-day-storage resins except for considerably increased MOE and MOR values for Resin 1.80. This behavior of Resin 1.80 is also puzzling. Comparing the three different type resins at the 30-day storage stage, the order of IB strength is Resin 2.10 > Resin 2.40 > Resin 1.80 and the order of the MOE and MOR values is Resin 2.40 > Resin 1.80 > Resin 2.10. At the 45- and 50-day storage times, with considerably increased resin viscosities, Resins 2.10 and 1.80 showed decreased IB and increased MOE and MOR values while Resin 2.40 showed increased IB and decreased MOE and MOR values. Overall, the results indicate that the various resin parameters discussed above had significant effects on the boards' strength properties. More detailed board making using various mat compaction speeds are needed to fully investigate the varying resin performances.

Two-hour Desiccator and Small-chamber Formaldehyde-emission Values of Boards

In the previous study,[17] the 2-h desiccator formaldehyde-emission levels for resins aged for 2 days were shown to be in the order of Resin 2.40 < Resin 2.10 < Resin 1.80, but the differences were relatively small. Formaldehyde-emission levels of PBs are dictated in large measure by the overall final F/U ratio used in the resin manufacturing.[10–13] With the F/U ratio being kept constant for all three resin types in this study, the formaldehyde-emission-level differences would reflect the different polymer structural compositions affected by the synthesis procedures and storage times. The 2-h desiccator test generally is viewed as reflecting the formaldehyde-emission levels of boards in the early life of boards after manufacturing due to a 2-day equilibration period in open air prescribed, before measuring. It is probable that free formaldehyde species trapped in the boards are the sources. In the 2-h desiccator emission data of the boards (Fig. 11), the emission level of Resin 2.40 was the lowest in the beginning, decreased a little at 15 days, but increased at 30 days and further increased at 45 and 50 days. Resins 2.10 showed the highest value in the beginning but decreased rapidly at 15 and 30 days and then increased to significantly higher values at 45 and 50 days, to the same level as those of Resin 2.40. Resin 1.80 showed intermediate emission values until 30 days but increased to a very high value at 50 days. Overall, the 2-h desiccator emission levels at the 15-day and 30-day storage times, which would correspond to the values of typical UF resins used in the industry, are in the order of Resin 2.40 ≥ Resin 1.80 ≫ Resin 2.10. The migration of hydroxymethyl groups seen predominantly until the
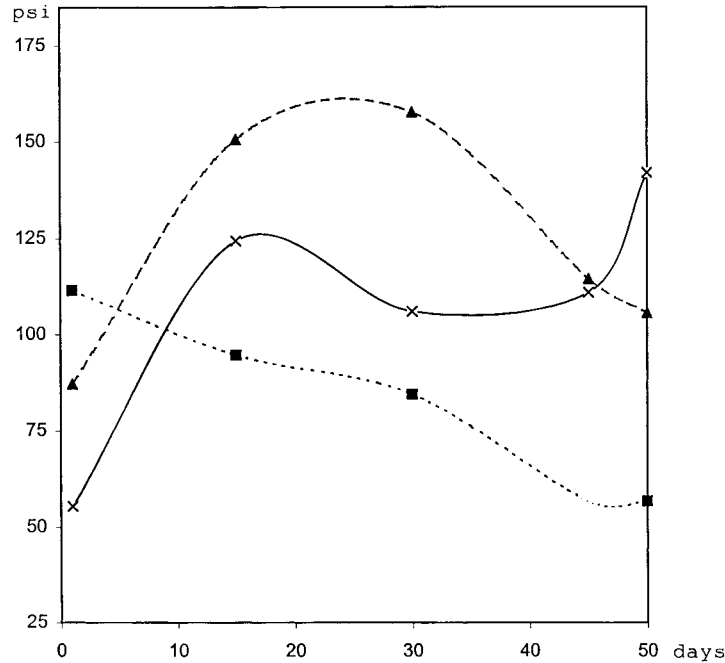
Figure 8 IB strength values of particleboards bonded with UF Resins (· · · ■ · · ·) 1.80, (–▲–) 2.10, and (—✕–) 2.40 stored at room temperature for 50 days.

15-day-storage samples lowered the formaldehyde-emission values for all three resins, while the increased degree of polymerization noted predominantly in the 30-day-storage samples lowered the formaldehyde-emission levels for Resins 2.10 and 1.80 but slightly increased them for Resin 2.40. Thus, the 2-h desiccator values reached minimum levels between 15 and 30 days of storage where mostly both the hydroxymethyl group migration and the degree of polymerization increased. In the 45-day-storage samples, where mostly the polymer agglomeration continuously increased, the 2-h desiccator values significantly increased for all three resins, and the emission levels remained the same at 50 days for Resins 2.40 and 2.10 while they further increased for Resin 1.80.

The small-chamber formaldehyde-emission tests were carried out after the prescribed 8 days of equilibration in open air, and, therefore, the more slowly defusing formaldehyde species or those in deeper layers were measured in comparison to the 2-h desiccator tests. In the small-chamber emission data (Fig. 11), the emission value of Resin 2.40 was higher than that of Resin 2.10 at 2-day storage and significantly increased at 15- and 30-day storage and then decreased to a very low level at 45- and 50-day storage. The emission value of Resin 2.10 was relatively low
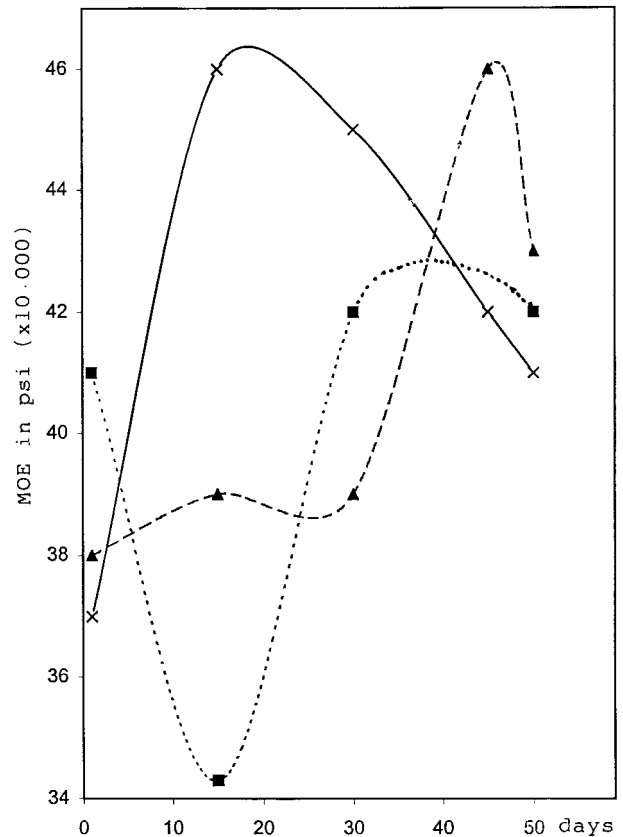

Figure 9 MOE values of PBs bonded with UF Resins (· · · ■ · · ·) 1.80, (–▲–) 2.10, and (—✕–) 2.40 stored at room temperature for 50 days.
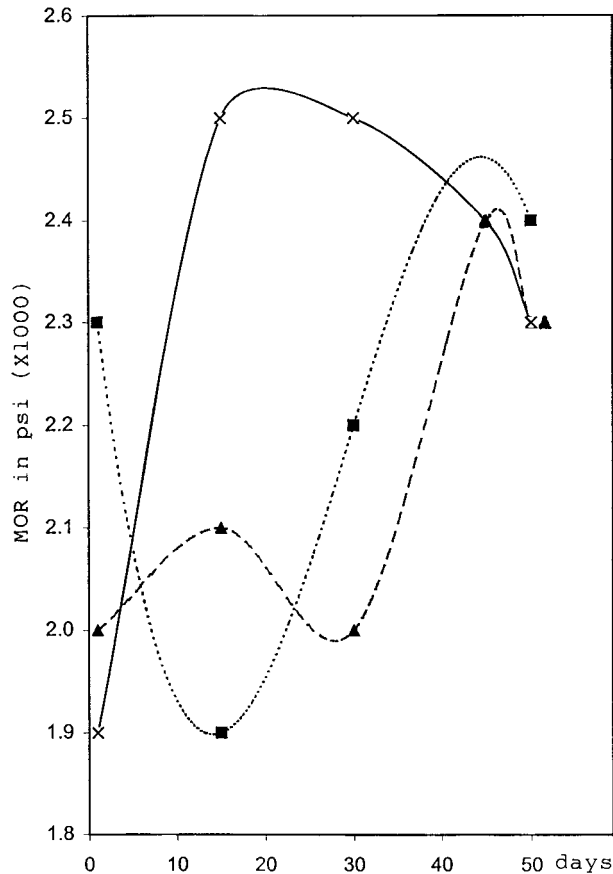
Figure 10   MOR values of PBs bonded with UF Resins ($\cdots\blacksquare\cdots$) 1.80, ($-\blacktriangle-$) 2.10, and ($-\times-$) 2.40 stored at room temperature for 50 days.

speculated that the limited mobility of the polymer resin molecules due to increased molecular agglomeration appeared to have decreased the formation of slow-diffusing formaldehyde species and increased the formation of fast-diffusing ones. Overall, the small-chamber emission levels at the 15-day and 30-day storage times, which would be comparable with typical resins used in the industry, are in the order of Resin 2.40 $\gg$ Resin 2.10 $\simeq$ Resin 1.80, while at longer storage times, the levels are in the order of Resin 1.80 $\gg$ Resin 2.0 $\sim$ Resin 2.40.

Applications to the UF Resin and PB Industry

In the UF resin manufacturing industry, the second urea addition step would start at about 70°C in the final cooling stage of resin manufacturing and take at least 2 h to reach room temperature. Depending on the efficiency of this mixing and cooling step and also on the following transportation and storage time until use, boards bonded with UF resins would show varying strength as well as formaldehyde-emission values. The F/U_1 mol ratio used in the first step of resin synthesis would also play an important role, although that parameter is usually not provided to resin users. The 2-day-storage resin samples are materials likely to be rarely encountered in industry because of the drastic batch cooling method used before the addition of the second urea in this work. The 15-day-storage resin samples would be more like freshly delivered industrial resins and, here, Resin 1.80 appears to be the least suitable because of the poor IB and MOE/MOR values of the boards, and Resin 2.40, similarly so due to the high formaldehyde-emission value in the small-chamber emission test in spite of good MOE/MOR values. Resin 2.10 would be the better resin type overall because of the good IB and decent MOE/MOR values as well as low 2-h desiccator and small-chamber formaldehyde-emission values. The 30-day-stored resin samples would be similar to about 2-week-aged industrial resins, which is commonly the maximum storage time recommended in the industry. Here, Resin 2.10 is again the better resin type overall due to the similar reasons as for the 15-day-storage resins.

It is interesting to note the Resin 2.40's high MOE/MOR values at intermediate storage times: It is possible that this resin cures adequately in the surface layers but does not attain the full cure in the core layer of boards to give the mediocre IB and high small-chamber formaldehyde-emission
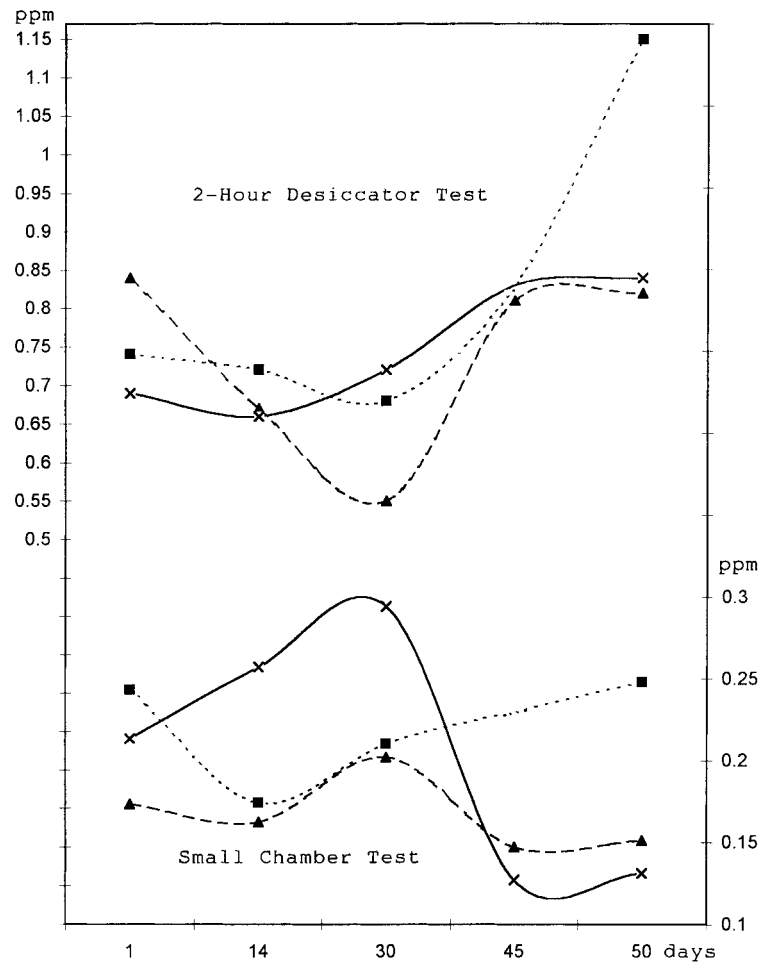
until 15 days and increased a little at 30 days and decreased to low values at 45 and 50 days. The emission value of Resin 1.80 was initially high but decreased at 15 days and then continuously increased thereafter, reaching the highest value among three resin types at 50 days. It is interesting to note that Resin 2.40 at 30 days reached the highest value among the three resins. The reason behind this phenomenon is unclear, but it appears that some slowly diffusing formaldehyde species such as residual hydroxymethyl groups are present in cured resins to slowly break down and diffuse out. An incomplete resin cure in the hot pressing of boards is suspected, especially in the core layer. A longer press time or higher press temperature might be needed to use with this resin. It is also interesting to note that Resins 2.40 and 2.10 at 45 or 50 days of storage times resulted in very low emission values, opposite to what was observed in the 2-h desiccator results. The underlying mechanism is unclear, but it is

Figure 11   Two-hour desiccator and small-chamber formaldehyde-emission values of particleboards bonded with UF Resins (· · · ■ · · ·) 1.80, (–▲–) 2.10, and (—✕–) 2.40 stored at room temperature for 50 days.

values due to residual hydroxymethyl groups in the cured resin layer. If it is used only in surface layers of boards with other resins such as Resin 2.10 used in the core layer, boards of good MOE/ MOR and lower formaldehyde-emission values may be obtained. Resin 1.80 is also interesting due to its relatively high IB value at 2-day storage and high MOE/MOR values at 30-day storage and might be useful as surface-layer resins.

For 45-day- and 50-day-storage resins, which would be less frequently encountered in the UF resins industry and quite inconvenient to produce intentionally, the results are interesting for Resins 2.10 and 2.40, which gave relatively good IB and MOE/MOR and very low small-chamber emission values, although their 2-h desiccator emission values were high. Since, in the UF resin and PB industry, the small-chamber formalde-hyde-emission levels of boards are viewed as a

better indicator in addressing the health concerns of the boards, these low small-chamber emission values effected by long storage times indicate a practical interest. The formaldehyde emitted from UF resin-bonded boards is thought to be mostly traced to the hydroxymethyl groups that break off during hot pressing and the residual hydroxymethyl groups present in cured resins.[10–12] In this formaldehyde-emission mechanism, the increased agglomeration of resin molecules due to long storage times appears to have effected certain molecular arrangements for polymers where more hydroxymethyl groups, possibly due to restricted access to urea amide groups, break off during hot pressing as formaldehyde and are trapped in boards to result in high 2-h desiccator values. One result of this increased breakage of hydroxymethyl groups would be a cured resin in boards that contain less residual

hydroxymethyl groups, to give lower small-chamber values. Therefore, for boards made with resins with 45- or 50-day storage times an airing would be a good method to obtain low formaldehyde-emission levels in both the 2-h desiccator and the small-chamber emission tests. An extended study is in progress.

CONCLUSIONS

When stored at room temperature over a period of 50 days, typical wood-adhesive UF resins in weak alkaline pH gradually undergo polymer structural changes that consist of migration of hydroxymethyl groups from the polymeric to the monomeric UF resin components and formation of mostly methylene and secondarily methylene–ether bonds involving the second urea.. The storage of resins also appears to be accompanied by associative interactions of polymer molecules, resulting in formation of bigger polymer clusters. In accord with these polymer structural changes, viscosity values of UF resins decrease initially and then begin to increase and reach very high values. These polymer structure variations and changes occurring due to different F/U_1 mol ratios, different cooling rates at the end of resin manufacture, and different storage times until use entail increases and decreases in UF resins' wood-bonding performances and formaldehyde-emission levels. The resin synthesis and room-temperature storage parameters defined in this work, in conjunction with the parameters obtained in the heating/stirring treatments of finished resins reported earlier, would be useful in optimizing UF resin manufacturing and PB manufacturing processes for improving board properties.

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