

# Effects of Urea and Curing Catalysts Added to the Strand Board Core-Layer Binder Phenol–Formaldehyde Resin

Sang M. Lee, Moon G. Kim

Department of Forest Products, College of Forest Resources, Forest and Wildlife Research Center, Mississippi State University, Mississippi State, Mississippi 39762-9820

Received 16 August 2006; accepted 20 December 2006

DOI 10.1002/app.26233

Published online 10 April 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Effects of adding urea to the strand board core-layer phenol–formaldehyde (PF) resin were investigated in conjunction with cure-accelerating catalysts. Ten percent urea based on the liquid resin weight was added at the beginning, at three different middle stages of polymerization, and at the end of PF resin synthesis. No significant cocondensation between the urea and PF resin components occurred as identified by  $^{13}\text{C}$  NMR analyses, which corroborated well with the curing and strand board bonding performance test results. The various urea addition methods resulted in resins that slightly differ in the various tests due to the urea's temporary holding capacity

of formaldehyde. The preferred method of urea addition was found to do it in the later part of PF resin synthesis for convenience, consistency, and slightly better overall performance. Some cure-accelerating catalysts were shown to reduce the thickness swelling of strand boards. This study showed the usefulness of adding some urea to strand board core-layer binder PF resins of replacing higher cost phenolic components with lower cost urea. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1144–1155, 2007

**Key words:** phenol–formaldehyde resins; urea; catalysts; strand board;  $^{13}\text{C}$  NMR; DMA analysis

## INTRODUCTION

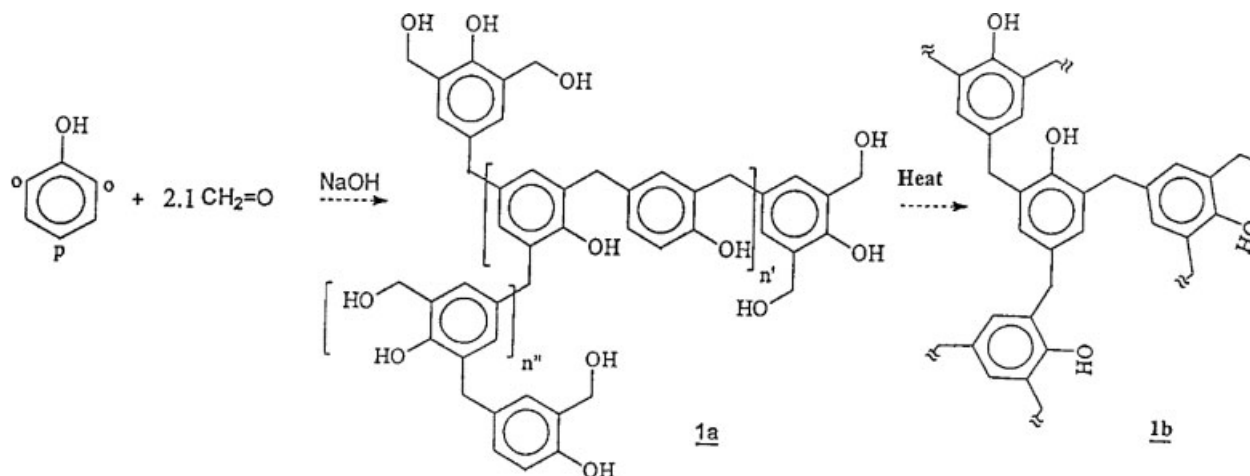
Phenol–formaldehyde (PF) resin resins are widely used as thermosetting binders for exterior-grade oriented strand board (OSB) and other wood composites and synthesized in the aqueous medium with sodium hydroxide as catalyst up to 0.6 mol sodium hydroxide per mol of phenol (Fig. 1).<sup>1–3</sup> In particular, OSB binder PF resins usually contain urea up to about 10% based on liquid resin solids weights,<sup>4</sup> where the lower cost urea reduces the overall binder cost as diluent. Liquid PF resin components are oligomeric poly(methylene-hydroxymethylphenol)<sup>3</sup> [Fig. 1(a)] where the phenolic hydroxyl groups present in the form of sodium phenolate anions are the basis of activation of the *o*- and *p*-hydroxymethyl groups in forming methylene groups in curing. The fully cured PF resin structure has been considered to be poly(methylene-phenol) with a 1.5 : 1.0 methylene : phenol ring ratio [Fig. 1(b)].<sup>5</sup> More recent solid-state  $^{13}\text{C}$  NMR studies of cured PF resins of F/P mol ratio of 2.1 indicated a more complex chemistry with less than 1.5 methylene groups incorporated per mole of phenol.<sup>6</sup>

OSB binder PF resins are available as core- and face-layer resins, the former being more advanced in

degree of condensation and having higher sodium hydroxide contents to effect a short hot-press time and minimal over-curing in the face layers. Since both core-layer and face-layer resins need to have viscosities at about 250 cP or less for atomizing operations, the core-layer resins have lower resin solids contents than the latter. Core-layer resins determine the hot-pressing time, often judged by the internal bond strength of boards, and therefore the effects of additives or catalysts are more clearly manifested in the core-layer resins. This study is mainly concerned with the core-layer resins.

OSB is commonly pressed at 200–240°C with PF resin binders at resin solids loading levels of 3–4% based on dry wood weight<sup>4,7</sup> and OSB manufacturing plants are bottlenecked at the hot press with the core-layer binder resin's curing speed determining the production rate. Therefore, the core-layer resin's formulation is often pushed to the limit for fast cure, mainly achieved by advancing the resin further in synthesis using higher sodium hydroxide and higher water contents. The advancement is limited by the active solids level required, resin's viscosity limit for spraying, and moisture level of wood mat to be achieved. Advancing of resin also increases the pre-curing tendency of resin characterized by a "lack of flow" of resin under the given hot-pressing temperature and time. A given core-layer PF resin can give poor bond strengths either by under-curing due to insufficient advancement or due to lack of flow from

Correspondence to: M. G. Kim (mkim@cfr.msstate.edu).



**Figure 1** Schematic representation of formation and curing reactions of phenol-formaldehyde resins.

an over-advancement. OSB core-layer binder PF resins are currently formulated in the 45–50% resin solids level including 4–6% sodium hydroxide catalyst and 5–10% levels of urea based on PF resin solids weight.<sup>4</sup> The cost-lowering urea addition to OSB binder PF resins has been practiced with minimal negative effects on the resin manufacturing procedure, hot-pressing time, and bond strength and thickness swell values of boards in water-soak tests. Adding urea to PF resins as inert diluent would slow down the resin curing speed, but this possible negative effect has been minimized by increasing the advancement of resin in resin manufacturing, made possible by the urea's viscosity-reducing effect.<sup>8</sup> Thus, Kim et al. reported that the effects of urea added to the thus-made PF core-layer resins up to 13% based on liquid resin weights decreased the curing speed to a minor extent and slightly lowered the OSB strengths,<sup>9</sup> confirming the role of urea as a diluent.

The cocondensation of urea and PF resin components has been investigated aiming at synthesizing useful phenol-urea-formaldehyde (PUF) resins. Tomita and Hse studied PUF resins made under the acidic condition,<sup>10,11</sup> identifying <sup>13</sup>C NMR chemical shift values of phenolic *o*-methylene group singly bonded to one urea nitrogen at ~ 40.6 ppm, phenolic *p*-methylene group singly bonded to one urea nitrogen at ~ 44.3, and two phenolic *p*-methylene groups bonded to one urea nitrogen at ~ 49.1 ppm. Further, Tomita et al. reacted phenol with a UF-concentrate (F/U = 2.5) under an acidic condition to obtain a PUF resin with a cocondensation extent of about 20%.<sup>12</sup> UF-concentrates are mixtures of various hydroxymethylureas and free formaldehyde, a good source of urea and free formaldehyde due to the reversibility of the hydroxymethyl groups.<sup>13</sup> In the acidic pH, however, PF resol resins or cocondensed PUF resins easily separate into the resin-rich and resin-poor phases making the resins unsuitable for

wood composite binder applications. Ohyama et al. studied this type PUF resins' curing behavior with acidic catalysts,<sup>13</sup> but the details are lacking. This type PUF resins would have varying proportions of two different hydroxymethyl groups, one bonded to phenolic rings and the other to urea amide groups. The former will behave as those of acid-curing PF resins and the latter as those of acid-curing UF resins, but the acidity level needed for the former is significantly greater than that for the latter.<sup>14</sup> Therefore, this type PUF resins will have a complicated curing chemistry, making it difficult to optimize the formulation/curing parameters in addition to the phase separation problem. Acid-curing PUF resins have not been used in the industry.

More recently, Zhao et al. claimed that urea additions made in the beginning of alkaline PF resin syntheses lead to cocondensation of urea and PF resin components to give single phase resins with urea levels up to 42 mol % of phenol,<sup>15</sup> with faster curing rates and better bond strengths of particleboard. However, the details on resin and board preparation parameters are lacking and the claims made for the wide ranges of resin viscosity (0.5–0.8 Pa/s), resin solids level, and F/P mol ratio were unusual. Also, nonquantitative interpretations of <sup>13</sup>C NMR spectra of resins were used with no peaks shown for the cocondensed phenolic methylene groups bonded to urea nitrogens in the range of 40.6–49.1 ppm.<sup>10,11</sup> Thus, a detailed investigation was made to probe the alkaline cocondensation approach by synthesizing PF resins with urea additions made at the beginning as well as at various middle and end stages of PF resin advancement. In addition, wood bonding performances of PF resins can be improved by an additional catalyst such as sodium carbonate, potassium carbonate, and triacetin, reported to accelerate the curing speed of resins or improve the bond strength for softwood plywood and laminated veneer lum-

ber<sup>15–21</sup> through a mechanism of an increased activation of *ortho*-hydroxymethyl groups of PF resins by a carbonate group.<sup>22,23</sup> Use of these potential catalysts in the current OSB core-layer PF resin binders has not been reported and, therefore, these catalysts were investigated in conjunction with the urea addition effects.

## EXPERIMENTAL METHODS

### Materials

Reagent-grade phenol, urea, and sodium hydroxide from Aldrich Chemical Company (Milwaukee, WI), and 50% formaldehyde aqueous solution and a commercial OSB core-layer PF resin donated by Georgia-Pacific Resins, Louisville, MS, were used.

### Resin preparation of core-layer resins

Core-layer resins were synthesized at a formaldehyde/phenol (F/P) mole ratio of 2.1 with 5.8% sodium hydroxide content and  $\sim (51.0 \pm 1.0)\%$  nonvolatile content. Urea was added at 10% level based on liquid resin weight at various points during the synthesis of resins. First, the synthesis of Resin PZ was carried out using the procedure of Zhao et al. with a slightly higher sodium hydroxide level than their NaOH/phenol ratio level of 0.35<sup>16</sup> and in a 2-L reactor equipped with a stirrer, thermometer, and condenser; 245.0 g of 90% phenol (2.35 mol), 100 g of 50% NaOH solution (1.25 mol; NaOH/P = 0.53), and 137.5 g of distilled water were charged in the given order with stirring. Then, 296.3 g of 50% formaldehyde solution (4.94 mol) was added in drops to the reaction mixture over 20 min (F/P = 2.1), followed by holding the temperature at  $\sim 45^\circ\text{C}$  for 10 min. Then, 88.9 g urea (1.48 mol; U/P = 0.63) was added and the temperature was raised stepwise to  $90^\circ\text{C}$  over 30 min and held at that temperature until the reaction mixture reached the viscosity "KL" by the Gardner–Holdt (GH) scale. The product resin was then cooled to room temperature to give a final viscosity of MN by GH scale. The same procedure and materials were used for other core-layer resins, except that the urea additions were carried out later after the reaction mixture of PF resin components has reached to the target GH viscosity: B for Resin PUB, E for Resin PUE, I for Resin PUI, and U for Resin PFU. Resin PFH was synthesized the same way but with an addition of 10% water as a control. A commercial OSB core-layer PF resin from Georgia-Pacific Resins, Resin COM, was also used as a control in board preparation. All resins were stored in a refrigerator until use.

### Face-layer resin

The face-layer resin was synthesized separately using the same procedure used above for core-layer resins at F/P mole ratio of 2.3, sodium hydroxide level of 4.26% based on the liquid resin weight, and the resin solids content of 62.0% including 3.2% urea, which was added after the PF resin was advanced to GH viscosity S. This face-layer resin was used in bonding all strand boards with no additional catalyst.

### Catalyst addition

The catalysts investigated were potassium carbonate, sodium carbonate, and triacetin with loading levels of 0, 2.5, 5.0, and 10.0% based on resin solids content of core-layer resins for preliminary curing speed test purposes and selected levels were used in board preparations.

### Measurements of physical properties of resins

As routine tests for confirming synthesis procedures and charged materials, all resins were characterized by measurements of viscosity, pH, specific gravity, gel times (at  $100^\circ\text{C}$ ), and hot-plate (at  $125^\circ\text{C}$ ) stroke cure times using the common laboratory methods. Nonvolatile solids of resins were measured with about 1.0 g of resin by heating in an oven at  $125^\circ\text{C}$  for 2 h.

### Dynamic mechanical analysis curing measurements of resins

DMA measurements of resins were carried out on TA Instruments DMA983 with a procedure designed mainly to compare different PF resins under a condition closely similar to the fast temperature increasing schedule used by OSB manufacturing plants.<sup>24</sup> The DMA data, therefore, may not be comparable with data obtained under the more gradual heating-up schedules commonly employed. Approximately 20 mg of resin sample was uniformly spread on a fiberglass braid ( $18.5 \times 11.2 \times 0.12\text{-mm}^3$  dimensions) and clamped horizontally between the two sample holding arms. Runs were carried out in the fixed displacement mode with 0.8 mm amplitude and 1.0 Hz oscillation frequency with the chamber temperature increasing from  $30^\circ\text{C}$  at a rate of  $25^\circ\text{C}/\text{min}$  to  $180^\circ\text{C}$  and then held isothermal for 20 min. The storage modulus ( $G'$ ), loss modulus ( $G''$ ), and  $\tan \delta$  ( $G''/G'$ ) curves were obtained. Although there are unsolved questions regarding curing interpretations of DMA results,<sup>25–27</sup> an earlier workers' comparative definitions were used to obtain the gel time as the time elapsed to the initial increasing point of storage modulus curve, the cure

TABLE I  
Properties of Various Core-Layer and Face-Layer Resins Used in OSB Manufacture

Resins <sup>a</sup>	PZ	PUB	PUE	PUI	PFH	PFU	COM	FACE
Urea content (%)	10	10	10	10	0	10	10 <sup>b</sup>	3.40
GH viscosity	MN	N	N	MN	I	MN	N	OP
Specific gravity	1.200	1.192	1.217	1.194	1.200	1.212	1.220	1.220
pH	11.65	11.62	11.58	11.61	10.70	11.68	11.51	10.38
Stroke cure (min)	2.50	2.50	2.45	2.25	2.35	2.40	3.15	3.15
Gel time (min)	19.20	19.90	19.90	21.65	33.40	26.45	19.20	20.60
Resin solids (%)	50.4	51.8	52.0	52.1	43.3	52.2	51.2	62.4

<sup>a</sup> Resin codes are described in the text.

<sup>b</sup> A value based on secondary information.

time as the elapsed time at the intersecting point of the maximum storage modulus rise and the final plateau line, and the cure rate as the maximum slope of the storage modulus curve,<sup>28</sup> as illustrated in Figure 1.

### <sup>13</sup>C NMR spectroscopic analyses of resins

<sup>13</sup>C NMR spectra of resins were obtained using a Bruker AMX-300 spectrometer at ambient temperature using a 12- $\mu$ s pulse width and 5-s delay time for maximum quantification results<sup>29</sup> with about 400 scans accumulated. Samples were prepared by mixing a liquid resin in deuterium oxide in 1 : 1 weight ratio. The spectral intensities were integrated and group concentration values were calculated.

### Wood strands

A batch of wood strands prepared for OSB manufacture was obtained from Norbord Corp., Guntown, MS, consisting of ~ 90% southern yellow pine and 10% mixed hardwoods.

### Strand board manufacturing procedure

The first set of boards were made for evaluating various synthesized core-layer resins against controls and the second set of board made for evaluating various catalysts added to core-layer resins. For all boards, the face-layer resin was the same with no catalyst added. Emulsion-type paraffin wax was sprayed at 1.0% level based on dry wood weights for all boards. The board manufacturing procedure was as follows: wood strands dried to a moisture content below 4% based on oven-dried wood weight were tumbled in a rotary blender and the emulsion-type wax, using a compressed-air sprayer, and the binder resin, using a spinning-disk type atomizer (Coil Model EL-2) at ~ 10,000 rpm, were blended. Core and surface layer strands were blended separately. Three-layer mats were then made without orientation of strands by felting the weighed amounts of wood strands as bottom, core, and top layers in a

30 : 40 : 30 weight ratio in a 76 cm  $\times$  76 cm forming box. The mat was then hot-pressed in a Dieffenbacher laboratory hot press using platen temperature of 204°C with press times of 3.5 and 4.0 min for the first set of boards. The second set of boards was pressed at 204°C for 3.5 min with the core-layer binder resins containing catalysts at indicated levels.

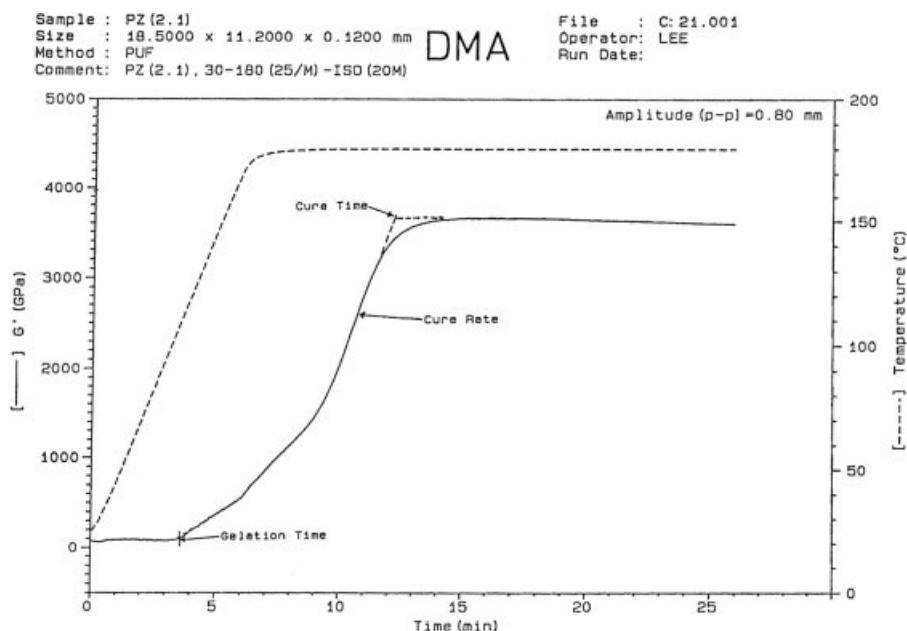
### Testing of strand boards

Pressed boards were tested according to ASTM D1037 (ASTM 2000) for internal bond (IB), modulus of elasticity (MOE), and modulus of rupture (MOR) values after cut specimens were equilibrated for 2 weeks in a conditioning room set at 7% EMC. The test results were also compared to CSA 0437-93 (CSA 1993) industrial standards. Board densities were measured with eight IB test specimens using the weights and volumes. IB strength was tested on an Instron testing machine and the average of eight sample values of a board was recorded. Wet IB values of samples were obtained after boiling eight IB specimens in water for 2 h and then drying in an oven at 103°C for 6 h to about 8% moisture content. Thickness swell (TS) and water absorption (WA) values were measured after soaking four specimens (15.2 cm  $\times$  15.2 cm) in water at room temperature for 2 and 24 h.

## RESULTS AND DISCUSSION

### Resin syntheses and resins' physical properties

The resin materials parameters and extent of polymerization (by resin viscosity) were kept relatively constant except Resin PFH, which differs due to the water added in place of urea and therefore a lower final viscosity. The various data obtained from synthesized core-layer PF resins, therefore, can be directly compared (Table I). The resin solids and final viscosity values of synthesized core-layer resins were close to the target value and to those of the commercial PF resin control. All synthesized resins' viscosity behaviors were normal and similar to those



**Figure 2** DMA curing diagrams of Resin PZ obtained with a heating schedule of 25°C/min increase to 180°C and then isothermal for 20 min.

of the commercial control, not showing any abnormal association tendency of resin molecules. Association tendency of PF resin molecules often becomes noticeable when PF resins were made with a low F/P ratio at low sodium hydroxide content or at a high extent of polymerization as well as when common PF resins were partially or fully acidified. These resins often show non-Newtonian viscosity behaviors, broad NMR peaks, and handling and performance inconsistencies. Thus, all synthesized core-layer resins were normal and expected to give reproducible analytical and bonding performance results as with the commercial control resin.

#### Effects of urea addition methods on stroke cure and gel times

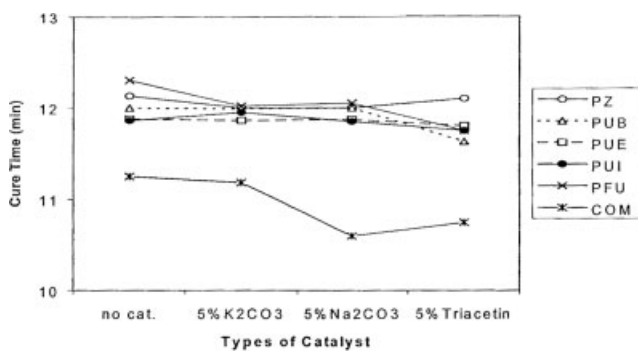
Stroke cure times of synthesized core-layer resins (Table I) varied little among the different urea addition methods and were in the same range with that of Resin PFH that contains no urea. This result indicates that in curing of resins at 125°C of stroke cure tests the curing speeds of all synthesized core-layer resins were about the same. The face-layer resin with lower sodium hydroxide content and lower extent of advancement showed a significantly longer stroke time.

Gel times of PF resins often do not reflect the average advancements of resins, since it is affected much by other factors such as resin solids levels due to the fact that the measurement is done at 100°C with little loss of content water. The gel times of Resins PZ, PUB, and PUE varied only a little, while Resin PFH

showed a significantly longer gel time due to its lower resin solids level. The face-layer resin, in spite of lower advancement and lower sodium hydroxide content, showed a similar gel time as the core layer resins due to the high resin solids content. Resins PUI and PFU showed slightly longer gel times than the other core layer resins to indicate that the method of adding urea in the later part of resin synthesis affects the molecular weight distribution of PF resin components. It is possible that the PF resin components made with early urea additions would make wider molecular weight distributions than those made with late additions to result in slightly shorter gel times. Overall, the various urea addition methods appear to make minimal differential effects on stroke cure and gel times of resultant resins.

#### Effects of urea addition methods on DMA curing of resins

The DMA storage modulus curve ( $G'$ ) of Resin PZ obtained by increasing the chamber temperature from 30 to 180°C at 25°C/min and then keeping isothermal for 20 min are shown in Figure 2. The storage modulus starts at near zero and begins to increase after about 3.5 min (gel time) at the chamber temperature of 117°C. It is likely that the sample at this point lost all water and the rigidity increase resulted from the formation of an infinite molecular network (gelation). The storage modulus then increases somewhat gradually and then very rapidly to reach the plateau value. The elapsed time to this plateau point is defined as the cure time and the



**Figure 3** DMA cure times of synthesized and commercial control core-layer PF resins with and without 5.0% catalysts with the same heating schedule of Figure 2.

slope of the fastest rising region as the cure rate of the resin. The storage modulus then changes little during the remainder of the run to indicate that the resin is completely cured at the cure time point and the cured resin is stable (not decomposing) at the temperature during the run time. The vitrification of the sample, i.e., the glass transition temperature of sample rising to above the DMA temperature due to the curing of resin, has occurred in the maximum rigidity rising region. The DMA cure times for synthesized core-layer and commercial control resins are shown in Figure 3. DMA gel times ranged from 2.75 to 3.25 min and the resins made with earlier urea additions showed slightly shorter gel times, but since their cure rates were smaller, the cure times differed little among all synthesized core-layer resins. All synthesized resins showed longer cure times than the commercial control, which might contain an unpublicized catalyst. Overall, DMA results indicate that although the different urea addition methods resulted in resins with subtle differences, no significant curing speed increases can be discerned such as that claimed by Zhao et al.,<sup>15</sup> although their resins were made at somewhat lower sodium hydroxide content.

#### Effects of catalysts on DMA curing of synthesized core-layer resins

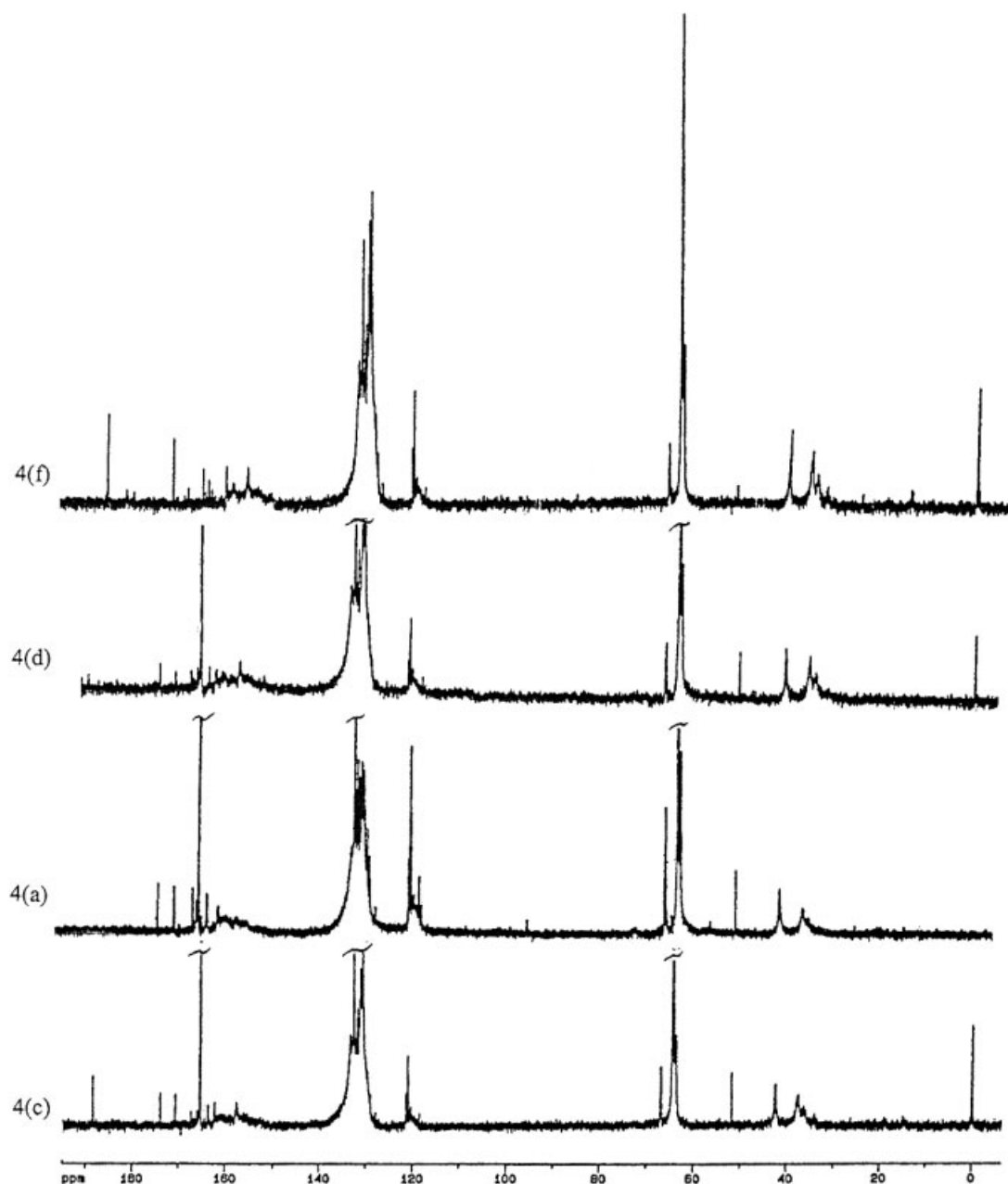
The DMA results indicate that potassium carbonate, sodium carbonate, and triacetin at 5.0% addition levels have some minor effects on DMA cure times for synthesized core-layer resins in Figure 3. The commercial control resin showed somewhat greater cure time decreases with sodium carbonate and triacetin.

#### <sup>13</sup>C-NMR spectra of various resins

Several urea-added PF resins in Zhao et al.'s report showed <sup>13</sup>C NMR spectra with some broadening of peaks,<sup>15</sup> indicating that molecular association

phenomenon is occurring.<sup>29</sup> Quantitative data derived from the spectra by integration would involve inaccuracies. On the other hand, all synthesized resins in this study showed no broadening and gave normal, relatively sharp <sup>13</sup>C NMR peaks and reasonable integration values [Fig. 4(a–e)]. Chemical shift values of PF resin components have been studied and they often change in small but significant measures with NMR solvents, sodium hydroxide contents, and internal standards used as spectral reference.<sup>30</sup> Trying to rigorously match chemical shift values with literature values for peak identification is often meaningless for PF or UF resins; rather, the overall matching of spectra by peak shapes and approximate chemical shift values is more useful. Thus, for synthesized core-layer resins, assuming formaldehyde losses during resin syntheses to be negligible, the NMR spectral integration results showed that *o*-hydroxymethyl groups (60.0–61.7 ppm), *p*-hydroxymethyl groups (64.2–64.8 ppm), and small amounts of urea-hydroxymethyl groups (65.2 ppm) amounted to 57.8–70.2% of charged formaldehyde. Methylene-ether group, free formaldehyde, and formaldehyde oligomers in the 68.0–95.0 ppm region were negligible. *op*-Methylene group (34.8–37.6 ppm), *pp*-methylene group (39.6–40.3 ppm), and *oo*-methylene group (30.0–30.5 ppm)<sup>30</sup> amounted to 29.3–42.2% of charged formaldehyde. No methylene groups were found between urea and phenolic ring (40.6–49.1 ppm),<sup>10</sup> i.e., no cocondensation has occurred. Also, little methylene bonds between two urea molecules (47–60.2 ppm)<sup>31</sup> were observed, i.e., no urea–formaldehyde type polymers were formed. Only a sharp small peak of methanol was present near at 50 ppm for all resins, including Resin PFH made with no urea addition, in amounts of 1.0–2.0% of charged formaldehyde. Industrial formaldehyde usually contain a small amount of methanol and it can also be formed during resin synthesis from the Cannizzaro reaction of formaldehyde.<sup>32</sup> The spectral features of PF resin components of all synthesized core-layer resins are very similar to each other and to the reported spectra for alkaline PF resins.<sup>30,33</sup> Overall, the various urea addition methods appear to have made no significant differences in the polymer structure of PF resins with no significant cocondensation occurring between urea and phenolic rings, opposite to the claims of Zhao et al.<sup>15</sup>

A quantitative chemical structure description of synthesized core-layer resins is needed to discuss the small differences of urea addition methods observed. Data obtainable from <sup>13</sup>C NMR spectra often digress slightly from the charged materials ratios of PF resins used in the absence of any material removal during synthesis. Some formaldehyde is destroyed by the Cannizzaro reaction but the loss from



**Figure 4**  $^{13}\text{C}$  NMR spectra of Resins PZ (a), PUE (c), PUI (d), and PUH (f).  $^{13}\text{C}$  NMR spectrum of Resin PUB (b) and PFU (e).

this route is commonly minimal. More often, the digression of NMR data arises from the slower relaxation of the nonhydrogen-bearing carbon nuclear spins in the pulse sequence in comparison to those of the hydrogen-bearing carbons. As mentioned above, also broadening of peaks due to restricted molecular motions can change integration values significantly often occurring in resins having a high viscosity or phase-separation. The pulse-delay time used in acquiring NMR spectra in this study was made relatively long to allow the nonhydrogen-bearing carbons fully recover to the equilibrium value before the subsequent pulse. Also, all spectra of PF

resins in this study were obtained after diluting the resin with water to further lower the viscosity. Further, the F/P mole ratio and sodium hydroxide content of all synthesized core resins were relatively high, so the resins and their NMR solutions were all clear and the resultant NMR spectral peaks are relatively sharp. The small broadening of methylene carbon peaks is apparent, ascribed to chemical shift value dispersions; similarly phenolic  $\text{C}_1$  carbon peaks dispersed more widely due to partial ionization and different substitution patterns on the *o/p*-carbons.<sup>30</sup> This type chemical shift dispersion effects would not affect integration results.

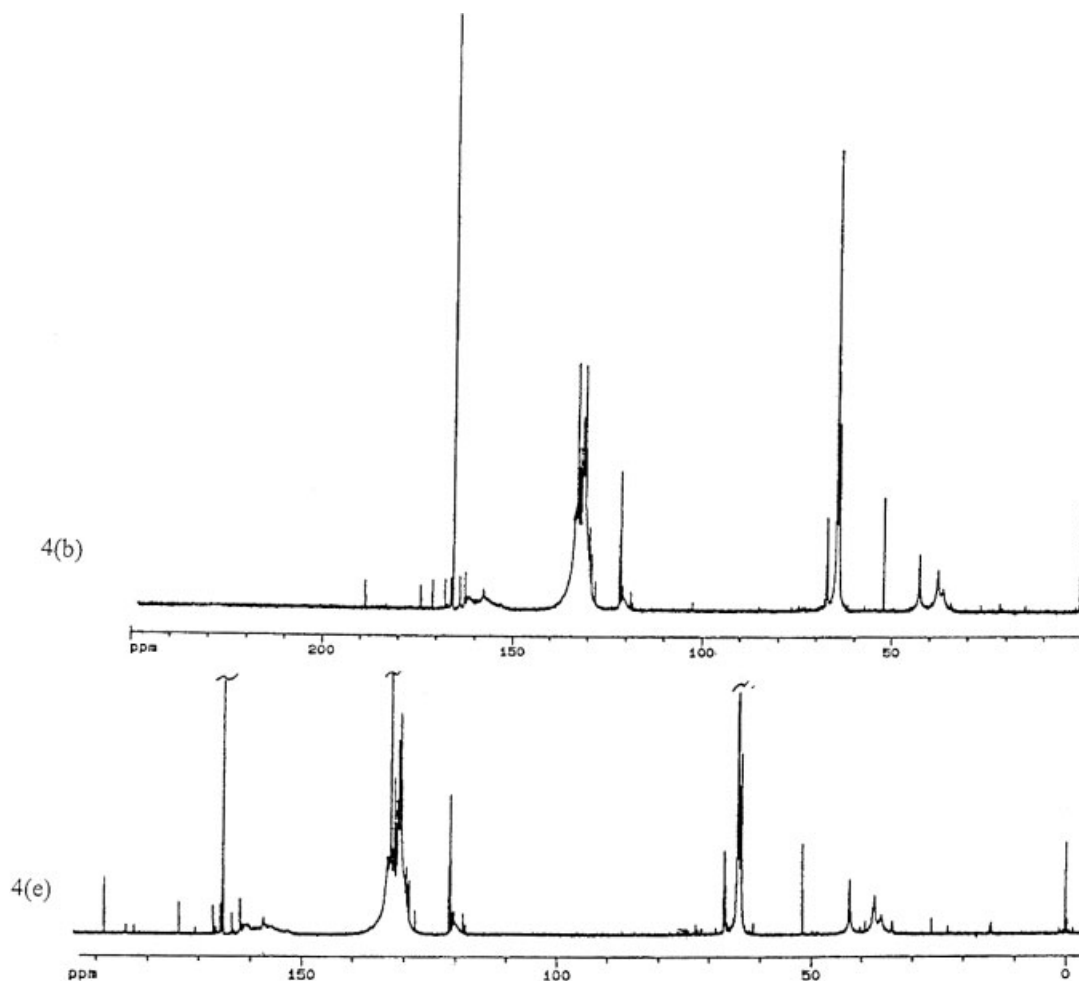


Figure 4 (Continued)

Firstly, the combined integrals of hydroxymethyl and methylene groups are compared to those of combined phenolic C<sub>2-6</sub> carbons to obtain the F/P ratio values (Table II). The NMR results are only slightly higher than the materials charge F/P ratio to indicate a satisfactory spectral integration data obtained. Approximately 30–40% of charged formaldehyde was transformed to *op*- and *pp*-methylene

groups and the rest to *o*- and *p*-hydroxymethyl groups. These values translate into a number-average 5–6-mer of poly(methylene)hydroxymethylphenols for the synthesized core-layer resins.<sup>33,34</sup> On the other hand, minor differences are apparent in NMR for Resins PZ and PUB in comparison to other resins made with later urea addition, although no cocondensation between urea and phenolic components

TABLE II  
Carbon Group Contents of Synthesized Core-Layer Resins from <sup>13</sup>C NMR Spectra

Resins	% Methylene (–CH <sub>2</sub> –)	% Methanol (CH <sub>3</sub> OH) <sup>a</sup>	% Hydroxymethyl (–CH <sub>2</sub> OH)	F/P molar ratio <sup>b</sup>	% Unreacted C <sub>2,4,6</sub> <sup>c</sup>
PZ	29.8	D	70.2	2.32	26.0
PUB	42.2	D	57.8	2.31	15.0
PUE	34.6	D	65.4	2.36	13.0
PUI	36.1	D	63.9	2.38	14.0
PFU	35.3	D	64.7	2.30	19.0
PFH	36.5	D	63.5	2.32	17.0

<sup>a</sup> Resins showed a small peak at ~ 50 ppm assigned to methanol.

<sup>b</sup> (Methylene + hydroxymethyl)/phenolic carbons.

<sup>c</sup> Phenolic unsubstituted C<sub>2,4,6</sub>/phenolic carbons.



was observed. These small NMR differences indicate that the urea added in the early part of synthesis appears to have affected the reaction path and rate of resin-forming processes. These small differences would make the small differences in gel time, curing speed, and wood bonding performance as observed.

For discussion of one of these small differential effects of resins made with early urea additions, firstly referencing the chemical shifts of phenolic ring carbons is in order. Phenolic *o*- and *p*-carbons' chemical shifts vary by sodium hydroxide contents of resin due to ionization of phenoxy group as well as by the kind of substituent groups over narrow ranges, while *m*-carbons are little affected.<sup>30</sup> In the synthesized core-layer resins, *meta*-phenolic carbons and substituted *o/p*-phenolic ring carbons are all bunched up in 126–134 ppm range, from which little detailed information can be extracted. Phenoxy carbon ( $C_1$ ) is spread in 150–163 ppm range and detailed interpretation is similarly difficult. On the other hand, unsubstituted *o/p*-phenolic carbons are bunched up in 116.2–119.2 ppm range, standing out from the rest of phenolic carbons, and give measures on the extent of substitution on *o/p*-phenolic carbons. The integral values of unsubstituted *o/p*-phenolic carbons varied depending on the urea addition methods with the highest value observed for Resins PZ (Table II). This result is interesting.

An idealized PF resol resin structure would be one in which all phenolic *o/p*-carbons are bonded either to a hydroxymethyl or a methylene group, the structure of which can be represented by the following equation with respect to the degree of polymerization ( $n$ ):<sup>33</sup>

$$F/P = 2.0 + 1.0/n$$

(F = methylene + hydroxymethyl groups). (1)

for  $n = 1$ ,  $F/P = 3$  and for  $n = 4$ ,  $F/P = 2.25$ , etc. In sodium hydroxide-catalyzed PF resins, *p,p*-methylene bonds (39.3–41.2 ppm) and *o,p*-methylene bonds (34.8–35.4 ppm) are more and *o,o*-methylene bonds (29.6–34.0 ppm) are small. Wood adhesive PF resins are commonly synthesized to have the maximum hydroxymethyl group content at the target degree of condensation and at the given sodium hydroxide content, i.e., a minimal content of unreacted phenolic *o/p*-carbons and minimal amount of free formaldehyde remaining, for the best curing speed and odor control. Alkaline PF resol resins have been assumed to cure through the formation of the quinonoid structure that is equivalent to the benzylic cationic species.<sup>35</sup> Therefore, if the extent of condensation and the sodium hydroxide content are kept constant among the resins, those resins with lower unsubstituted phenolic *o/p*-carbon contents, i.e., higher hydroxymethyl group content, would have a higher

reactivity than resins with higher unsubstituted phenolic *o/p*-carbons. One important criterion of resin selection in OSB industry is the curing speed attainable in the hot press, bottle neck of the plant.

In alkaline PF resin synthesis, formaldehyde reacts with phenol to form hydroxymethyl phenols, which then react with each other to form methylene bonds. The hydroxymethylation reaction proceeds preferentially at 60–70°C commonly in the beginning of synthesis, but if the temperature is kept higher in this stage, the methylene bond-forming condensation reaction also proceeds. Therefore, depending on the temperature and also on the base catalyst level and other factors, unreacted *o/p*-carbons and free formaldehyde can remain in the resin when the condensation reaction has progressed to give the target viscosity value. Although the F/P mole ratio value (2.1) and average degree of polymerization values (5–6) of the synthesized core-layer resins predict the presence of some unreacted *o/p*-carbons by eq. (1), resin PZ showed the highest unreacted *o/p*-carbon value. This result can be explained that the urea added in the beginning of resin synthesis inhibits the hydroxymethylation reaction, probably by limiting the availability of formaldehyde. Part of formaldehyde in this stage would be tied up in the form of various hydroxymethylureas, from which free formaldehyde is released to determine the rate of the reaction. The small but significantly different amounts of unreacted phenolic *o/p*-carbon contents for synthesized core-layer resins would have made the differences in curing characteristics and strand board bonding performances.

The urea and urea derivatives of synthesized core-layer PF resins can be estimated by the urea carbonyl peaks. In common urea–formaldehyde (UF) resins, the unreacted urea occurs at ~ 164.0 ppm, monosubstituted ureas at ~ 162.2 ppm, and di- and trisubstituted ureas at ~ 160.7 ppm in nearly neutral water medium.<sup>31,36</sup> For all synthesized core-layer resins in alkaline water medium, the major peak at 163.5 ppm, accounting for about 90% of total urea added, is sharp and has no reason to be assigned for other than free urea. This result indicates that most urea remained as free urea in the end (no reaction). The small amounts of monosubstituted ureas, accounting for the rest of urea, occur at 162.5 ppm, most likely of monohydroxymethylurea with the hydroxymethyl groups occurring close to the right hand side of the phenolic *p*-hydroxymethyl groups at about 65.0 ppm. No (urea-)methylene-phenol peaks were observed in the aliphatic region as discussed above. Di- and trisubstituted urea carbonyl groups are almost none, again indicating that no urea molecules would be present as structural units of the supposed urea–phenol–formaldehyde condensation polymers. The small carbonyl peaks observed

**TABLE III**  
**Dry and 2-h Boil Internal Bond Strengths of Strand Boards Pressed at 204°C with Indicated Press Times<sup>a</sup>**

Press time (min)	IB tests	Core-layer resins (MPa)							
		PZ	PUB	PUE	PUI	PFU	AVE	PFH	COM
3.5	Dry	0.59	0.63	0.60	0.53	0.63	0.60	0.69	0.55
	2-h boil	0.12	0.13	0.16	0.18	0.15	0.15	0.14	0.16
4.0	Dry	0.65	0.69	0.68	0.60	0.71	0.67	0.65	0.64
	2-h boil	0.12	0.19	0.22	0.18	0.19	0.18	0.21	0.17

AVE: average values of five urea-containing resins.

<sup>a</sup> Dry board densities ranged from 0.73 to 0.77 g/cm<sup>3</sup>.

in 165–189 ppm range of all synthesized core-layer resins appear to indicate that some urea is broken by the sodium hydroxide catalyst during resin synthesis as well as of forming of formate and keto-group-containing species from PF resin components.<sup>6</sup>

#### Board performance and different urea addition methods

All boards showed density values in the narrow range of 0.73–0.77 g/cm<sup>3</sup> (Table III), indicating that the strength values of boards measured could be compared with respect to different urea addition methods. Dry internal bond (IB) strength values of boards ranged from 0.53 to 0.72 MPa and were generally higher for 4.0 min press times than 3.5 min press times as expected and they compared well with the IB values of commercial control resin. The dry IB values were not much affected by the different urea addition methods for both press times. All IB values exceeded the minimum industrial standard values of 0.345 MPa (50 psi). Two-hour boil IB values of boards were also higher for 4.0 min press time than for 3.5 min press times reaching to 20–30% of dry IB values and they were slightly higher for the resins made with late urea additions than resins made early urea additions. The faster curing resin characteristics

claimed by Zhao et al.<sup>15</sup> were not apparent especially at 3.5 min press times. A faster curing resin would have manifested itself to give higher dry or higher wet IB strength values. Water absorption (WA) and thickness swell (TS) values of boards in 2 and 24 h water soak tests (Table IV) showed only minor differences for the different urea addition methods. On the other hand, Resin PFH showed slightly lower WA and TS values than synthesized urea-added resins and also commercial control resin, probably a result of resin PFH not having the hygroscopic urea. This observation agrees with the conclusion of an earlier report.<sup>9</sup> MOR strength values of boards ranged 28.1–38.0 MPa and the variations due to resin kind and press times were minor and the values were above the minimum industrial MOR standard values of 17.2 MPa (data not reported). MOE strength values of boards ranged 3710–4430 MPa with no significant differences from the different urea addition methods or different press times and values are above the minimum industrial MOE standard of 3100 MPa (data not reported). MOR and MOE values of boards depend much on the quality of the face-layer binder resins and the relatively good MOR/MOE values indicate that the face-layer resin used in this study was adequate for the press temperature and times used, allowing an adequate evaluation of the core-layer res-

**TABLE IV**  
**Water-Soak (2 h/24 h) Water Absorption (WA) and Thickness Swell (TS) Values (%) of Strand Boards for Which Internal Bond Strengths Were Tested in Table III**

Press time (min)	WA tests	Core-layer resins								
		PZ	PUB	PUE	PUI	PFU	AVE	PFH	COM	
3.5	2 h	WA	15.8	14.0	12.5	14.3	14.3	14.2	14.3	18.0
		TS	17.0	15.5	16.8	16.1	16.4	16.4	14.6	18.6
	24 h	WA	60.0	55.5	52.3	52.0	53.2	54.6	45.3	61.2
		TS	36.6	35.3	37.8	43.9	33.7	37.5	32.1	37.7
4.0	2 h	WA	17.5	15.1	16.3	16.3	17.5	16.6	13.5	16.9
		TS	17.1	15.7	17.4	21.5	16.2	17.6	14.8	18.5
	24 h	WA	59.5	56.7	61.3	63.3	52.9	58.7	52.6	55.3
		TS	35.7	34.3	34.9	40.1	33.9	35.8	33.6	35.9

AVE: average values of five urea-containing resins.

**TABLE V**  
**Dry and 2 h Boil Internal Bond Strengths of Strand Boards Pressed at 204°C for 3.5 min with Core-Layer Resins Having 2.5% Catalysts Based on Resin Solids Weight<sup>a</sup>**

Catalysts	IB tests	Binder resins							
		PZ	PUB	PUE	PUI	PFU	AVE	PFH	COM
None	Dry	0.59	0.63	0.60	0.53	0.63	0.60	0.69	0.55
	2 h boil	0.12	0.13	0.16	0.18	0.15	0.15	0.14	0.16
K <sub>2</sub> CO <sub>3</sub>	Dry	0.62	0.72	0.64	0.66	0.61	0.65	0.67	0.69
	2 h boil	0.12	0.14	0.13	0.16	0.15	0.14	0.13	0.18
Na <sub>2</sub> CO <sub>3</sub>	Dry	0.61	0.60	0.57	0.65	0.57	0.60	0.60	0.58
	2 h boil	0.12	0.13	0.12	0.12	0.14	0.13	0.11	0.11
Triacetin	Dry	0.66	0.70	0.67	0.53	0.58	0.63	0.52	0.59
	2 h boil	0.14	0.15	0.13	0.12	0.09	0.13	0.12	0.12

<sup>a</sup> Dry board densities ranged 0.68 to 0.76 g/cm<sup>3</sup>.  
 AVE: average values of five urea-containing resins.

ins. Overall, the different urea addition methods used for resin synthesis resulted in only minor differences in board performance values, indicating that urea added either early or late in resin synthesis does not lead to resins having accelerated curing speed nor bring any significant performance improvement/deteriorations. The board test results indicate that little chemical interactions have occurred between urea and phenolic components, i.e., urea acted as a diluent.

#### Effects of catalysts added to synthesized core-layer resins on board performance

Boards bonded with synthesized core-layer resins having 2.5% potassium carbonate, sodium carbonate, or triacetin based on the resin solids content showed density values ranging from 0.68 to 0.76 g/cm<sup>3</sup> (Table V). The board density values were slightly lower for boards made with catalysts (0.71 g/cm<sup>3</sup>)

than for boards made without catalyst (0.75 g/cm<sup>3</sup>), indicating that the core-layers of all boards made with catalysts may have been less well consolidated. Dry IB strength values of boards made with potassium carbonate and triacetin catalysts were only slightly better for core layer resins made with early urea additions. Sodium carbonate did not show any significant effect on dry IB strength values. Two-hour-boil IB strength values of boards bonded with and without catalyst additions were similar and also no significant differences were observed from the different urea addition methods of resin synthesis. On the other hand, 2- and 24-h water absorption (WA) and thickness swell (TS) values were lower for boards bonded with catalyst additions than without catalysts (Table VI) regardless of the different urea addition methods. The reasons for this improved performance are obscure at this time, but the result appears useful for OSB industry, deserving a re-

**TABLE VI**  
**Water-Soak (2 h/24 h) Water Absorption (WA) and Thickness Swell (TS) Values (%) of Strand Boards for Which Internal Bond Strengths Were Tested in Table IV**

Catalysts	WA test	Core-layer resins								
		PZ	PUB	PUE	PUI	PFU	AVE	PFH	COM	
None	2 h	WA	16.0	14.0	13.0	14.0	14.0	14.2	12.0	14.0
		TS	17.0	16.0	17.0	17.0	17.0	16.8	14.0	18.0
	24 h	WA	60.0	55.0	52.0	52.0	63.0	56.4	45.0	60.0
		TS	37.0	37.0	42.0	42.0	36.0	38.8	36.0	41.0
K <sub>2</sub> CO <sub>3</sub>	2 h	WA	6.1	6.2	7.5	7.2	7.0	6.8	6.7	6.9
		TS	8.0	9.0	8.5	11.0	9.5	9.2	11.5	9.5
	24 h	WA	35.0	36.0	43.0	46.0	37.0	39.4	39.0	41.0
		TS	28.0	32.0	33.0	35.0	32.0	32.0	33.0	32.0
Na <sub>2</sub> CO <sub>3</sub>	2 h	WA	7.2	7.4	8.3	8.2	8.0	7.8	7.5	8.0
		TS	9.5	9.0	11.0	10.0	10.0	9.9	11.0	10.0
	24 h	WA	39.0	39.0	40.0	40.0	39.0	39.4	39.0	40.0
		TS	35.0	34.0	36.0	34.0	36.0	35.0	38.0	36.0
Triacetin	2 h	WA	5.8	5.8	6.3	6.0	6.1	6.0	6.0	5.8
		TS	8.0	8.5	9.0	9.5	8.5	8.7	9.0	8.0
	24 h	WA	37.0	39.0	40.0	40.0	40.0	39.2	41.0	38.0
		TS	29.0	32.0	31.0	35.0	32.0	31.8	36.0	33.0

AVE: average values of five urea-containing resins.

examination. MOR values of boards bonded with catalysts, ranging from 23.50 to 36.24 MPa, were higher than the minimum industrial MOR standard of 17.2 MPa and no significant differences were observed from different urea addition methods (data not reported). MOE values of boards bonded with catalysts were similarly higher than the industry standard values and no significant differences were observed from different urea addition methods.

### CONCLUSIONS

Effects of adding 10% urea based on liquid resin weight to strand board core-layer PF resins in the early, middle, and later part of a typical resin synthesis procedure were investigated to see if any cocondensation occurs between the urea and phenolic components with improved bonding performances. The different urea addition methods did not show any cocondensation products by  $^{13}\text{C}$  NMR spectra, corroborating well with DMA curing and strand board bonding results in contrast to the literature claims of cocondensation. However, the various urea addition methods did result in slightly "different" resins in each case showing slightly different test results, which was explainable as arising from the urea acting as a temporary holding reservoir of formaldehyde during resin synthesis. Overall, this research showed that the optimum method of adding urea to strand board binder PF resins is to add it in the later part of resin synthesis for consistency and convenience of resin manufacture. Use of auxiliary catalysts improves the 2-h TS value considerably and 24-h TS value to a small but useful extent for OSB industry. Overall, this study shows the usefulness of adding some urea to PF resins in strand board binder applications with little negative effects on bond strength performance, while the lower cost urea ( $\sim$  \$0.15/lb) replaces the phenolic resin solids ( $\sim$  \$0.45/lb) up to about 10% by liquid resin weight.

### References

1. Van Epps, C. F. U.S. Pat. 2,360,376 (1944).
2. Knop, A.; Plato, L. A. *Phenolic Resins*; Springer Verlag: Berlin, 1985.
3. Megson, N. J. L. *Phenolic Resin Chemistry*; Academic press: New York, 1958.
4. Sellers, T.; Kim, M. G.; Miller, G. D.; Haupt, R. A.; Strickland, R. C. *Forest Prod J* 1994, 44, 63.
5. Hultzsich, K. *Chemie, der Phenolharze*; Springer Verlag: Berlin, 1950; p 7.
6. Kim, M. G.; Wu, Y.; Amos, L. W. *J Polym Sci Part A: Polym Chem* 1997, 35, 3275.
7. Davis, C. R. *Personnel Communication* 2000.
8. Buschfeld, A.; Lattekamp, M.; Ripkens, G.; Schitteck, H. U.S. Pat. 5,011,186 (1991).
9. Kim, M. G.; Watt, C.; Davis, C. R. *J Wood Chem Technol* 1996, 16, 21.
10. Tomita, B.; Hse, C. Y. *J Polym Sci Part A: Polym Chem* 1992, 30, 1615.
11. Tomita, B.; Hse, C. Y. *Mokuzai Gakkaishi* 1993, 39, 1276.
12. Tomita, B.; Ohyama, M.; Hse, C. Y. *Holzforchung* 1994, 48, 522.
13. Ohyama, M.; Tomita, B.; Hse, C. Y. *Holzforchung* 1995, 49, 87.
14. Robitschek, P.; Lewin, A. *Phenolic Resins*; Iliffe and Sons: London, 1950; p 160.
15. Zhao, C.; Pizzi, A.; Garnier, S. *J Appl Polym Sci* 1999, 74, 359.
16. Daisy, N. K.; Leeper, D. L. U.S. Pat. 4,758,478 (1988).
17. Clarke, M. R.; Steiner, P. R.; Anderson, A. W. U.S. Pat. 4,824,896 (1988).
18. Reuther, et al. Ger. Pat. 2,110,264 (1972).
19. Baxter, G. F. U.S. Pat. 4,915,766 (1990).
20. Creamer, A. W. U.S. Pat. 4,909,516 (1990).
21. Black, E. P. U.S. Pat. 5,763,559 (1998).
22. Higuch, M.; Tohmura, S.; Sakata, I. *Mokuzai Gakkaishi* 1994, 40, 604.
23. Tohmura, S.; Higuchi, M.; Hattoru, Y.; Sakata, I. *Mokuzai Gakkaishi* 1994, 40, 390.
24. Lofthouse, M. G.; Burroughs, P. *J Therm Anal* 1978, 13, 19.
25. Winter, H. H. *Polym Eng Sci* 1987, 27, 1698.
26. Harran, D.; Laudouard, A. *Rheol Acta* 1985, 24, 597.
27. Núñez, L.; Gómez-Barreiro, S.; Garcia-Fernández, C. A. *Rheol Acta* 2005, 45, 184.
28. Kim, M. G.; Nieh, W. L.-S.; Meacham, R. M. *Ind Eng Chem Res* 1991, 30, 798.
29. Levy, G. C.; Nelson, G. L. *C-13 NMR for Organic Chemists*; Wiley-Interscience: New York, 1972.
30. Kim, M. G.; Tiedeman, G. T.; Amos, L. W. *Weyerhaeuser Science Symp* 1981, 2, 263.
31. Kim, M. G.; Amos, L. W. *Ind Eng Chem Res* 1990, 29, 203.
32. Walker, J. F. *Formaldehyde*. Reinhold: New York; 1964. p 493.
33. Kim, M. G.; Amos, L. W.; Barnes, E. E. *Ind Eng Chem Res* 1990, 29, 2032.
34. Kim, M. G.; Amos, L. W. *Ind Eng Chem Res* 1991, 30, 1151.
35. Lenghaus, K.; Qiao, G.; Solomon, D. H. *Polym Preprints* 1999, 40, 242.
36. Kim, M. G. *J Polym Sci Part A: Polym Chem* 1999, 37, 995.