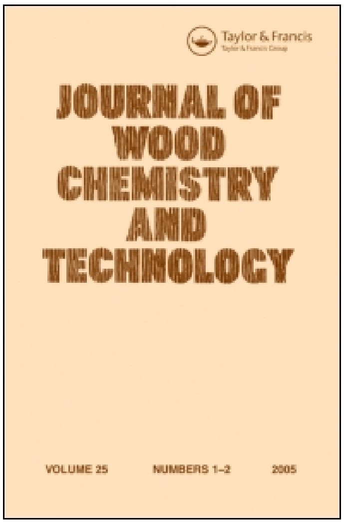

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Effects of Urea Addition to Phenol-Formaldehyde Resin Binders for Oriented Strandboard

Moon G. Kim; Christopher Watt; Charles R. Davis

To cite this Article Kim, Moon G. , Watt, Christopher and Davis, Charles R.(1996) 'Effects of Urea Addition to Phenol-Formaldehyde Resin Binders for Oriented Strandboard', Journal of Wood Chemistry and Technology, 16: 1, 21 — 34
To link to this Article: DOI: 10.1080/02773819608545780
URL: http://dx.doi.org/10.1080/02773819608545780

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(1), 21-34 (1996)

EFFECTS OF UREA ADDITION TO PHENOL-FORMALDEHYDE RESIN BINDERS FOR ORIENTED STRANDBOARD

Moon G. Kim and Christopher Watt
Mississippi Forest Products Laboratory, Mississippi State, MS 39762,
and
Charles R. Davis
Georgia-Pacific Corporation, Crossett, AR 71635

ABSTRACT

Effects of urea addition to oriented strandboard (OSB) binder phenol-formaldehyde (PF) resol resins were investigated at 0, 10, 18, and 26% urea addition levels. PF resins were synthesized at these urea levels with the resin solids levels and viscosities being kept approximately constant at 50% and 150 - 250 cP, respectively. Analysis results of synthesized resins indicated that the urea additions lowered the free formaldehyde content and increased the degree of polymerization but decreased the curing rates. Evaluation of the laboratory OSBs manufactured using the synthesized resins as binders showed that the internal bond (IB) strength and the water soak properties were decreased gradually as the urea addition level was increased.

INTRODUCTION

In North America, PF resol resins used as binders for OSB manufacture contain urea currently at about 10 - 20% levels based on the resin solids weight.[1] This practice of urea addition has been generally known to have effected a substantial decrease of formaldehyde odor in the resin blending and matting areas of OSB manufacturing plants and a significant reduction of the resin unit cost because the lower cost urea solids are undistinguished from the PF resin solids. The urea addition is carried out at the end of the polymerization step and known to reduce the viscosity of resin apparently due to the hydrogen bond-breaking effect of urea.[2] Furthermore, it necessitates an additional amount of water to be added during resin synthesis becuase of the adjustment of urea solids level to the targeted resin solids level, currently being in the range of about 45 - 55%. Because of these reasons, it was claimed that the phenolic resin components can be advanced to higher molecular weights than where no urea is added.[3]

The reaction of urea with formaldehyde to form various hydroxymethylureas in aqueous alkaline solution is well known as the first phase reaction in the manufacture of urea-formaldehyde resins.[4] OSB binder-type PF resol resins are manufactured in alkaline pH and a small amount of formaldehyde is usually remained after the polymerization is completed. This formaldehyde similarly reacts with the added urea to form hydroxymethylureas,[5] which do not polymerize among themselves in the alkaline pH[4] but may react at elevated temperatures with PF resol resin components to form PF resol - urea copolymer products[6] similarly to the copolymer products obtainable in the acidic pH.[7,8] In the current resin manufacturing practice, the post-addition of urea carried out at low temperatures (about 60°C and below) does not favor any significant copolymerization reaction in the uncured resin stage,[5] but the reaction is likely to proceed in the curing stage to positively affect adhesive performances in comparison to the addition of non-reacting diluent additives. A preliminary study indicated that the post-added urea modifies the resins' curing characteristics[9], but its effects on adhesive performance or other resin curing properties have not yet been reported. In order to investigate these effects OSB binder-type PF resins were synthesized at four urea addition levels and two formaldehyde/phenol (F/P) ratios at constant resin solids and viscosity levels. Synthesized resins were analyzed and curing rates were determined and OSBs bonded with these resins were evaluated.

EXPERIMENTAL SECTION

Resin Syntheses

Eight PF resins were formulated with target resin solids levels of 50%, sodium hydroxide contents of 4.6%, and formaldehyde/phenol (F/P) mole ratios of 2.16 and 2.47. The urea addition levels were 0, 10, 18, and 26% based on the resin solids weight, where the phenolic resin solids levels were reduced accordingly to maintain the resin solids levels at 50%. Duplicate resins were made for each resin formula, resulting in sixteen resins in total. In calculating the targeted resin solids levels, charged phenol, sodium hydroxide, and urea solids values were taken as such and formaldehyde-derived solids were taken as the methylene group (CH_2) values, obtained by multiplying the charge weights with a factor of 14/30. The order of resin synthesis was randomized.

A typical resin synthesis procedure for a 2.0 kg-batch was as follows: phenol, water, and one-half of the sodium hydroxide (50% solution) were charged into a stirred reactor and the reaction mixture was heated to 65 - 70°C. Formaldehyde solution (50% conc., Georgia-Pacific Corp. Louisville, MS) was then added drop-wise to the reaction mixture over a period of 30 minutes while keeping the reaction temperature remain in the same range by intermittent cooling using an ice bath. After the formaldehyde addition is completed, the reaction temperature was maintained at the same range for about 10 minutes and then was gradually increased to 90°C over a period of 30 minutes. This reaction temperature was maintained until the resin reached a "D" viscosity by the Gardener-Holdt (G-H) viscosity scale. The reaction temperature was then lowered to 80°C and the remaining sodium hydroxide and the water needed to attain the targeted resin solids level were added. The reaction was continued at 80°C until the resin reached an "H" viscosity by the G-H scale (approximately 200 cP). Resins made with no urea additions were cooled directly to room temperature at this viscosity point. For resins to be synthesized with urea additions, the reaction time at 80°C was extended until higher viscosities were reached: approximately 380 cP, 550 cP, and 850 cP, respectively, for 10%, 18% and 26% urea addition levels. The resin was then cooled to about 60°C, urea (Aldrich Chem.) stirred in, cooled further to room temperature, and stored frozen until analysis or use.

Resin Analyses

Viscosity, pH, and specific gravity of synthesized resins were measured using the standard equipment at 25°C. Gel time was measured using a Sunshine gel timer at 100°C. Resin solids level was determined by heating one gram of resin on an aluminum pan at 125°C for 2 hours. Free formaldehyde content was measured by the hydroxylamine hydrochloride method.[10] Molecular weight was determined by a gel filtration chromatographic method using 0.10N sodium hydroxide solution as eluant, Sephacryl 400 gel, and a UV detector set at 280nm.[9] Since the molecular weight calibration of this analysis was made by using available linear polystyrene sulfonate molecular weight standards (Polymer Laboratory), the obtained molecular weights are only relative measures because of the branched polymer chains.[11,12] Furthermore, the UV detector used is effective only on phenolic resin components leaving the urea and urea-formaldehyde condensates undetected. Therefore, urea-weighted molecular weight values were calculated by weighting the obtained molecular weight values with urea addition levels. Resin analyses results reported are averages of duplicate resins (TABLE 2).

Resin Curing Rate Determination

A Du Pont DMA 982 dynamic mechanical analyzer (DMA) was used[9,13] in the fixed displacement mode. A glass cloth having measuring dimensions of 15(l) x 12.5(w) x 0.3(t) mm was impregnated with approximately 16 - 20 mg of liquid resin and clamped horizontally between the two arms. The oscillation of test sample, set to run at its natural frequency, increased from about 2 Hz to 25 Hz as the resin cured during the run. The sample chamber temperature was initially jumped from room temperature to 75°C and then increased at a rate of 25°C per minute to predetermined isothermal run temperatures of 110, 125, and 150°C. The

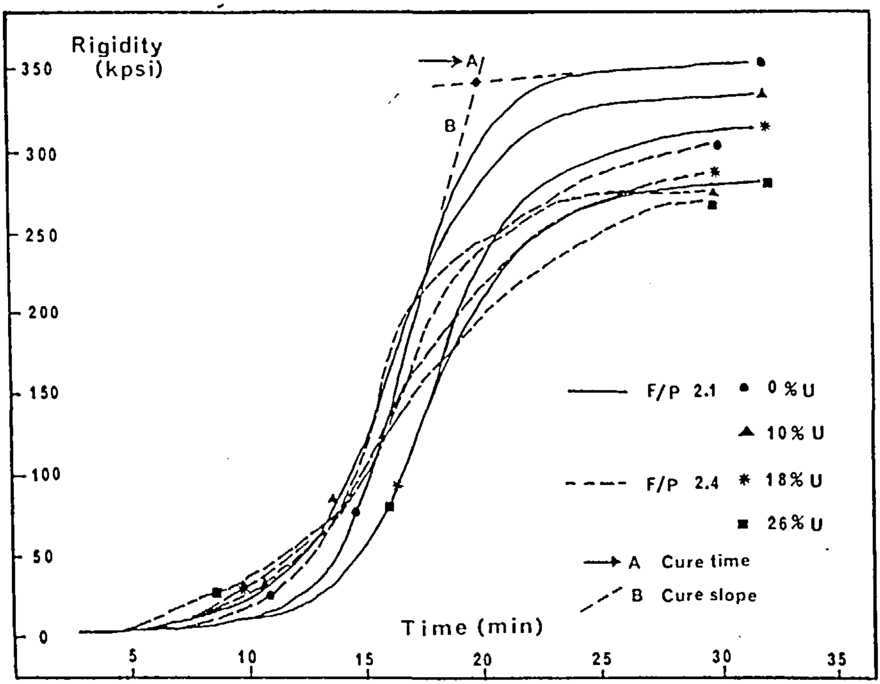

FIGURE 1. DMA Rigidity Developments vs. Urea Addition Levels at 125°C for OSB-type PF Resins Synthesized with F/P Ratios of 2.16 and 2.47.

increasing oscillation frequency and changing damping values were monitored for 30-50 minutes, from which the sample's rigidity modulus was derived as a function of time. The rigidity modulus reflects the density of the crosslinked polymer network formed in the oscillating sample. On this rigidity versus time curve, *cure time* was defined as the time at which the rigidity curve peaked out and *cure slope* as the maximum slope of the rigidity curve,[9] as shown in Figure 1.

OSB Manufacture and Performance Testing

Southern pine boles (Pinus sp., 35 - 40 years old) obtained in the southern Arkansas region were flaked with a CAE disc flaker into 0.025"-thick, 1"-wide,

TABLE 1. Laboratory OSB Manufacturing Parameters.

Mat formation: 55.9 cm x 61.0 cm, one-layer, no flake orientation.
Mat moisture content: 6.0 - 9.0%. Target density: 672.8 kg/m^3.
Press temperature: 177°C. Press pressure schedule: 5.5 - 2.75 - 0 MPa.
Press times: 4.0 and 4.5 minutes. Post-cure: 2 hours at 90°C.
Replication: 2 boards, from one blending (total: 128 boards)
Resin loading: 3.2% and 4.2%. Wax loading: 1.0% slack (Indrawax 210).
Board conditioning: 14 days at 21°C in a 56% RH room (Equil. MC = 10%).

and 3"-long wood strands, screened to eliminate fines smaller than 0.25"-square in size, and dried to a moisture content of 2 - 5% based on the oven dry wood weight. Laboratory OSBs were then manufactured using the processing parameters reported in TABLE 1. In board manufacturing, the resin order, resin loading level, and hot-pressing time were randomized, but replicate boards were made from one resin blending. A factorial design with sub-sampling was used to analyze the resulting data. Using the test specimens cut from boards (Figure 2), internal bond (IB), boil IB, modulus of elasticity (MOE), modulus of rupture (MOR), and 2-hour and 24-hour water-soak water absorption (WA) and thickness swell (TS) values were determined in accordance with the American Society for Testing and Materials (ASTM) procedure D 1037. Small sample edge-bending tests were also conducted in accordance with the American Plywood Association (APA) procedure S-6 using the APA accelerated-aging procedure D-4. Aged MOR tests were performed after aging the specimens according to the APA procedure D-4. Loads were measured using a Tinius-Olsen Universal Property Testing Machine (Model 92797) and an Instron Universal Property Testing Machine (Model TTCML).

Six IB specimens derived from one board sometimes showed varying densities and, therefore, averaging of the IB strength values was done by linear regression of the strength and density values and then selecting the IB value at the target density of 672.8 kg/m^3, which is the typical value for commercial southern

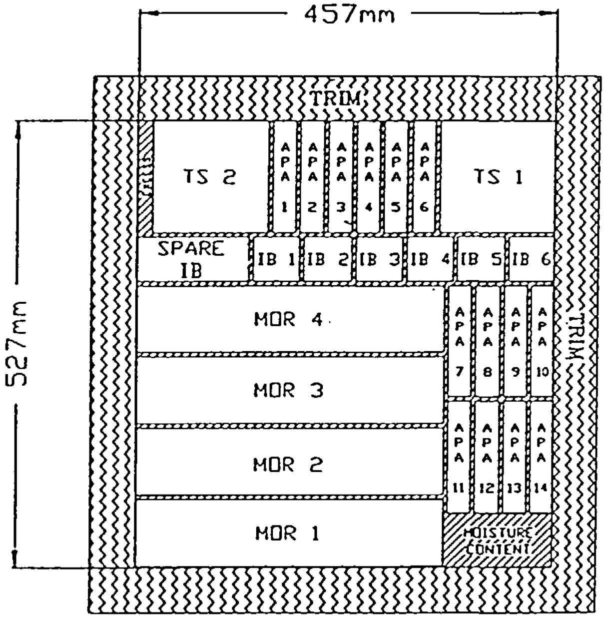

FIGURE 2. Cutting Diagram of Laboratory OSBs for Property Test Samples.

pine OSBs manufactured in North America.[14] Board property test results were statistically analyzed using the Statistical Analysis System program.[15] It was assumed that all panel properties adhered to the central limit theorem, the experimental units were homogeneous, and the between-treatments variance had to be greater than the total variance to be considered significant. Analysis of variance was used to generate within treatment, between treatment, and total variances. F-test was used to determine the significance of variances at less than 0.05 probability. Ficher's Protected t-Test {least significant difference (LSD)} was used to generate comparisons for physical properties at the 95% confidence (0.05) level.[16]

TABLE 2: Resin Properties of Eight Synthesized PF Resins.*

Resin #	1	2	3	4	5	6	7	8
Urea level	0%	0%	10%	10%	18%	18%	26%	26%
F/P Ratio	2.16	2.47	2.16	2.47	2.16	2.47	2.16	2.47
pH	10.5	10.4	10.7	10.6	10.8	10.8	10.9	11.1
Viscosity (cP)	172	160	162	244	186	265	123	230
Solids level (%)	53.7	51.4	49.7	50.5	51.2	50.1	49.7	49.3
Gel Time (min)	29.8	22.7	25.7	21.6	25.5	19.9	23.9	18.3
Free Form.(%)	0.31	1.95	0.0	0.0	0.0	0.0	0.0	0.0
Specific Grav.	1.23	1.22	1.21	1.22	1.23	1.22	1.23	1.22
Mol. Weight	530	670	1230	1250	1740	2290	2910	8430
Mol. Weight-U	530	670	1110	1130	1440	1890	2170	6250

* All values are averages of duplicate resins. Mol. Weight-U: molecular weight values calculated by weighting the urea levels used in resin syntheses.

RESULTS AND DISCUSSION

Resin Analyses Results

The resin solids levels ranged from 49.3% to 53.7% and the resin viscosities ranged from 123 cP to 265 cP (TABLE 2). These spreads of properties should have caused some molecular weight variations unrelated to the urea addition levels, but they were deemed to be acceptable in this work. All resins made with urea additions showed very low free formaldehyde contents as expected. An estimation for the amount of urea necessary to obtain a low formaldehyde odor level in use would be useful at this point. Assuming that the free formaldehyde content of the resin synthesized at an F/P ratio of 2.46 without urea addition, 1.95%, is applicable to other PF resins made at the same F/P ratios, the resin with a 10% urea addition will have a formaldehyde/urea (F/U) mole ratio of about 0.80. This mole ratio appears to be low enough for odor controls desired in OSB manufacturing plants considering the fact that the F/U ratios of urea-formaldehyde resins used as particleboard binders currently run at about 1.00 - 1.15.[17]

Thus, urea levels used at about 10% appear to be more than necessary for odor control purposes. Also, as the urea addition level increased, the average molecular weight increased as expected from the synthesis schemes used. Furthermore, shorter gelation times were observed for resins made with urea additions, which appears to be due to the increased resin reactivity becuase of the reaction between the PF resol components and urea.[6] PF resins made with the higher F/P ratio showed higher molecular weights and shorter gel times in comparison to the PF resins made with the lower F/P ratio, reflecting the higher functional group contents. Possible benefits such as a shorter board pressing time are indicated, but the higher amounts of hydroxymethylureas may result in emitting increased amounts of formaldehyde into the environment during board pressing.

Resin Curing Rates Determined by DMA

The rigidity modulus curves obtained from DMA experiments carried out at 125°C are presented as typical examples (Figure 1). Graphic averaging was done for duplicate runs and duplicate resins for these modulus curves. The rigidity moduli began to rise at about 5 minutes of heating and increased thereafter slowly until about 13 minutes. During this early period of heating the resins appear to have lost most of water and passed the gelation points. The rigidity curves then rapidly increased in a short time to reach about 80% or more of the ultimate rigidity values. The time to reach this major curing point and the slope of the curve at this curing phase have been shown to be the characteristics of the resin synthesis parameters used.[9] The cure time and cure slope values obtained this way are reported in TABLE 3. As observed for alkaline PF resol resins,[9] the DMA cure times were shortened and the cure slopes increased as the curing temperature increased. Most of all, it should be noted that PF resins made with higher urea addition levels showed longer cure times and smaller cure slopes in spite of the increased molecular weights and shorter gel times observed above and also the anticipated urea copolymerization effects. Thus, some deterioration of bond strength is implicated for these resins if boards are compared at the same press

TABLE 3. DMA Cure Time and Cure Slope Values of Synthesized PF Resins

		Cure Time (min.)			Cure Slope*		
F/P	Urea	90°C	125°C	150°C	90°C	125°C	150°C
2.16	0%	33.0	20.0	12.9	21.6	29.7	55.2
	10%	32.5	20.5	12.8	16.8	25.9	46.6
	18%	34.3	21.4	13.4	17.3	23.6	54.0
	26%	35.0	21.9	14.4	14.2	24.3	50.2
2.47	0%	30.8	19.7	14.4	15.9	24.9	41.4
	10%	31.1	20.0	12.7	15.7	23.8	41.8
	18%	32.6	21.0	13.9	13.8	22.5	37.0
	26%	34.8	22.2	14.1	11.1	16.0	26.2

* In 10^8 dynes/cm^2/minute.

times. Another interesting result is that the PF resins made at the higher F/P ratio showed, in general, a faster incipient rigidity rise in comparison to the resins made at the lower F/P ratio (Figure 1). This tendency appears to have a commonality with the shorter gel times observed for these resins.

OSB Performance Results

Results of board performance tests and statistical analyses are reported in TABLE 4. Ficher's grouping comparison analyses were made at the 95% confidence level for urea addition levels and other variables effects. Most of all, dry and boil IB strengths and 24-hour water soak properties showed significant decreases as the urea addition level increased. On average, one percentage increase in the urea addition level effected decreases of dry and boil IB strength values by 6.21 MPa and 4.83 MPa, respectively, and the water soak TS and WA values by 0.20% and 0.35%, respectively. Dry and aged MOR, MOE, and APA edge-bending values decreased in smaller extents. These decreasing board performances appeared like a dilution effect by urea on the PF resin polymer and

TABLE 4. OSB Physical Property Means and L S D Letter Groupings.*

		IB (MPa)		MOR (MPa)			APA S-6			Water Soak (%)			
	Density (kg/m^3)	Dry	Boil	Dry	Agd (/dry)	MOE (GPa)	Dry (MPa)	1-cyc. /dry	6-cyc. /dry	2-hour TS	2-hour WA	24-hour TS	24-hour WA
Urea													
0%	740.1a	1.055a	0.627a	46.26a	0.91ab	3.30a	3.18a	0.76a	0.76a	2.7a	5.8a	12.0a	23.1a
10%	741.7a	0.986ab	0.586ab	41.02ab	0.94a	2.50a	3.12a	0.79ab	0.76a	3.0a	7.9a	13.8b	26.1b
18%	736.9a	0.958ab	0.510bc	42.95a	0.87bc	2.39a	2.79b	0.85bc	0.74a	2.7a	5.8a	14.2b	27.0b
26%	724.1b	0.986b	0.489c	39.02b	0.84c	1.68a	2.81b	0.88c	0.72a	3.7ab	8.3b	17.4c	32.0c
F/P ratio													
2.16	738.5a	1.034a	0.572a	42.06a	0.86b	2.87a	3.01a	0.83a	0.75a	2.8a	6.5a	13.7a	26.2a
2.47	735.3a	0.917b	0.537a	40.33a	0.92a	2.41a	2.94a	0.82a	0.74a	3.3b	6.9a	15.0b	27.9b
Resin load													
3.2%	735.3a	0.958a	0.482a	40.40a	0.89a	2.79a	2.90a	0.81a	0.75a	3.2a	6.7a	15.6a	28.7b
4.2%	738.5a	1.055b	0.627b	42.00a	0.89a	2.48a	3.04a	0.84a	0.75a	2.9a	6.8a	13.1b	25.4b
Press time													
4.0 min	738.5a	0.992a	0.544a	41.09a	0.89a	2.41a	2.95a	0.83a	0.75a	3.2a	7.1a	14.9a	27.7a
4.5 min	735.2a	0.958a	0.565a	41.30a	0.89a	2.87a	3.00a	0.81a	0.75a	2.9b	6.4a	13.8b	26.5b

*L S D Letter groupings and means with same letter are not significantly different. Strength values of aged samples presented as fractions of the dry strength values. Agd: Aged. Cyc.: Cycle. TS: Thickness swell. WA: Water absorp.

agree with the decreasing resin cure rates observed by DMA. The fundamental chemistry must be studied and optimized in the future especially with respect to the copolymerization reactions between urea and PF resin components[6] in order to utilize the low cost urea more effectively.

Other resin synthesis variables also affected board performance properties. The higher F/P mole ratios used in resin synthesis resulted in poorer IB strength values and poorer water soak properties, indicating that certain limitations may exist in obtaining increased non-phenolic resin solids or faster gelation times by using this approach. Also, the lower resin loading level used in boards resulted in lower board performances in comparison to the higher resin loading level, an expected result but with an implication that high urea addition levels would be of limited applicability if low resin solids loadings are to be employed. Thus, urea addition level, F/P ratio, and resin solids loading level together showed accumulative degradation effects on board performance properties. The most apparent is the dry IB values, where a strength decrease from 1.055 MPa to 0.758 MPa was observed when boards made at the 26% urea addition level, 2.47 F/P ratio, and 3.2% resin loading level were compared with boards made at the 0% urea addition level, 2.16 F/P ratio, and 4.2% resin loading level. Therefore, all relevant parameters must be considered together against the reduced resin unit cost attained by urea addition.

In closing, it should be noted that within the urea addition levels studied in this work, the board performance properties decreased only gradually without any drastic reductions. This would indicate that an unacceptably high urea addition level was not reached by the highest level studied. Since sodium hydroxide content is relatively high, urea at high addition levels would undergo hydrolysis reaction during board pressing to produce gaseous ammonia and disrupt board consolidation. In this limited sense, the results of this study indicate that urea addition levels up to about 26% would be acceptable for OSB-type PF resins. It should also be mentioned that the IB strength values obtained in this study were relatively very high in comparison to the industry norms of 50-70 psi.[14] It was probably due to the high quality of wood strands used, which was necessary to have the effects of urea addition levels more clearly be differentiated. However, the high IB strength values did not allow the results of this study be directly useful in predicting the optimum urea addition levels for OSB industry. The question for OSB manufacturers is whether the board property reductions due to a urea addition level can be compensated by changing other process variables at a cost less than the savings derived from the reduced unit resin cost. Furnish moisture content and quality, hot-pressing time and temperature, resin loading level, and other processing variables can be utilized for this purpose. Therefore, the results of this study would provide a useful guide in achieving the optimum urea addition levels.

CONCLUSION

OSB binder PF resins synthesized with urea addition levels up to 26% based on the resin solids weight showed increased molecular weights and drastically reduced formaldehyde contents. But DMA experiments and evaluation of laboratory OSBs bonded with these resins showed reduced curing rates and also gradually decreasing board performance properties as the urea addition level increased. Most IB strength and water absorption property decreases were statistically significant at the 95% confidence level. However, no abrupt board performance decreases were observed within the urea addition levels studied. Results of this study would be useful for OSB manufacturers in making decisions on the urea addition level to be used in their PF resin binders with respect to the resin loading level, hot-pressing time and temperature, and the resulting IB strength and water absorption properties. At the lowest urea addition level studied (10%), the board performance property deteriorations were minimal and the free formaldehyde contents in the resins were very low.

ACKNOWLEDGEMENT

The work was supported by a USDA Wood Utilization Grant (90-34158-5034) and was carried out as a partial requirement for the M. S. Degree of Christopher Watt. The authors appreciate the technical help of Messrs. Louis Wasson and George Miller of MFPL and Doug Meacham of Georgia-Pacific Corp.

REFERENCES

1. T. Sellers, M. G. Kim, G . D. Miller, R. A. Haupt, and R. C. Strickland, Forest Products. J., *44*, 63 (1994).

2. T. Gramstad and J. Sandstroem, Spectrochim. Acta, *25A*, 31 (1969).

3. A. Buschfeld, M. Lattckamp, G. Ripkens, and H. Schittek, United States Patent 5,011,886 (1991).

4. J. De Jong and J. De Jonge, Recl. Trav. Chim. Pays-Bas, *71*, 3731 (1952).

5. M. G. Kim, L. W. Amos and E. E. Barnes, Ind. and Eng. Chem. Resch., *29*, 2033 (1990).

6. D. Scopelitis and A. Pizzi, J. Appl. Polymer Sci., *47*, 351 (1993). A. Pizzi, Advanced Wood Adhesives Technology, p 126 and 192, Dekker, New York (1994).

7. B. Tomita, Polymer Preprints, Volume 24, p. 165, Am. Chem. Soc., Washington, D. C. (1983).

8. B. Tomita and C.-Y. Hse, J. Polymer Sci.: Part A: Polymer Chem., *30*, 1615 (1992).

9. M. G. Kim, W. L. -S. Nieh and R. M. Meacham, Ind. and Eng. Chem. Research, *29*, 798 (1991).

10. J. F. Walker, Formaldehyde, p. 493, Reinhold, New York (1964).

11. A. L. Wooten, M. L. Prewitt, T. Sellers, Jr., and D. C. Teller, J. Chrom., *445*, 371 (1988).

12. M. G. Kim, W. L. S. Nieh, T. Sellers, Jr., W. W. Wilson and J. Mays, Ind. and Eng. Chem. Resch., *31*, 973 (1992).

13. M. G. Lofthouse and P. Burroughs, J. of Therm. Anal., *13*, 439 (1978).

14. E. Biblis, Forest Products J., *39*, 55 (1989).

15. Statistical Analysis User's Guide, p. 1028, Statistical Analysis Software Institute, Cary, NC (1982).

16. R. G. D. Steel and J. H. Torrie, Principles and Procedures of Statistics, 2nd Ed., p. 631, McGraw-Hill, New York (1980).

17. G. Graves, G., Proc. of 27th Intern. Particleboard and Composite Materials Symp., 221, Washington State University, Pullman, WA (1993).