

FURFURYL ALCOHOL EMULSION RESINS AS CO-BINDERS FOR UREA-FORMALDEHYDE RESIN-BONDED PARTICLEBOARDS

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ABSTRACT

An approach to using water-insoluble furfuryl alcohol (FA) resins as a co-binder for particleboard (PB) urea-formaldehyde (UF) resins was evaluated. Sprayable FA/UF mixed resins were made by emulsifying FA resins of varying advancements and mixing with various formaldehyde to urea (F/U) ratio UF resins in various proportions. The binder performance of the mixed FA/UF resins was then evaluated by bonding laboratory PBs using a weakly acidic ordinary UF resin curing catalyst at various hot pressing temperatures. The PBs were also heat-treated and were aged for two years at room temperature. The test results of bond strengths and formaldehyde emission levels of PBs showed promising improvements at about 30% FA resin additions, although the results were preliminary due to the variable performance nature of such binder systems.

Keywords: Furfuryl alcohol, polyfurfuryl alcohol emulsion resin, urea-formaldehyde resins, particleboard binder resins.

INTRODUCTION

Furfural is manufactured from renewable biomass materials by acid digestion, and furfuryl alcohol is manufactured from furfural by a simple hydrogenation process. Furfural and furfuryl alcohol are widely used as industrial solvents and as monomers for various furan and furan-phenolic resins (Dunlop and Peters 1953; McKillip and Sherman 1980; Brown 1952). A large volume of furfural would be produced in the future as a by-product when large-scale acid-catalyzed hydrolysis processing of wood and other biomass materials,

which is currently under development, is realized for fuel alcohol production (Barrier and Bulls 1992). Potentially large volume uses of furfural as an aldehydic copolymer component of phenol-formaldehyde (PF) resol wood adhesive resins were shown (Baxter and Redfern 1958; Kim et al. 1993), and although PB binder-type UF resins appear to be another candidate for furfural utilization, past research indicates that the aldehydic reactivity of furfural toward urea is too low under the ordinary synthesis or curing conditions of UF resins (Novotny and Johnson 1924). Furfuryl alcohol is

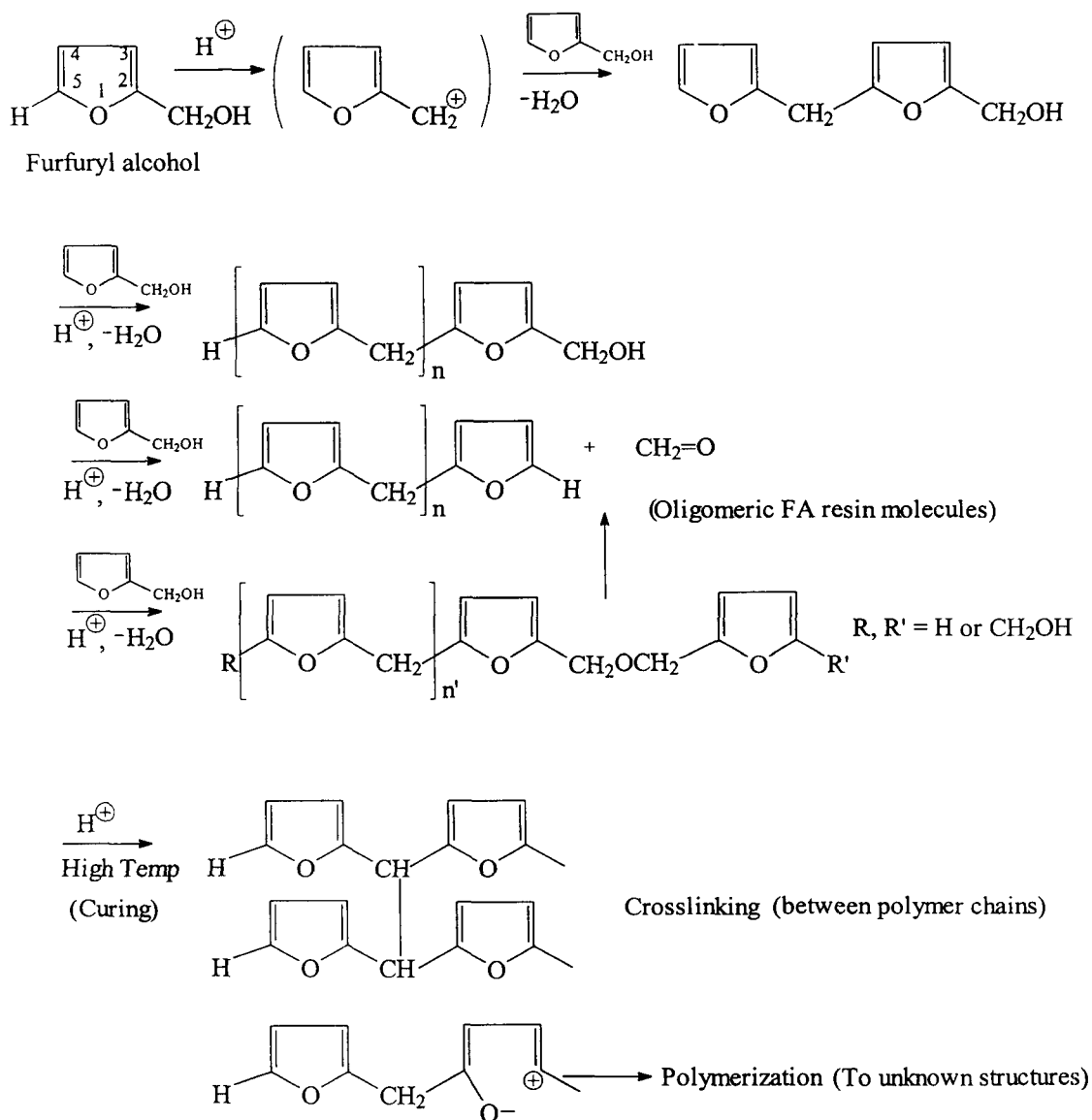


FIG. 1. Furfuryl alcohol resin formation and curing reactions.

the sole monomer of oligomeric FA resins, which are currently widely used as highly durable thermosetting metal-coating resins (Dunlop and Peters 1953; Schmitt 1974). Oligomeric FA resins are manufactured by acid-catalyzed polymerization of furfuryl alcohol, and they cure (thermoset) by a strong acid catalysis at elevated temperatures. Very low molecular weight FA resins are soluble in water,

but moderately advanced molecular weight FA resins are soluble only in organic solvents. Although detailed chemical curing mechanisms are not well understood, oligomeric FA resin structures have been documented using NMR and gel permeation chromatography methods as depicted in Fig. 1 (Werwerka et al. 1971; Milkovic et al. 1979; Fawcett and Dadamba 1982; Laslo-Hedvig et al. 1984; Maciel et al.

1982). Thus, the hydroxymethyl group of furfuryl alcohol is activated by acid to form a carbenium ion, which attacks mostly on either 5-carbon position of another furfuryl alcohol to form a methylene-bonded dimer, and this reaction continues to form FA oligomer resins. The carbenium ion attack also occurs on the 2-carbon position of furfuryl alcohol to replace the hydroxymethyl group as formaldehyde. Also, the reaction occurs on the oxygen atom of another hydroxymethyl group to form methylene ether bonds, but they eventually transform into methylene groups by expelling a formaldehyde molecule. It has been suggested that the crosslinking curing of FA resins arises from the bonds formed between methylene groups and/or the ill-defined furan ring opening and subsequent polymerization reactions, but details are very few (McKillip and Sherman 1980). Furfuryl alcohol is currently about five times as expensive as UF resins but is expected to become competitive when large-scale acid hydrolysis processing of wood and other biomass materials is practiced in the future. Some oligomeric FA resins have been investigated as sole binders for plywood and particleboard (Kelly et al. 1982; Leitheiser et al. 1980, 1982; Schultz 1990). In those studies, the resin application on wood substrate was carried out either by using organic solvents as carriers, or by selecting very low molecular weight FA resins that are dispersible in water; and it was also necessary to use a strong acid catalyst to cure the resins even at elevated temperatures. Major drawbacks of these approaches stem from the fact that use of organic solvents in wood products manufacturing plants presents environmental and safety problems that are difficult to solve, and the use of strong acid catalysts imparts deterioration potential to bonded wood products. More recently, a water-soluble furfuryl alcohol/urea-formaldehyde resin was reported to result in PBs having slightly lower internal bonds than a control urea-formaldehyde resin (Schneider et al. 1996). Although the chemistry or origin of the resin systems was not described, again the FA resin component used

was indicated to be a low molecular weight water-soluble resin, and an addition of zinc chloride at a 10% level was used to cure the resin system. Zinc chloride produces a strong acid in contact with water.

Particleboards are widely used in interior and furniture applications. They are manufactured from wood residues using UF resin thermosetting binders at about 8–10% loading levels, based on dry wood weight. The hot pressing of PBs is done at elevated temperatures (149–177°C) and a mild acid catalyst such as ammonium sulfate is often used to speed up the hot-pressing process. There are many favorable characteristics of PBs, but their long-term water resistance is very poor because of the inherently poor water resistance of cured UF resins (Myers 1984, 1990). Uncured PB binder UF resins are water emulsions of low molecular weight polymers (Kim and Amos 1990) and they are immiscible with organic solvent-soluble polymers such as solvent-borne FA resins. In recent years, the water resistance of PBs has become a more critical parameter in board manufacturing because of keeping the formaldehyde to urea (F/U) mole ratio of UF resin binders at a very low value (about 1.15) to minimize the formaldehyde emission of boards. Further lowering of the F/U ratio of UF resins does not appear to be feasible because of the resulting reduction in strength and water resistance properties of the boards (Myers 1984).

Our continuing interest in finding new uses for furfural or furfuryl alcohol as raw materials derived from renewable biomass led to the highly durable FA resins (when optimally cured) as an investigation candidate in fortifying UF resins for bond and water resistance improvements. Moderately advanced water-insoluble FA resins were the preferred material over low molecular weight water-soluble resins for apparent reasons. The thermosetting curing regime of FA resins is similar to that of UF resins, except that the former needs a strong acid, while the latter needs a weak acid as catalyst. Thus, the first key question was whether water-insoluble FA resins can be used

along with UF resins without causing incompatible processing problems such as balling up of PB mats or having them stick to cauls and press platens. The second question was whether the mixed FA/UF resins formulated with a weak acid catalyst can be adequately cured within the PB manufacturing and board handling parameters. A practicable spraying method for water-insoluble FA resins was needed. Based on a good possibility for converting them into oil-in-water type emulsions to make them miscible and sprayable with UF resins in various proportions, modest exploratory work was planned and carried out to examine the approach. The problem of the curing rate of FA resins was increased by using more advanced water-insoluble resins than those studied previously (Kelly et al. 1982; Leitheiser et al. 1982; Schneider et al. 1996) as well as by employing higher hot-pressing temperatures, post-curing steps, and longer board storage times. The formaldehyde emission potential of the boards was also investigated selectively since this is currently one of the major concerns of the PB industry.

EXPERIMENTAL PROCEDURE

Syntheses of FA resins

Following a reported general synthesis procedure of oligomeric FA resins (Laslo-Hedvig et al. 1982), two FA resins, FA_a and FA_b, were prepared by varying the reaction time. Thus, water (445.0 g) and furfuryl alcohol (445.0 g) were charged into a 2-L stirred reactor, and the reaction mixture was heated to, and held, at 70°C. Then, 10% sulfuric acid solution (26.0 g) was added drop-wise over a period of 10 minutes, and measurement of the reaction time was begun. The exotherm from reaction was dissipated by cooling the reaction mixture intermittently with an ice bath; and when the exotherm subsided, heat was applied to maintain the reaction mixture at 70°C. The reaction mixture separated into two phases in about 20 minutes. The reaction was continued with vigorous stirring until the reaction time reached 45 minutes for Resin FA_a and 65 minutes for

Resin FA_b. The resulting two-phase reaction mixture was then cooled to 60°C, and 20% sodium hydroxide solution (about 11 g) was added to adjust the pH to 7.0. Molecular weights were not measured, but Resin FA_b is considered to have a higher value than Resin FA_a. The residual free furfuryl alcohol content of Resin FA_a and FA_b were both 5.30% by gas chromatographic analysis; and the formaldehyde content, derived from breakage of hydroxymethyl groups of furfuryl alcohol (Werwerka et al. 1971), was 2.33% and 2.40%, respectively, by titration analysis.

Preparation of oil-in-water emulsions of FA resins

Resin FA_a or FA_b made above was stirred vigorously at about 60°C, a gum slurry and a surfactant were added (see below), and small amounts of water were added to lower the viscosity of the emulsion to about 700 cP. The oil-in-water emulsion formed was gradually cooled to room temperature over a period of an hour. The FA emulsion resins obtained were stable for ordinary handling operations; but after standing for about 10 hours, they showed some stratification, which it was possible to disperse again simply by stirring. From various gums and emulsifiers screened, a combination of Jaquar 8920 (Rhone-Poulenc Inc.) at a level of 72 g of 5% slurry in water and Schercomid TO-2 (Scher Chemicals) at a level of 1.0 g for a 900 g batch of emulsion was found to work well. The emulsion Resins FA_a and FA_b had nonvolatile resin solid levels of 42.1% and 37.7%, respectively, determined by drying 1 g samples at 110°C for 2 hours in an oven.

Preparation of more stable oil-in-water emulsions of FA resins

In the second stage of the work, Resin FA_c was made using a similar procedure but by conducting the acid-catalyzed polymerization reaction at 80°C for 60 minutes. Resin FA_c is considered to have advanced more than Resin FA_b because of the higher temperature used.

Although the emulsification of Resin FA_c could be accomplished by the method described above, an emulsion of improved stability was sought and achieved by using a different combination of emulsifiers. Thus, 3,600 grams of Resin FA_c were heated to 60°C in a water bath, and 36.0 grams of Jaguar C-162 (10% solution in water), 36.0 grams of Synperonic 88 (10% solution in water), and 21.6 grams of Synperonic 92 were added (all three emulsifiers from ICI Chemical Co.). The mixture was stirred vigorously to result in an oil-in-water emulsion, and the resulting emulsion was cooled to room temperature by stirring slowly for an hour. It showed a viscosity of about 300 cP, and it was stable for more than a month when kept at about 7°C. The residual free furfuryl alcohol content of Resin FA_c was 5.0% by gas chromatographic analysis; and the formaldehyde content, derived from breakage of hydroxymethyl groups of furfuryl alcohol (Werwerka et al. 1971), was 2.53% by titration analysis. All three FA resin emulsions were dispersible with water to any desired resin solids level or viscosity. The FA resins obtained from reactions that were kept longer than that for Resin FA_c failed to give emulsions by the above method or with other emulsifiers examined due to the formation of hard particles.

US resins of various F/U mole ratios and a reference UF resin

First, a typical UF resin used by the PB industry was prepared according to a reported procedure (Kim and Amos 1990; De Jong and De Jonge 1952). Thus, a weighed amount of formaldehyde (50% solution, Georgia-Pacific Corp.) was charged into a stirred reactor, and the pH was adjusted to 7.5 with an 8% sodium hydroxide solution. The reaction mixture was then heated to 70°C, and a sufficient amount of urea (Aldrich Chem.) was slowly added to bring the initial formaldehyde to urea (F/U) mole ratio to 2.10. The exotherm from the reaction was allowed to raise the reaction temperature to about 90°C, which was maintained

for 30 minutes initially by intermittent cooling and later by external heating. Then, using an 8% sulfuric acid solution, the pH of the reaction mixture was lowered to 5.0–5.1; and by heating, the reaction temperature was raised to, and held at, 95°C for about 110 minutes until the viscosity of the reaction mixture reached 550 cP. The reaction mixture was neutralized to pH 7.5 with sodium hydroxide and then divided into three portions. Enough urea was added to each portion to bring the final F/U mole ratio to 1.15 for Resin UF_a, 1.0 for UF_b, and 0.90 for UF_c. A commercial PB binder UF resin (Georgia-Pacific, GP-3588), UF_d, was obtained as a reference resin.

Preparation of mixed resins from FA and UF resins

Combining and stirring an FA emulsion resin and a UF resin resulted in mixed resins. The mixed resins were uniform, with viscosities ranging between 100 and 200 cP, depending on mix ratios. Ammonium sulfate (25% solution in water) at a level of 0.30% by weight based on liquid resin was added before mixed resins were sprayed on wood particles. This level of catalyst is commonly used in the particleboard industry. The catalyzed FA/UF mixed resins remained homogenous and stable for several hours, allowing the ordinary atomizing operation to be easily carried out using compressed air nozzles.

Preparation of laboratory particleboards

Single-layer homogeneous PBs were manufactured using the parameters reported in Table 1. In the first stage of board preparation, three sets of boards were prepared using emulsion Resin FA_a or FA_b combined in various increasing ratios either with reference resin UF_d or Resin UF_a, both of which have a F/U mole ratio of 1.15. The press temperature was either kept constant at 300°F or varied upwards to 360 or 380°F. The boards were tested within 2 weeks of preparation. In the second stage of board preparation, the FA/UF resin mix was made with 25% Resin FA_c and UF_a,

TABLE 1. *Experimental parameters and methods used in PB manufacture and testing.*¹

Wood particles: southern pine with about 25% mixed hardwoods.
 Panel size: 63.25 × 55.66 mm × 12.65 mm.
 Replication: 2 boards for 1st–3rd stage boards and 8 for 4th stage test; replication boards were made from one blending.
 Resin blending: 15 min.
 Matting: 15 min after resin blending for 10 min.
 Hot pressing: 5 min after matting and for 4.5 min at given temperatures.
 Mat moisture content: 9–10%.
 Target board density: 800 kg/m³.
 Resin and wax loads: 8.0% and 1.0%, respectively, on oven-dry wood weight.
 Pressing mode: 1.0 min compression to ~2,760 kPa (~400 psi) for 3.0 min, and 0.5 min decompression.
 Catalyst: all resin mixes contained 0.3% of ammonium sulfate.

FA/UF resin mixes and press temperatures used were as follows:

First stage board preparation:
 0–50% FA_a + 100–50% UF_d, at 149°C
 0–50% FA_a + 100–50% UF_a, at 149–182°C
 0–50% FA_b + 100–50% UF_a, at 149–193°C

Second stage board preparation:
 25% FA_c + 75% UF_a, at 162°C
 25% FA_c + 75% UF_b, at 162°C
 25% FA_c + 75% UF_c, at 162°C

Postcure: subsets were heated at 121°C for 5 hours.
 Conditioning: in 55% humidity room, up to 2 years.

¹ FA_a, FA_b, FA_c, UF_a (F/U = 1.15), UF_b (F/U = 1.00), UF_c (0.90) and UF_d (F/U = 1.15, commercial), as defined in the text.

UF_b, or UF_c resin; and the press temperature was kept constant at 325°C. Also, a post-cure (122°C for five hours) was applied on subsets of boards, and both sets of boards were stored at room temperature in a 55% relative humidity room (~10% equilibrium wood moisture content). Selected strength properties were tested over a period of two years.

Tests of particleboards

Internal bond (IB), modulus of rupture (MOR), and 2-hour and 24-hour water-soak thickness swell (TS) values were selectively measured in accordance with the American Society for Testing and Materials Procedure D 1037. Eight IB samples, two MOR samples, and two water-soak samples were cut consistently using a pattern from each board and were then used for tests. The average values of two boards are reported. Detailed statistical analyses were not conducted due to the exploratory nature of the investigation. For the 2-hour desiccator formaldehyde emission tests done by the National Particleboard Associa-

tion laboratory (Gaithersburg, Maryland) the hot-pressed PBs were first allowed to stand at room temperature for 24 hours, cut into samples, sanded lightly on both surfaces, immediately wrapped tightly with polyethylene plastic film, and then sent by air.

RESULTS AND DISCUSSION

FA resins and emulsions

The preparation method of the oil-in-water emulsions of FA resins developed in the initial phase of the work allowed water-insoluble FA resins, more advanced than those studied previously, to be evaluated as a co-binder of UF resins in PB manufacturing. Ordinary atomizing methods used in the PB industry can be used, and no organic solvents are needed. The emulsifiers used may make boards more susceptible to moisture absorption, but this can probably be minimized later by a more rigorous screening of emulsifiers. However, since FA resins in current applications are optimally cured only with a strong acid catalyst, and UF

resins in PBs must be cured with a weak acid catalyst, the present approach of using an ordinary weak acid catalyst for FA/UF mixed resins faced the prospect of inadequate curing for the FA resin components. In addition to the various hot-pressing conditions and other methods examined in this work, the FA emulsion resin approach will allow future investigators to experiment with other curing catalysts and methods that befit the PB processing condition and at the same time improve water resistance of boards.

Also, the emulsion approach allowed the evaluation of FA resins advanced to different extents (different cooking times) beyond water insolubility, another avenue of maximizing the cure rate of FA resins, which is useful under the requisite curing condition of using a weak acid catalyst and limited hot-pressing temperature and time. However, the FA resins obtained by carrying out the reaction beyond the stage of Resin FA_c, although their resin-rich phases were fairly mobile, were difficult to emulsify and binder evaluation was not possible. It appeared that hard unstable particles were formed during the emulsification, which might well be due to their molecular weights being too high or the hydrophilic hydroxymethyl group content too low. This problem would also be aggravated if the molecular weight distribution becomes too wide, resulting in forming a high molecular weight end fraction due to nonuniformity of the two-phase stage polymerization reaction. Also, relatively large amounts of unreacted furfuryl alcohol, about 5% based on the total liquid weight, detected in synthesized FA resins, would arise from the two-phase reaction. Being a thermosetting system that results in highly water-resistant cured products, oligomeric FA resins were expected to exhibit an emulsification limit at some extent of polymerization. Attempts to conduct the FA polymerization reaction in an oil-in-water emulsion regime for a more uniform polymerization reaction using various emulsifiers failed. An effective molecular weight-distribution control would be highly necessary, especially for reducing the

high free furfuryl alcohol content, a severe problem to the FA/UF mixed resin approach since free furfuryl alcohol would remain unreacted when FA/UF mixed resins are cured in wood composites.

The cooking time and temperature schedules chosen in synthesizing FA_a, FA_b, and FA_c resins were intended to define the emulsification limit as well as to gauge the binder effects of these parameters on curing. The polymerization chemistry of FA is complex (Fig. 1), and the free formaldehyde and free furfuryl alcohol content determinations did not appear to illuminate much on the extent of polymerization. The resultant effects observed of these parameters could be due to the molecular structure and molecular weight distribution effects. Further optimization of the FA resin polymerization chemistry to improve emulsification and binder performance (see below) was beyond the scope of this exploratory work.

Test results of PBs

Each of the three sets of PBs prepared in the first-stage experiment (Table 2) were made at different times with differences in air humidity and temperature inside the laboratory, and the data therefore are not directly comparable. The first set of PBs were bonded at a constant press temperature of 149°C using mixed binder resins from adding the least advanced Resin FA_a to commercial Resin UF_d (F/U = 1.15) at 0–50% levels. The IB and bending strength values increased as the FA resin level increased in the mix and peaked at 30% level, decreased slightly at 40% level, and decreased further to values slightly lower than those of UF resin alone at 50% level. Thickness swell values did not show much effect from FA resin additions. The second set of PBs were bonded by increasing the hot-pressing temperature as well as the FA resin mix level using the same Resin FA_a but using the laboratory-made Resin UF_a (F/U = 1.15). Since it was expected that PBs bonded with UF resins alone at increased hot-pressing tem-

TABLE 2. Test results of PBs bonded with mixed resin binders made from FA and UF resins using various mix ratios and 3.0 min press times at various press temperatures.¹

FA/UF ² ratio ²	Press temp (°C)	IB (kPa)	MOR (kPa)	Thick. swell (%)		FE ³ (μg/ml)
				2 h	24 h	
FA_a : UF_d						
0 : 100	149	503	8.89	14.4	45.5	ND
20 : 80	149	510	11.03	16.9	50.7	—
30 : 70	149	648	15.03	14.2	47.8	—
40 : 60	149	614	12.13	14.6	50.5	—
50 : 50	149	551	8.00	16.3	60.5	—
FA_a : UF_a						
0 : 100	149	648	8.96	23.4	74.8	—
30 : 70	160	682	14.00	17.0	62.5	—
40 : 60	171	648	13.31	16.0	59.3	—
50 : 50	182	510	11.03	17.8	64.9	—
FA_b : UF_a						
0 : 100	149	745	7.93	7.4	22.2	1.73
20 : 80	160	827	9.93	6.6	26.1	0.70
30 : 70	171	800	9.85	6.2	25.8	1.00
40 : 60	182	620	8.89	7.0	40.1	0.49
50 : 50	193	689	8.55	6.4	38.5	0.50

¹ IB strength values reported are values obtained by normalizing each data set at a 800 kg/m³ board density; actual IB sample densities ranged from 770 to 890 kg/m³. Control boards were not made in the latter two sets for varying press temperature. 2. FA_a, FA_b, FA_c, UF_a (F/U = 1.15, lab synthesis) and UF_d (F/U = 1.15, commercial) as defined in the text. 3. FE: formaldehyde emission values obtained by the 2-hour desiccator method with samples sent to testing lab one day after board manufacture. IB: Internal bond strength value obtained as an average of 8 test samples from each of two boards, in kPa (1 psi = 6.894 kPa). MOR: Modulus of rupture value obtained as an average of 2 test samples from each of two boards, in 1,000 kPa. ND: Not determined. Thick. Swell: Water-soak thickness swell values.

peratures would result in similar strength properties, the experiment did not include control PBs bonded with UF resin alone at each hot-pressing temperature. The board strengths increased again at 30% and 40% FA resin additions, and thickness swell performances did not show any significant differences. In both sets of boards, the increases in strength values might be partially explained as due to the extra formaldehyde added to the UF_d resin from the FA_a resin, which contains about 5% free formaldehyde. However, it appears that Resin FA_a is at least able to replace the UF_d or UF_a resin up to about 30% by weight without incurring deleterious effects at ordinary or increased hot-pressing temperatures without.

The third set of PBs were bonded similarly with the second set of boards except that Resin

FA_b, which was cooked longer than Resin FA_a by about 20 minutes, was used to determine the effect of an increased average molecular weight. The data cannot be directly compared to those of the previous sets of PBs due to the fact that PBs were made at different times. However, higher strength and lower thickness swell values were obtained due to the particular board manufacturing condition. The data trends of this set of boards are similar to the board strength improvement obtained at 20–30% Resin FA_b addition levels, and some deteriorations at higher levels. Although whether Resin FA_b was a better co-binder than Resin FA_a was not ascertained; the results indicate that Resin FA_b is within the range to improve board performance.

The fourth set of PBs were made somewhat later in the second stage of the project (Table 3). All boards were hot-pressed at 162°C using mixed binders made by adding 25% Resin FA_c (most advanced resin) to Resin UF_a (F/U = 1.15), Resin UF_b (F/U = 1.00), and Resin UF_c (F/U = 0.90), respectively, as well as control PBs using Resin UF_a only. Furthermore, binder resin components in the PBs were investigated to determine whether they undergo any post-curing by a heat-treatment at 121°C for 5 hours and also by aging for two years at room temperature in a 55% humidity room. The overall results were somewhat confusing in that the control PBs bonded with Resin UF_a unexpectedly showed appreciably higher IB and bending strengths than the previous three sets of boards. This made the PBs bonded with FA/UF mixed resin binders look comparatively inferior to what was observed in the previous sets of PBs. A better board manufacturing condition (probably related to mat moisture content) present in the laboratory at the time of the control board manufacture is a likely partial explanation since our PB manufacturing laboratory was open to outside and often experienced this phenomenon of drastic swings of board strength properties. Then, since all PBs of this set were made in the same period, the apparently lower IB strengths of PBs bonded with FA_c/UF_a mixed resins in

TABLE 3. Test results of PBs bonded with Resin UF_a (F/U = 1.15) and with 75:25 ratio FA/UF mixed binders made by mixing Resin FA_c with Resin UF_a, Resin UF_b (F/U = 1.00), and Resin UF_c (0.90), respectively, hot pressed at 162°C, with and without heat treatment at 121°C for 5 hours, and aged over a two-year period at room temperature in a 55% humidity chamber.¹

Board/Time	FE ²	0.5 Month			6 Month			12 Month			2 year average	
		IB	MOR	MOE	IB	MOR	MOE	IB	MOR	MOE	IB	B. Dens.
UF _a												
As is	1.20	882	15.03	3,916	1,199	17.99	4,895	1,282	19.03	5,053	1,186	792 ± 18
Heat tr.	0.52	924	14.55	4,026	1,103	17.17	4,743	1,365	16.96	4,667	1,089	789 ± 19
UF _a /FA _c												
As is	1.00	772	15.44	4,508	869	18.20	4,770	1,041	16.75	4,647	882	788 ± 16
Heat tr.	0.36	696	14.20	4,315	861	14.82	4,495	1,000	15.79	4,529	958	788 ± 13
UF _b /FA _c												
As is	0.94	675	11.79	3,888	806	14.00	4,467	889	14.82	4,412	710	781 ± 19
Heat tr.	0.22	627	13.31	4,012	751	13.65	4,164	861	13.93	4,488	772	779 ± 17
UF _c /FA _c												
As is	0.48	524	12.27	3,874	593	12.27	3,244	593	13.03	4,474	593	779 ± 17
Heat tr.	0.18	517	15.72	4,689	558	14.96	5,108	572	13.17	4,309	586	782 ± 19

¹ Bd. dens.: Board density values reported are averages of the four IB sample density averages, with standard deviations; actual board density values ranged between 770–820 kg/m³. ² FE: Formaldehyde emission values in µg/ml obtained by the 2-hour desiccator method with samples sent to testing lab one day after board manufacture. IB: Internal bond strength value obtained as an average of 8 test samples from each of two boards, in kPa (1 psi = 6.894 kPa). MOR: Modulus of rupture value obtained as an average of 2 test samples from each of two boards, in 1,000 kPa. MOE: Modulus of elasticity in 1,000 kPa.

comparison to the control PBs could well be due to the higher advancement imparted to the Resin FA_c used beyond the stage of Resin FA_b. And, for both UF control resin and FA/UF mixed resins, the heat treatment in general resulted in slightly lowered or slightly increased IB values in comparison to untreated boards over the entire two-year aging period. In view of the industrial practice of hot pressing boards at about 150–160°C and resulting board degradation with a slow board cooling, the temperature and time used for the heat treatment used here could have been only of marginal severity with no appreciable post-curing. Another unexpected trend was that IB and bending strength values of almost all PBs, including the heat-treated ones, increased as the board aging time increased to about one year, after which they decreased slightly. The reasons for this seemingly undercuring of manufactured boards and a continuous curing thereafter at room temperature are not clear. The phenomenon may be pronounced only with small laboratory PBs which, after the hot pressing, are normally cooled down faster than industrial boards because of the former's

smaller sizes. Once laboratory boards are cooled, the functional groups that remained unreacted at the time can be locked in, not readily revived by a later heat treatment, and only slowly react to increase the binder strength. Since the effects of heat treatment and aging of boards occurred to a similar degree for both the control UF and FA/UF mixed resin binders, they could well be arising from an inherent property of cured UF resins, and the effects of FA resin components were not ascertained. Therefore, the experiments in the fourth set of boards were carried out with an FA resin advanced to more than an optimum level, and the heat treatment and aging procedure used did not show any improvements derived from using the FA_c resin.

The IB strengths of PBs bonded with the FA_c/UF mixed resins decreased when the UF resin was changed from UF_a to UF_b and UF_c, i.e., the F/U ratio used in the resin was reduced from the current value of 1.15 to 1.00 and to 0.90, a trend expected for the current UF PB binder resins due to the decreasing amounts of crosslinking functional groups. This trend of board weakening occurring when

lowering the F/U ratio in UF resins was thus not stemmed by the addition of the FA_c resin. As discussed above, this effect may have been adversely affected by the over-advancement of the FA_c resin used, but also from the moderate bond strength increases observed in previous sets of boards for FA/UF mixed resins; it is also likely that FA resins are not very effective in remedying lower F/U ratios in UF resins.

Overall, more detailed FA resin optimization and evaluation work would be necessary. This would include determining the dependence of board strength values on the resin loading levels to further evaluate the effects of FA resins. The results of this study indicate that FA resins, if optimized, may moderately improve the bonding strengths and water-soak TS properties of PBs but at levels below that expected from the highly durable nature of well-cured metal coating FA resins (Brown 1952). On the other hand, the results also indicate that FA resins containing up to about 30% in UF resins would act as decent extender resins, a finding that could still become useful when the price of furfuryl alcohol comes down to that of UF resins in the future. The concept of an extender function given to FA resins appears to be in accord with the fact that the lower strengths were obtained for PBs bonded with FA resin levels of 40–50% due to the dilution of UF resins. If FA resins cured appropriately, such binder dilution effects would not be observed. Thus, our approach of using mixed FA/UF resins as binders for PBs appeared to reveal its limitation of minimal binder effectiveness, probably due to ineffective curing. A catalyst system that would cure FA resins adequately under the PB hot-pressing condition as well as a method that would maximize the synergy with UF resin will be a highly desirable objective of future research endeavors. Use of FA resins resulted in boards of darker colors with intensity increasing as the FA resin usage increased, which may be a problem in certain applications of PBs.

Formaldehyde emission test results

The sampling method used for the 2-hour desiccator method was the same as that used

by the PB industry, and the formaldehyde emission values observed for control PBs are comparable to those of industrial PBs (Graves 1993). A gradual reduction of the emission value was indicated as the FA resin addition level and the hot-pressing time were increased. An increased hot-pressing temperature would favor a more thorough cure of UF resins and result in boards that contain lower total amounts of formaldehyde (Plath 1967). However, the initial formaldehyde emission values are not directly affected by moderate levels of increases in the hot-pressing temperature. Therefore, the gradual reduction of formaldehyde emission values appears to be due mainly to the replacement effect by FA resins in spite of the latter's free formaldehyde content of about 5% mentioned above. Therefore, although the curing mechanisms of FA resins in current coating uses are not well understood and could involve some formaldehyde emission (Fig. 1), FA resins as used in this work appear to emit little formaldehyde in comparison to UF resins. The use of increased hot-pressing temperatures to reduce the formaldehyde potential of UF resin-bonded PBs has not been common in industry because of the strength degradation of boards due to the overcuring of UF resins. The PBs pressed at 182°C with the 40:60 FA_b/UF_a mixed resin (Table 2) showed a very low formaldehyde emission. However, the IB and MOR values were also somewhat lower due to either or both of the high FA resin content and the high hot-pressing temperature. From the standpoint of the formaldehyde emission problem of PBs, this low emission result merits a further investigation. The formaldehyde emission data in Table 2 indicate that the lowering trend of formaldehyde emission is reversed between 20% and 30% FA resin additions, which appears to be a data scatter in comparison to the formaldehyde emission data in Table 3 or to have arisen from some unknown parameters possibly related to the matting and hot-pressing method used.

The formaldehyde emission values of the second stage PBs (Table 3) show that the low-

ering of the F/U mole ratio of UF resin reduced the formaldehyde emission, which would have a practical application if the board strength property decreases were prevented by the FA resin component as discussed above. The more drastic reduction of formaldehyde emission observed for the heat-treated PBs indicates that the heat treatment method can be useful even for PBs bonded only with UF resins. The cost of the treatment needs to be considered. The board strength degradations that occur when the cooling of hot-pressed PBs is delayed in the PB industry appear to have a steep dependence on the temperature since the heat treatment conditions used, 125°C for 5 hours and two-year aging at room temperature, caused almost no changes in board strengths. Thus, the overall results still indicate that FA resins might show merit for further investigations as formaldehyde emission reduction additives.

CONCLUSIONS

Water-insoluble oligomeric FA resins were made into oil-in-water emulsions successfully, enabling them to be sprayed effectively as PB binder-type mixed FA/UF resins using the ordinary atomizing methods used in the PB industry. Additions of 20–30% of optimized FA resins to UF resins appear to produce increased strength properties and reduced formaldehyde emissions. These effects were also shown to be potentially magnified when the hot-pressing temperature was increased and a post-heat-treatment was applied. However, the study was carried out as preliminary and exploratory work, and the binder and other materials interactions occurring in the hot pressing of PBs in relation to these improvements were not investigated. Those need to be examined to establish a more solid foundation for the approach. Optimization of the FA resin polymerization reaction, including the reduction of free furfuryl alcohol content, would also be an essential step in realizing the full potential of this approach.

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