

Behavior of Amine-Modified Urea-Formaldehyde-Bonded Wood Joints at Low Formaldehyde/Urea Molar Ratios

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SYNOPSIS

Urea-formaldehyde-bonded wood products are limited to interior nonstructural applications because of their poor durability under cyclic moisture or humid environments. The stability of solid-wood joints and particleboards can be enhanced by bonding with urea-formaldehyde adhesives modified with di- and trifunctional amines at an effective resin formaldehyde-to-urea mol ratio (F/U) of 1.6; however, particleboard formaldehyde emissions were not improved over those from boards made with unmodified adhesives and were unacceptably high. The relative effectiveness of selected modifications was investigated at resin formaldehyde-to-urea (F/U) molar ratios of 1.4 and 1.2. Solid-wood joints and particleboards made with modified adhesives, an unmodified adhesive, and a phenol formaldehyde (PF) resin were subjected to cyclic soak-dry (cyclic stress) treatments and moist-heat aging. Formaldehyde emissions from particleboards were also determined. At F/U 1.4, the resistance of solid-wood joints made with modified adhesives to cyclic stress and moist-heat aging was equal to that of PF-bonded joints and superior to that of joints bonded with unmodified adhesive. The resistance of particleboards made with modified adhesives was greater than that of boards made with unmodified adhesive but less than that of PF-bonded board. Solid-wood joints and particleboards made with F/U 1.4 resins performed better than did those made with F/U 1.2 resins. Particleboards made with F/U 1.2 resins had formaldehyde emissions well below the standard, and room temperature aging or bonding at high temperature reduced emissions substantially. © 1994 John Wiley & Sons, Inc.*

INTRODUCTION

Urea-formaldehyde (UF) resins are used in large quantities for the production of wood products such as plywood and particleboard. However, UF-bonded wood products are normally confined to interior nonstructural applications because UF resins undergo stress rupture and/or hydrolytic degradation under cyclic moisture or warm, humid environments. Hydrolysis is often accompanied by formaldehyde emission, which constitutes a potential health haz-

ard. Formaldehyde emission is, consequently, subject to regulation and is a major concern of the forest products industry.

In previous work, we postulated that a primary cause for the poor durability of UF-bonded wood products was the susceptibility of the UF polymer chains to scission of bonds under the stresses imposed by dimensional changes in the wood during cyclic moisture changes.¹ We postulated further that incorporating flexible di- and trifunctional amines into the UF chains should reduce sensitivity to those cyclic stresses and lead to improved durability of UF-bonded wood products. To validate this approach, we incorporated flexible amines into the resin in two ways: First, urea-terminated amines were substituted for a small fraction of the urea during resin synthesis. Second, amine hydrochlorides were substituted for ammonium chloride as the catalyst for resin cure. This approach significantly improved the durability of both solid-wood joints and

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Journal of Applied Polymer Science, Vol. 52, 689-700 (1994)
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CCC 0021-8995/94/050689-12

particleboards at an effective formaldehyde to urea (F/U) molar ratio of 1.6.¹⁻³

Not surprisingly, formaldehyde emissions from particleboards bonded with modified and unmodified adhesives at the molar ratio 1.6 did not meet accepted standards.² It is well recognized, however, that formaldehyde liberation by wood products decreases with decreasing F/U ratio.⁴ Therefore, the objective of the present study was to investigate the effectiveness of modifying UF resins with selected flexible amines at F/U ratios of 1.4 and 1.2. As in earlier work, we evaluated the effectiveness in terms of the resistance to cyclic soak-dry and moist-heat aging and in terms of the formaldehyde emission of bonded wood products.

Throughout this report, a resin is defined as the synthesized polymer in aqueous solution. An adhesive is defined as a resin mixed with a curing agent (catalyst). A modified resin is one into which the urea derivative of an amine was incorporated during resin synthesis. A modified adhesive is a resin (modified or unmodified) cured with an amine hydrochloride or a modified resin cured with a non-amine curing agent.

EXPERIMENTAL

The experimental methods are summarized because most details have been presented previously.¹⁻³ The chemicals employed are described in Table I. Following our previous convention, we used code names; e.g., hexamethylenediamine is HMDA, purified bis-hexamethylenetriamine is BHMTA, and crude BHMTA is C-BHMTA. For urea-capped amines, the final A in the code name is replaced by U; e.g., HMDA becomes HMDU and C-BHMTA becomes C-BHMTU. The hydrochloride salts of the amines are designated, e.g., as HMDA·2HCl and TEATA·3HCl. The preparation of concentrated aqueous formaldehyde has been described.¹

Curing Agents

The cure of UF resins is induced by lowering the pH. This can be effected in a number of ways, including the addition of ammonium salts or amine hydrochlorides, which liberate hydrogen chloride by reaction with free formaldehyde in the resin. However, F/U 1.2 resins contain relatively little free

Table I Test Materials

| Material | Source | Remarks |
|---|---|--|
| Hexamethylenediamine (HMDA) | DuPont Petrochemicals, Wilmington, DE | Pure (+ 99.9%) aliphatic diamine anhydrous solid |
| Bis-hexamethylenetriamine, crude (C-BHMTA) | DuPont Petrochemicals | Brown viscous liquid, bp 249°C at 100 mmHg, vapor pressure 7 mmHg at 180°C |
| Triethylaminetriamine (TEATA, Tren) | W.R. Grace & Co., Organic Chemicals Div., Lexington, MA | High-purity grade with < 2% ethylene amine |
| Triethyleneoxidediamine (TEODA, Jeffamine EDR 148) | Texaco Chemical Company, Austin, TX | Liquid, viscosity 8 cp at 25°C, total amine 13.5 meq/g, mol wt ~ 148 |
| Poly(propyleneoxide)tri-amine (PPOTA, Jeffamine T-403) | Texaco Chemical Co. | Pale yellow liquid, viscosity 70 cp at 25°C, total amine 6.4 meq/g, mol wt ~ 440 |
| Poly(ethylene oxide)di-amine (PEODA-11, Jeffamine ED 600) | Texaco Chemical Co. | Liquid at 27°C, Viscosity 72 cp at 20°C, total amine 97.5 wt % or 3.19 meq/g, mol wt ~ 600 |
| Poly(propylene glycol)di-amine (PPGDA-3, Jeffamine D230) | Texaco Chemical Co. | Liquid at 27°C, mol wt ~ 230, total amine 8.4 meq/g |
| Paraformaldehyde | Aldrich Chemical Co., Milwaukee, WI | 95%, mp 163-165°C |
| Urea | Aldrich Chemical Co. | Mp 134°C |
| Ammonium chloride | Aldrich Chemical Co. | Moist white crystals, 97%, mp 119-121°C |

formaldehyde for such acid liberation. Moreover, the resin synthesis usually involves adding triethanolamine as a buffer. Consequently, preliminary experiments showed that ammonium chloride or amine hydrochlorides in F/U 1.2 resins did not drop the pH sufficiently for adequate cure. Therefore, for those systems, we investigated other curing agents, such as aluminum chloride, citric acid, and formic acid.

With ammonium chloride or amine hydrochlorides as curing agents, the adhesives were made by mixing the resin with 5 wt % of the curing agent. Preliminary experiments showed that the direct mixing of 5 wt % of either formic acid (85% solution), aluminum chloride, or citric acid with the resin resulted in almost instantaneous gelation. Therefore, these curing agents were used as 30 wt % aqueous solutions sprayed directly on the substrate rather than mixed into the adhesive. The hydrochloride derivatives of amines were prepared as reported previously.³

Amine Urea Derivatives

The urea derivatives of amines (urea-capped amines) were made in the presence of the total urea to be used in a particular resin synthesis, as reported previously.² The weight and molar compositions of the urea-amine mixture are shown in Table II. After refluxing for about 4 h, the hot liquid product was poured with vigorous stirring into excess ethanol (2–3 L) in a beaker immersed in an ice bath. The resulting precipitate was filtered under suction, washed several times with ethanol, and dried to constant weight in a vacuum oven (about 0.1 MPa) at 80°C.

Resins

All resins were synthesized by adding the urea (or the combined urea and urea-amine derivative) in

two steps (Table III). The first step yielded an effective F/U ratio of 2.0, and the second step, a final F/U ratio of either 1.4 or 1.2. After the second urea addition for F/U 1.2 resins, the reaction mixture was held at 90°C and pH 6.5 until reaching L-viscosity on a Gardner-Holt[†] bubble viscometer scale instead of the H-viscosity for F/U 1.6 or 1.4 resins. The detailed resin synthesis and characterization procedures were reported previously.^{1,2} Initial values of pH, viscosity, solids content, and free formaldehyde for the unmodified and modified resins are given in Table IV.

Bonded Joints and Particleboard

Solid-wood Joints

Solid-wood assemblies were bonded with both modified and unmodified adhesives as described.³ However, different press platen temperatures were used in the present study. For the UF joints, platen temperature was 20°C above the exotherm peak temperature determined from differential scanning calorimetry (DSC) measurements for the particular adhesive (Table V); for the PF joints, platen temperature was 177°C.

Compression shear-block specimens, of reduced size from the standard specimen,⁵ were cut from each assembly. During specimen preparation, an offset was formed at each end of the specimen by sawing away a portion of the adherend. The adhesive layer was often exposed directly to the atmosphere in this offset area.

Particleboard

With F/U 1.4 resins, particleboards were made as described previously³ but at platen temperatures noted in Table V. Total heating time was 10 min.

With F/U 1.2 resins, the general procedure was the same as that for making boards bonded with F/U 1.4 resins with the following exception: For aluminum chloride, formic acid, and citric acid curing agents, a 30 wt % solution of the curing agent was initially sprayed on the furnish and then the resin was applied. The amount of curing agent solution used was such that the curing agent was 5 wt % of the resin (solid basis). For all the F/U 1.2 resins, platen temperature was 20°C above the DSC exotherm peak (Table V). With PF resins, the conditions were the same as for the UF-bonded parti-

Table II Composition of Urea and Urea Derivative Mixture

| Resin | Urea Substitution (Percent) | |
|---------|-----------------------------|-----------|
| | Molar | By Weight |
| HMDA | 8.33 | 14.9 |
| C-BHMDA | 8.33 | 22.3 |
| TEODA | 4.55 | 10.5 |
| PPOTA | 7.69 | 37.9 |
| | 4.35 | 25.0 |
| | 2.33 | 14.9 |

[†] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Table III Resin Synthesis Compositions^a

| F/U Ratio and Resin | Formaldehyde | Urea + Urea Derivative | |
|---------------------|--------------|------------------------|-------------------|
| | | 1st Addition | 2nd Addition |
| 1.4 F/U | | | |
| Control | 41.0 | 41.0 ^b | 18.0 ^b |
| HMDU | 36.0 | 44.0 | 20.0 |
| PPOTU (7.7 mol %) | 27.0 | 50.0 | 23.0 |
| C-BHMTU | 33.7 | 45.8 | 20.5 |
| 1.2 F/U | | | |
| Control | 37.5 | 37.5 ^b | 25.0 ^b |
| TEODU | 34.5 | 39.3 | 26.2 |
| PPOTU | | | |
| (7.7 mol %) | 24.5 | 45.3 | 30.2 |
| (4.4 mol %) | 29.6 | 42.2 | 28.1 |
| (2.3 mol %) | 33.1 | 40.1 | 26.7 |

^a Units are percentage of weight, based on total solids.

^b Urea only.

cleboards except that the platen temperature was 177°C.

Treatment, Aging, and Testing of Bonded Specimens

Slightly different vacuum-pressure soak-dry (VPSD) treatments were used for solid-wood (VPSD-1) and particleboard (VPSD-2). Each VPSD-1 cycle consisted of submerging specimens in cold water for 30 min at about 0.1 MPa vacuum and 30 min at 0.4 MPa pressure, followed by drying for 20 h in a forced-draft oven at 43–45°C. Groups of three solid-wood specimens of each adhesive were allocated to each of 1, 2, 6, or 10 cycles. An additional group of

three specimens was left untreated to serve as controls. The vacuum-pressure soak portion of the VPSD-2 cycle was the same as used in VPSD-1, but drying was elevated to 80°C and extended to 24 h. Groups of four particleboard specimens of each adhesive type were allocated to each of 1, 2, 6, or 10 cycles. An additional set of four specimens was left untreated to serve as controls.

Solid-wood shear-block specimens and particleboard specimens were subjected to moist-heat aging at 70°C and 80% relative humidity (RH) for up to 80 days as described.³ After treatment or aging, all specimens were equilibrated to 6% moisture content before testing. All mechanical testing was performed on an Ametek/Riehle universal testing machine.

Table IV Initial Resin Properties

| Resin | pH | Viscosity (cps) | Solids Content (%) | Free Formaldehyde (%) |
|-------------------|------|-----------------|--------------------|-----------------------|
| 1.4 F/U | | | | |
| Control | 7.98 | 1210 | 60 | 0.24 |
| HMDU | 7.78 | 450 | 64 | 0.25 |
| PPOTU (7.7 mol %) | 7.91 | 1100 | 69 | 0.17 |
| C-BHMTU | 7.86 | 390 | 64 | 0.32 |
| 1.2 F/U | | | | |
| Control | 8.00 | 1590 | 61 | 0.18 |
| TEODU | 7.90 | 874 | 62 | 0.18 |
| PPOTU | | | | |
| (7.7 mol %) | 7.90 | 2020 | 70 | 0.14 |
| (4.4 mol %) | 8.08 | 4450 | 65 | 0.17 |
| (2.3 mol %) | 8.10 | 938 | 62 | 0.19 |

Table V Press Platen Temperatures for Bonding of Solid-wood Joints^a

| Resin | NH ₄ Cl | HMDA · 3HCl | TEATA · 3HCl | PPOTA · 3HCl | C-BHMTA · 3HCl |
|---------|--------------------|-------------|--------------|--------------|----------------|
| 1.4 F/U | | | | | |
| Control | 125 | 130 | 125 | 135 | 135 |
| HMDU | 120 | 125 | 120 | 130 | 130 |
| PPOTU | 120 | 125 | 120 | 130 | 130 |
| C-BHMTU | 120 | 130 | 120 | 135 | 140 |
| 1.4 F/U | | | | | |
| Control | 125 | 135 | 125 | 135 | 140 |
| PPOTU | 120 | 130 | 120 | 130 | 130 |

^a Units in °C.

The solid-wood shear-block specimens were tested according to ASTM Method D 905,⁵ and the strength of the particleboard perpendicular to the plane of the panel (internal bond) was tested according to ASTM Method D 1037.⁶ The residual thickness swelling of the particleboard was measured on the specimens used for the internal bond test after soaking, redrying, and equilibrating to 6% moisture content.

Specimens were sent to the National Particleboard Association to determine formaldehyde emission values by the standard 2 h desiccator test (FMT-1).⁷ Before determining the emission, each specimen was edge-coated with wax and conditioned for 24 h in a room at 24 ± 3°C, 50 ± 5% RH, and a maximum ambient formaldehyde concentration of 0.1 p/m. After the initial emission value was obtained, the specimens were reconditioned for 30 days and the emission value was redetermined.

RESULTS

Because resin quantities were limited and the experiments were regarded as screening efforts, only three specimens were tested for each data point shown in the figures. For solid-wood joints, standard deviations from the test values varied between approximately 5 and 15% when the joints were strong and wood failure predominated; when joints were weak, however, standard deviations often exceeded those levels. For particleboard, standard deviations were usually between 5 and 10%. To simplify the figures, we did not attempt to supply error bars. Instead, we drew a smooth curve through each group of data that we considered significantly different from other groups, using two standard deviations spread as an approximate criterion.

Cyclic Soak-Dry Treatments

Solid-wood Joints

Figures 1 and 2 summarize the effects of cyclic VPSSD-1 treatment on the shear strength of solid-

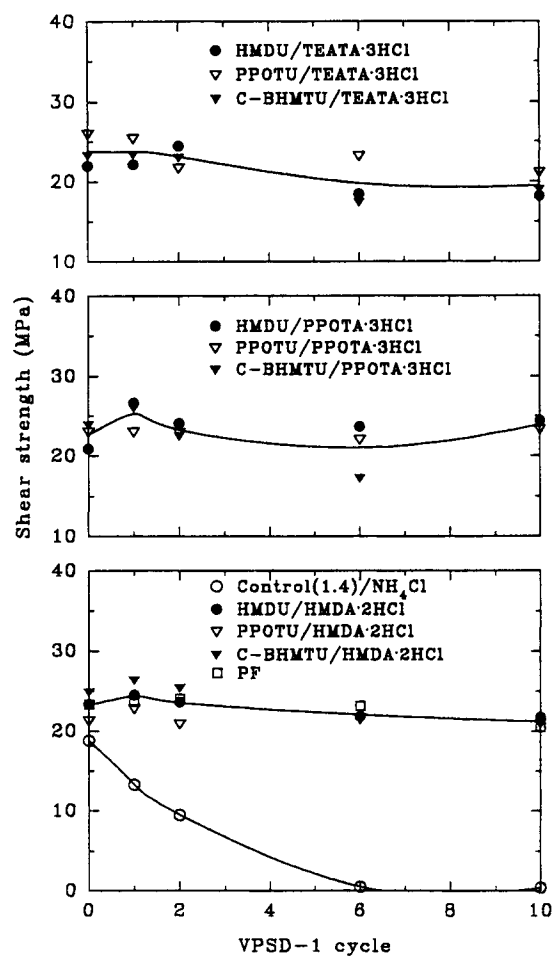


Figure 1 Effect of cyclic soak-dry stress on shear strength of solid wood joints made with F/U 1.4 resins.

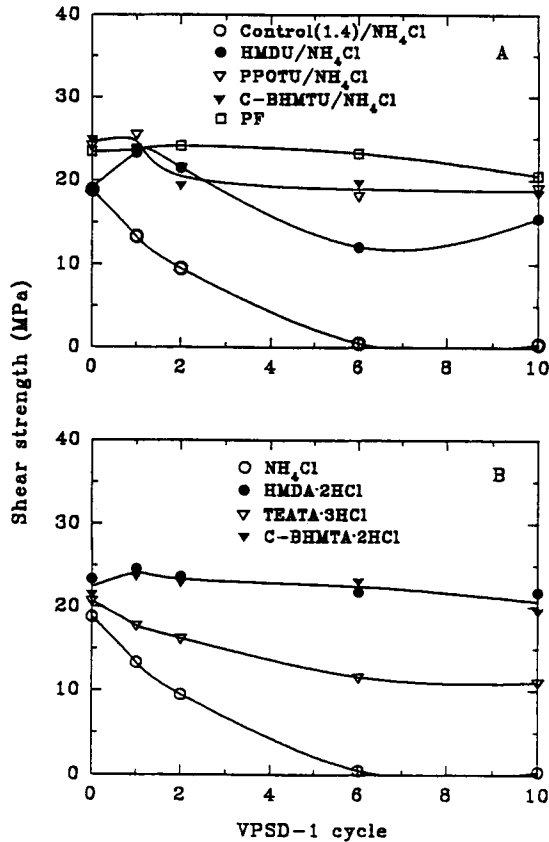


Figure 2 Improved cyclic soak-dry stress resistance caused by resin modification at F/U 1.4: (A) modified resin/ammonium chloride; (B) unmodified resin/amine hydrochloride).

wood joints made with F/U 1.4 resins. In general, the results are consistent with those for joints made with F/U 1.6 resins. Specifically, we note the following:

1. Joints bonded with modified resins cured with HMDA·2HCl, TEATA·3HCl, and PPOTA·3HCl retained > 80% of their initial strength after 10 VPSD-1 cycles, irrespective of the resin. Most of these joints had strengths comparable to that of joints bonded with PF resin (Fig. 1).
2. The strength of joints made with the control resin cured with ammonium chloride was decidedly inferior to that of joints made with the modified adhesives. The control system started at a lower value and dropped virtually to zero after six VPSD-1 cycles (Figs. 1 and 2).
3. The strength of joints bonded with the modified resins cured with ammonium chloride

[Fig. 2(A)] and that of joints bonded with the control (unmodified) resin cured with the hydrochloride amine salts [Fig. 2(B)] were higher than that of joints made with the control resin cured with ammonium chloride.

Figure 3 compares the shear strength of joints bonded with F/U 1.4 and 1.2 resins cured with ammonium chloride (A) and PPOTA·3HCl (B). The behavior of the joints made with resins cured with PPOTA·3HCl is typical of the other amine hydrochlorides. Irrespective of the curing agent, the performance of the joints made with F/U 1.2 resins was inferior to that of joints made with F/U 1.4 resins. With F/U 1.2 resins, however, the strength of joints bonded with PPOTU-modified resin was higher than that of joints bonded with the control resin.

Particleboard

The internal bond strength of all the UF-bonded particleboards followed similar behavior as a function of VPSD-2 cycles (Figs. 4 and 5). In general,

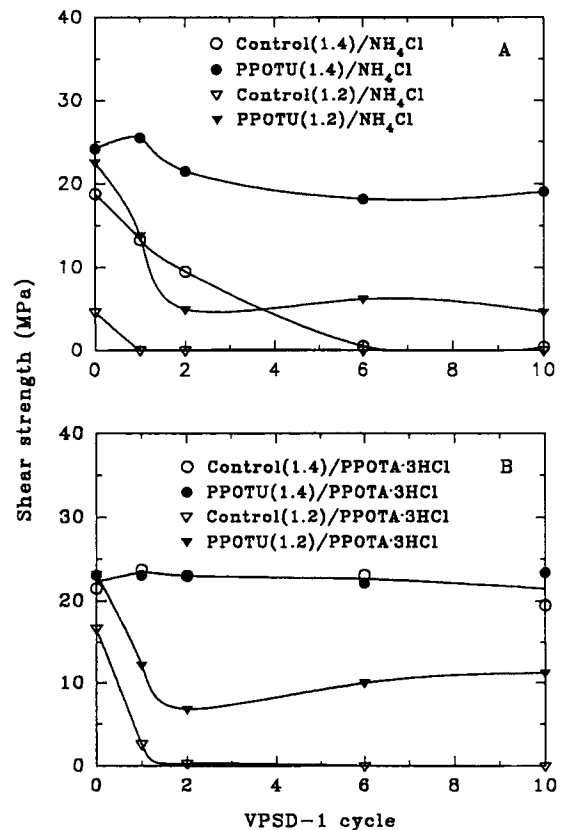


Figure 3 Relative cyclic stress resistance of solid-wood joints made with F/U 1.4 and 1.2 resins: (A) ammonium chloride; (B) PPOTA·3HCl).

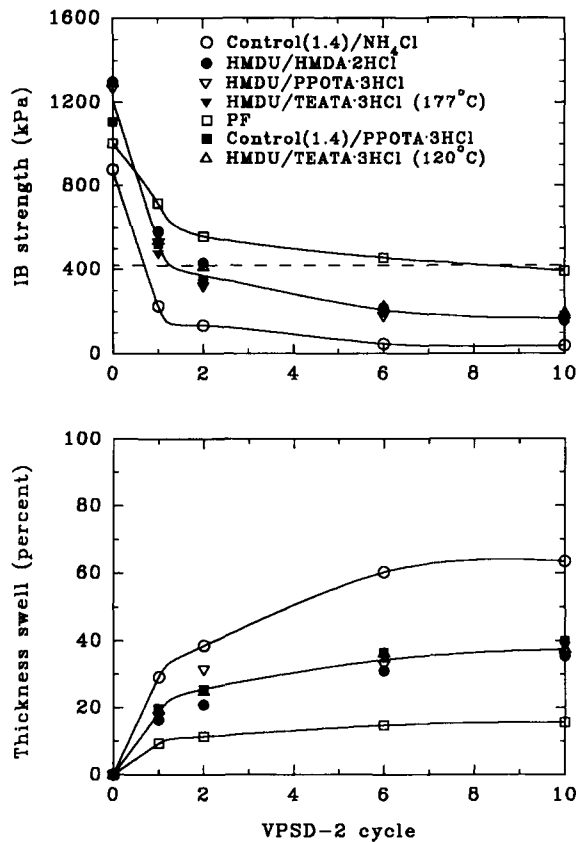


Figure 4 Effect of cyclic soak-dry stress on internal bond (IB) strength and thickness swell of particleboards made with F/U 1.4 resins. Dashed line indicates IB strength requirement for unaged mat-formed particleboard.⁸

the primary difference among the UF-bonded boards at a given molar ratio was the initial strength. At F/U 1.4, e.g., all the modified adhesives produced higher initial strengths than those of the unmodified adhesives (Fig. 4) and met the American National Standard Institute (ANSI) requirement of 414 kPa for medium-density particleboard⁸ until approximately the second cycle, whereas the unmodified system fell below the ANSI standard during the first cycle. The modified systems retained their advantage over the unmodified systems through the tenth cycle. On the other hand, the PF-bonded board possessed lower initial strength than that of the boards bonded with modified adhesives but resisted degradation much better and met the ANSI requirements through 10 cycles.

At F/U 1.2 (Fig. 5), the performance was generally inferior to that at F/U 1.4. However, boards bonded with some modified adhesive possessed higher initial strength than that of those bonded

with the unmodified system and, consequently, they retained slightly higher strength during cycling.

The effect of adhesive modification on dimensional stability generally paralleled its effect on internal bond strength (Figs. 4 and 5). After 10 VPSD-2 cycles at F/U 1.4, the thickness swell of particleboards made with the control adhesive was 65%, whereas that of boards made with some modified adhesives was 34–40%. With F/U 1.2 resins, the thickness swell of most boards was in the range of

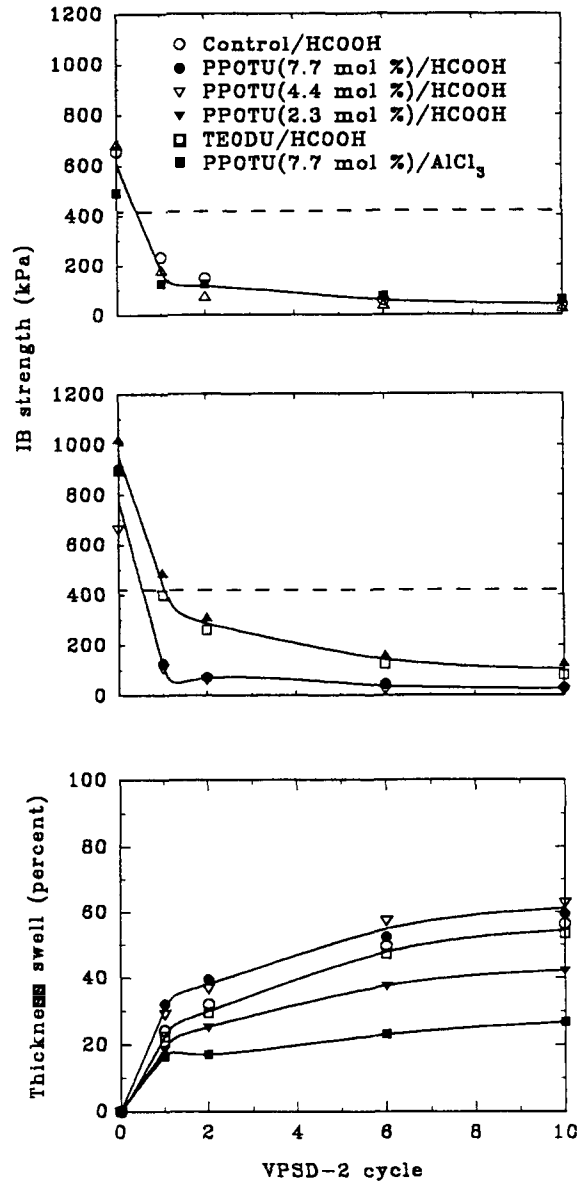


Figure 5 Effect of cyclic soak-dry stress on IB strength and thickness swell of particleboards made with FU 1.2 resins. Dashed line indicates IB strength requirement for unaged mat-formed particleboard.⁸

52-65% after 10 VPSD-2 cycles (Fig. 5). The PF-bonded board swelled only 18%.

Moist-heat Aging

Solid-wood Joints

Figure 6 shows the effect of moist-heat aging on the behavior of solid-wood joints made with modified UF adhesives compared to those made with PF and unmodified UF adhesives. The UF resins had an F/U ratio of 1.4. Joints made with adhesives modified with trifunctional amines retained > 80% of their strength even after 40 days of moist-heat aging. Their behavior was comparable to that of PF-bonded joints and clearly superior to that of the joint bonded with the unmodified UF adhesive.

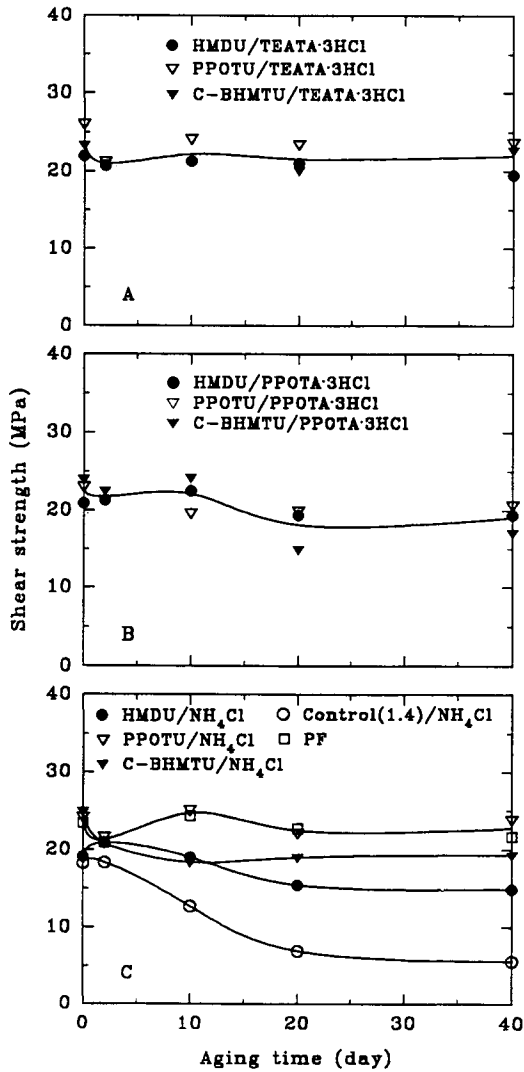


Figure 6 Resistance to moist-heat aging of solid-wood joints made with FU 1.4 resins.

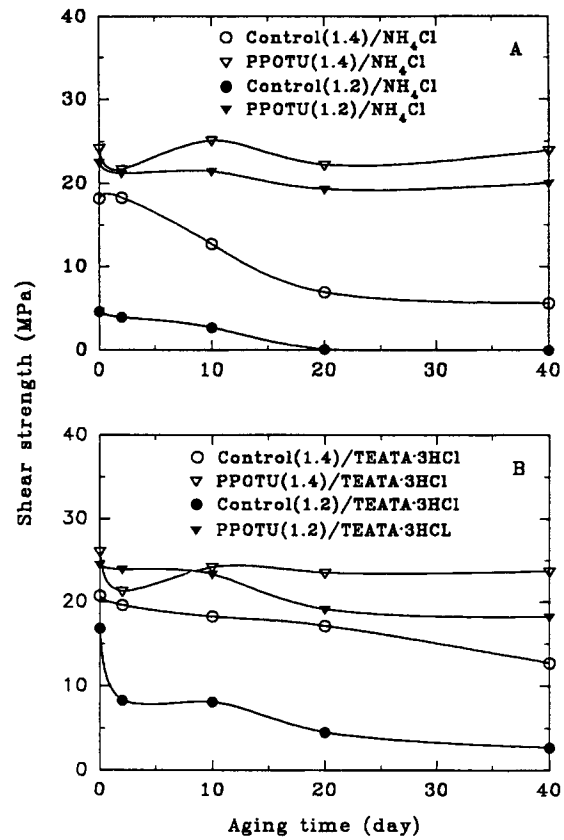


Figure 7 Resistance to moist-heat aging of solid-wood joints made with F/U 1.4 and 1.2 resins cured with (A) ammonium chloride and (B) TEATA·3HCl.

Figure 7 compares the behavior of joints made with F/U 1.4 resins with those made with F/U 1.2 resins for the unmodified control and PPOTU-modified resins cured with ammonium chloride (A) and TEATA·3HCl (B). Although joints made with F/U 1.4 resins had better resistance to moist-heat aging than did those made with F/U 1.2 resins, the trifunctional PPOTU proved very effective in improving the resistance, even at F/U 1.2.

Using a low-power microscope, we examined specimens bonded with unmodified and modified adhesives having the greatest resistance to moist-heat aging. The unmodified adhesives showed pervasive shrinkage cracking in both the unaged and aged specimens and crack erosion typical of unmodified UF adhesive in the aged specimens.⁹ The modified adhesives, PPOTU(1.4)/NH₄Cl and BHMTU(1.4)/NH₄Cl, did not show shrinkage cracking in unaged specimens. The shrinkage cracking did appear after 40 days of aging in the offset ends of the shear-block specimens where the modified adhesive layer was directly exposed to the atmosphere. There was also crack erosion in this

area, indicating thermal degradation. However, crack erosion was much less severe than observed in the offset area of specimens bonded with unmodified adhesives and subjected to the same aging treatment. Most importantly, no shrinkage cracking or thermal aging effects appeared in the actual bond area with these modified adhesives.

As with the two modified adhesives at F/U 1.4, the PPOTU(1.2) resin, cured with ammonium chloride or the hydrochloride salt of the difunctional HMDA, was quite resistant to moist heat and developed shrinkage cracks and crack erosion only in the exposed offset specimen. However, it is notable that when cured with the hydrochloride salts of trifunctional amines (TEATA and PPOTA), PPOTU(1.2) adhesives did not develop shrinkage cracks or show signs of erosion in the offset or bond areas. Some specimens maintained strengths as high as 18–20 MPa and maintained considerable wood failure after 40 days of moist-heat aging. These combinations of trifunctional resin and curing agent seem to hold the most promise for improving the hydrolytic stability of UF adhesives.

Particleboard

Up to at least 20 days, boards made with modified adhesives at F/U 1.4 possessed better resistance to moist-heat aging than did boards made with the unmodified adhesive (Fig. 8). After 40 days, however, this difference largely disappeared, and all the UF boards tested were well below the ANSI standard of 414 kPa. All UF-bonded boards were considerably less resistant to moist-heat aging than were the PF-bonded particleboards.

With F/U 1.2 resins, the boards made with TEODU/HCOOH and with two of the PPOTU/

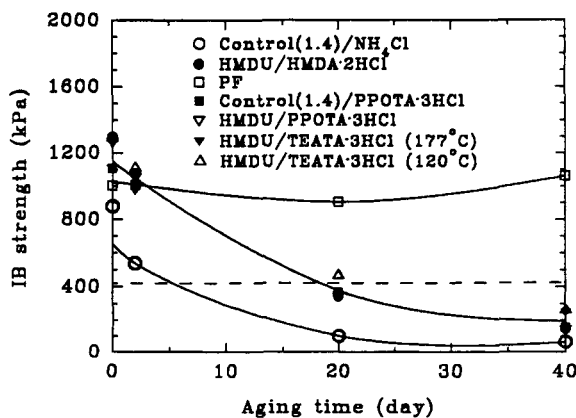


Figure 8 Resistance to moist-heat aging of particleboards made with F/U 1.4 resins.

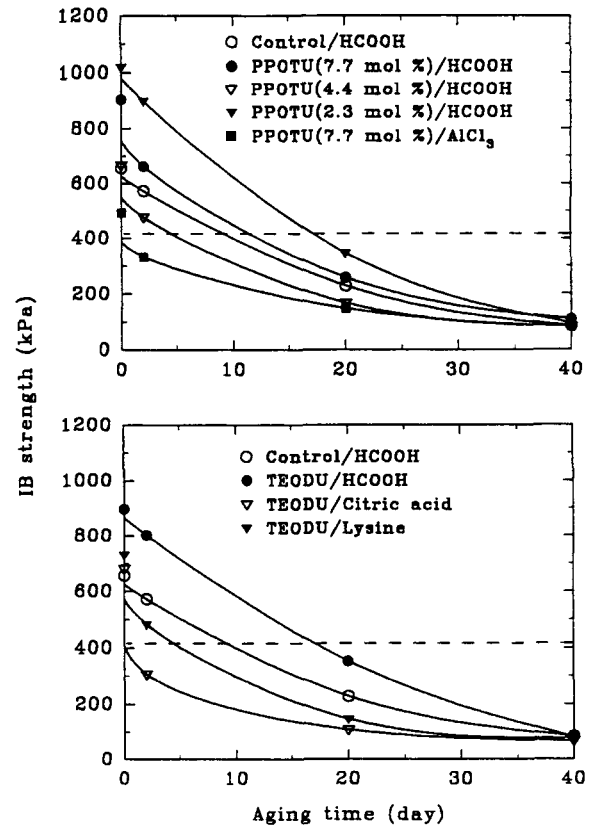


Figure 9 Resistance to moist-heat aging of particleboards made with F/U 1.2 resins.

HCOOH adhesives possessed greater initial strength than did the board made with unmodified adhesive (Fig. 9); the modified systems met the ANSI requirement of 414 kPa for at least 10 days. However, none of the boards met the requirement after 20 days, and all internal bond strength values were nearly identical after 40 days of moist-heat aging. The board made with the resin with the lowest viscosity (2.5 mol % PPOTU, Table IV) was better than those with resins of higher viscosity, similar to the effect noticed after cyclic aging. Therefore, if resin viscosity is well controlled, organic acids, Lewis acids, and proteins show promise as curing agents for low F/U resins.

In general, results with F/U 1.4 and 1.2 resins, indicate the following:

1. Many modified UF adhesives performed better than did the unmodified adhesives and were more effective in solid-wood joints than in particleboard. The performance of solid-wood joints bonded with modified UF adhesives at F/U 1.4 approached that of PF-bonded joints.

Table VI Formaldehyde Emission for 1.4 F/U Particleboard^a

| Curing Agent/Resin | None | | NH ₄ Cl | | HMDA · 3HCl | | TEATA · 3HCl | | PPOTA · 3HCl | |
|--------------------|---------|------|--------------------|------|-------------|------|--------------|------|--------------|------|
| | Initial | Aged | Initial | Aged | Initial | Aged | Initial | Aged | Initial | Aged |
| Control | 2.20 | 0.79 | 1.94 | 0.61 | — | — | — | — | 3.98 | 1.07 |
| HMDU | 2.80 | 1.04 | — | — | 3.96 | 1.10 | 3.79 | 1.36 | 3.66 | 0.89 |
| HMDU ^b | — | — | — | — | — | 1.46 | 0.65 | — | — | — |
| PPOTU | 1.93 | 0.89 | — | — | 1.72 | 0.70 | 1.97 | 0.54 | 2.14 | 0.70 |
| C-BHMDU | 2.58 | 0.75 | 1.98 | 0.66 | — | — | 3.62 | 0.95 | 4.28 | 1.02 |
| PF | 0.47 | 0.26 | — | — | — | — | — | — | — | — |

^a Units expressed in $\mu\text{g}/\text{mL}$. Approximate HUD limit is $1.1 \mu\text{g}/\text{mL}$.

^b Board made at 177°C instead of temperatures listed in Table V.

2. PF-bonded particleboards had superior resistance to swell/shrink cycling and moist-heat aging compared to modified or unmodified UF-bonded particleboards.
3. Decreasing the F/U molar ratio from 1.4 to 1.2 tended to decrease the initial strength of solid-wood joints and particleboard. The F/U 1.2 systems, with a few exceptions, exhibited lower resistance to cyclic stress and moist-heat aging.

Formaldehyde Emission from Particleboard

Tables VI and VII summarize the particleboard formaldehyde emission results. We note the following:

1. At F/U 1.4, all the initial emissions were above the approximate Housing and Urban Development (HUD) regulatory limit of $1.1 \mu\text{g}/\text{mL}$. However, after the 30-day aging period, all but one emission fell below that limit. Emissions of the F/U 1.2 UF-bonded boards and the PF-bonded boards all were below the limit before aging.

2. At F/U 1.4 and at the standard curing temperature, the initial emissions of boards made with PPOTU resin were below those of boards made with unmodified resin or HMDU- and C-BHMTU-modified resins. These differences probably reflect the free formaldehyde contents of the resins (Table IV). In addition, the higher emission of boards made with amine hydrochloride curing agents compared to ammonium chloride probably reflects the greater formaldehyde-scavenging capability of ammonium chloride due to its presence at greater molar levels.
3. Emissions were substantially reduced by curing at higher temperature (HMDU at F/U 1.4) and by the 30-day ambient aging.

DISCUSSION

Several factors could have contributed to the poorer performance of the modified systems in particleboard compared to solid-wood joints. The first factor relates to structural and stress concentration differences. Particleboard essentially consists of a large

Table VII Formaldehyde Emission for 1.2 F/U Particleboard^a

| Curing Agent/Resin | HCOOH | | AlCl ₃ | | Lysine | | TEATA · 3HCl | | Citric Acid | |
|--------------------|---------|------|-------------------|------|---------|------|--------------|------|-------------|------|
| | Initial | Aged | Initial | Aged | Initial | Aged | Initial | Aged | Initial | Aged |
| Control | 0.39 | 0.26 | — | — | — | — | — | — | — | — |
| TEODU | 0.51 | 0.33 | — | — | 0.47 | 0.22 | — | — | 0.79 | 0.41 |
| PPOTU (7.7 mol %) | 0.44 | 0.27 | 0.69 | 0.35 | — | — | 0.41 | 0.33 | — | — |
| PPOTU (4.4 mol %) | 0.55 | 0.33 | — | — | — | — | — | — | — | — |
| PPOTU (2.3 mol %) | 0.63 | 0.44 | — | — | — | — | — | — | — | — |

^a Units expressed in $\mu\text{g}/\text{mL}$. Approximate HUD limits is $1.1 \mu\text{g}/\text{mL}$.

number of compressed wood particles held together by a relatively small quantity of adhesive. Different particles in the bonded assembly have different sizes, orientations, and degrees of compression. Consequently, as the moisture content of the board cycles, the rates and levels of swelling and shrinking vary for different particles. We should therefore expect the stress developed in such a bonded assembly to be much higher than that in solid-wood joints where the bonded area and compression are smaller and orientations more ordered. The second factor is the difference in drying temperature between VPSD-1 for solid-wood (43°C) and VPSD-2 for particleboard (80°C). Irle and Bolton¹⁰ and Dinwoodie¹¹ argued that under mild soak-dry conditions mechanical rupture rather than hydrolytic degradation of adhesive bonds appears to be responsible for the loss in strength of UF-bonded particleboards. In the present case, however, the influence of bond hydrolytic scission would certainly be more pronounced at the higher drying temperature for particleboard; this plus the higher stress levels in particleboards would lead to a more rapid decline in the strength of particleboards than in solid-wood joints. A third factor contributing to the poorer performance of modified resins in particleboard is that the solid-wood joints were made within 1–2 months of resin synthesis, whereas the particleboards were made 6–7 months after synthesis. Despite storage of the resins in a refrigerator, that age difference could well have altered the resin structure and increased viscosity, resulting in decreased resin effectiveness.

The faster and greater strength loss of UF-bonded particleboard compared to PF-bonded boards has often been attributed to the lower resistance of UF resins to hydrolysis,^{12,13} and there is every reason to expect that some UF hydrolysis occurred during both the VPSD-2 cycles and the moist-heat aging employed here. However, from exposing UF and PF films to different environments and from the soak-dry treatment of particleboards made from these adhesives, Bolton and Irle^{10,14} concluded that the short-term room-temperature breakdown of UF-bonded particleboard cannot be due to hydrolysis. This conclusion is shared by Dinwoodie.¹¹ In further studies of the creep behavior of UF and PF films, Irle and Bolton¹⁵ showed that UF resins were considerably more rigid and crept less than did PF resins. They concluded, therefore, that higher stresses and lower stress relaxation would occur in UF-bonded boards than in PF-bonded boards.

A number of reports have also indicated reductions in the properties of UF-bonded plywood,¹⁶ particleboard,¹⁷ and UF films¹¹ as the F/U ratio de-

creases. The internal bond strength of UF-bonded particleboards depends largely on the strength of the adhesive and its bonding to wood; these, in turn, depend on the degree of hydrogen bonding between molecules and the condensation reactions between methylol and amide groups. As the F/U ratio decreases, the number of methylol groups and the free formaldehyde content of the resin decrease, leading to a decline in hydrogen bonding and cross-link density in the cured resin. Indeed, Horioka et al.¹⁸ suggested that methylol ureas create the adhesive bond between the resin and wood, whereas higher condensation products provide resin cohesion. The overall reduction in these reactions for lower F/U ratio resins translates into a higher moisture sensitivity of the bonded wood products.

CONCLUSIONS

We conclude from all our results to date that bonded wood products made with formaldehyde-to-urea (F/U) molar ratios 1.6 and 1.4 resins generally possess better durability than those made with F/U 1.2 resins, whether the adhesives are amine-modified or unmodified. However, particleboards made with the F/U 1.2 resins did meet the current formaldehyde emission standard, and we expect that adjusting resin synthesis conditions to reduce both buffer capacity and viscosity, coupled with the use of amino acids, Lewis acids, or organic acids as curing agents, will significantly improve the durability of products bonded with these resins.

Overall, the results support our hypothesis that the stability and durability of UF-bonded wood products can be enhanced by altering the structure to produce a more flexible cured network. That conclusion is supported by fracture analysis of solid-wood joints. The results reported here affirm that the most promising modifiers studied to date are as follows:

1. Urea-terminated amines with ammonium chloride curing agent:
 - a. linear, difunctional, aliphatic materials such as C-BHMTU and HMDU,
 - b. branched, trifunctional, aliphatic TEATU, and
 - c. branched, trifunctional, aliphatic ether PPOTU.
2. Hydrochloride salts of amines such as
 - a. aliphatic amine hydrochlorides, linear or branched, e.g., HMDA · 2HCl and TEATA · 3HCl, and

- b. branched, aliphatic ether amine hydrochloride, e.g., PPOTA · 3HCl.

We thank Texaco Chemical Co., the National Particleboard Association, Georgia Pacific Corp., and Borden, Inc., for financial support. We acknowledge the support of the Competitive Research Grants Office/USDA, Agreement 90-37291-5772. We also thank the National Particleboard Association for carrying out the formaldehyde measurements, E. Arnold Okkonen for preparing and testing the specimens and preparing the data, and Wesley Rork for preparing the specimens and analyzing the resin.

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Received June 9, 1993

Accepted August 2, 1993