Polyamine-Modified Urea–Formaldehyde-Bonded Wood Joints. III. Fracture Toughness and Cyclic Stress and Hydrolysis Resistance

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SYNOPSIS

The objective of this study was to improve the durability and stability of urea–formaldehyde-bonded wood products by decreasing the internal stress developed during the resin cure and by improving the ability of the cured system to withstand cyclic stresses. Urea–formaldehyde resins were modified either by incorporating urea-capped di- and trifunctional amines into the resin structure or by using the hydrochloride derivatives of some of these amines as the curing agent, or by both methods. This study supplements our previous work by examining the effects of additional amines and subjecting bonded products to additional testing. Solid wood joints bonded with a variety (7 of 15) of modified adhesives had resistance to cyclic stress superior compared to that of joints bonded with unmodified urea–formaldehyde adhesive; at least three of the modified adhesives approached the behavior of phenol–formaldehyde-bonded joints. Resistance to moist heat aging, although still inferior to that of phenol–formaldehyde-bonded joints, was significantly improved for joints bonded with modified adhesives over joints made with unmodified resins. The fracture behavior of joints made with modified adhesives was different from that of joints made with unmodified resins. The fracture energy was greater for joints made with three of four modified adhesives than for joints made with unmodified resins. Modified adhesives produced particleboards with enhanced cyclic stress resistance. Formaldehyde emission from particleboards made with resins modified with urea-terminated amines was less than emission from boards made with unmodified resins. However, emissions from particleboards made with amine hydrochlorides were not improved compared to those from boards made with an ammonium chloride curing agent. © 1993 John Wiley & Sons, Inc.†

INTRODUCTION

Large quantities of urea–formaldehyde (UF) resins are used by the forest products industry as adhesives in the production of wood products such as decorative plywood and particleboard. Phenol–formaldehyde (PF) resin is also a major wood adhesive. In some wood applications, replacement of PF resins by UF resins is desirable because UF resins result in lower bonding costs, are less sensitive to com-

mercial bonding variables, and are less dependent on petroleum. However, the poor durability and stability of UF-bonded wood products, particularly under cyclic moisture or warm and humid environments, limits them to interior nonstructural applications. The applicability of UF resins could be expanded if the durability of UF-bonded wood products could be improved.

In Parts I and II of this series, we described our approach to improving the durability of UF-bonded wood products and presented preliminary results that support this approach.[1,2] Our approach involves modifying UF resins by incorporating di- and trifunctional flexible amines into the resin to produce a cured system that possesses greater resistance to stress because of the increased flexibility and possibly more random distribution of cross-links. We
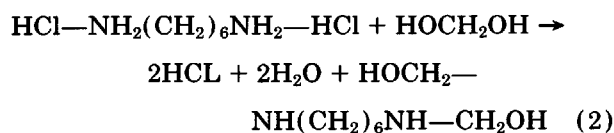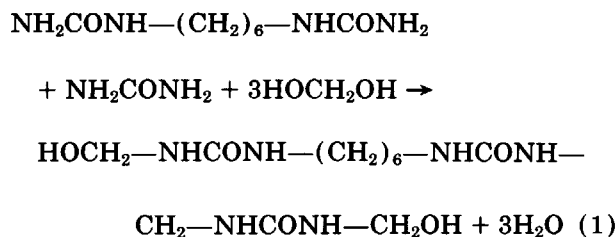
incorporated the amines in two ways: The urea-terminated amines were substituted for a small fraction of the urea during resin synthesis; eq. (1) illustrates the chemistry. Alternatively, the amine hydrochlorides were substituted for ammonium chloride prior to cure to provide a hydrogen chloride catalysis of the resin cure. The chemistry here is potentially more complex, but eq. (2) illustrates one possible reaction to produce hydrogen chloride and hydroxymethylamine, the latter then being free to react with amine functionalities on the resin:

$$NH_2CONH—(CH_2)_6—NHCONH_2$$

$$+ NH_2CONH_2 + 3HOCH_2OH →$$

$$HOCH_2—NHCONH—(CH_2)_6—NHCONH—$$

$$CH_2—NHCONH—CH_2OH + 3H_2O \quad (1)$$

$$HCl—NH_2(CH_2)_6NH_2—HCl + HOCH_2OH →$$

$$2HCL + 2H_2O + HOCH_2—$$

$$NH(CH_2)_6NH—CH_2OH \quad (2)$$

In Part III, we expand the scope of amine modifiers to provide several comparisons of structural effects, which could be expected to have different influences on resin properties such as flexibility, water sensitivity, and cross-linking efficiency. These include (a) the length of aliphatic backbone (materials a, b, and c in Table I), (b) aliphatic as opposed to aliphatic ether backbone (materials a, b, and c as opposed to d, e, and f in Table I), (c) length and type of ether backbone (materials d, e, and f in Table I), and amine functionality. Material b in Table I is also of interest because it is less pure than the others but is less costly. In addition, we expand the testing to include the following: (a) effects of the curing agent and modified resin on the cure rate

Table I Experimental Materials

Material	Source	Remarks
a. Hexamethylenediamine (HMDA)	DuPont Petrochemicals Wilmington, DE	
b. Bishexamethylenetriamine (C-BHMTA)	DuPont Petrochemicals	Brown viscous liquid with boiling point 249°C at 13.33 kPa and vapor pressure 0.93 kPa at 180°C
Triethylaminetriamine (TEATA, Tren)	W. R. Grace and Co., Organic Chemicals Division, Lexington, MA	High-purity grade with < 0.93 kPa, 2% ethylene amine
Triethyleneoxidediamine (TEODA, Jeffamine EDR 148)	Texaco Chemical Co. Bellaire, TX	Liquid with viscosity 0.008 Pa-s at 25°C, total amine 13.5 meq/g, molecular weight about 148
d. Poly(propylene oxide)triamine (PPOTA, Jeffamine T-403)	Texaco Chemical Co.	Pale yellow liquid, viscosity 0.07 Pa-s at 25°C, total amine 6.4 meq/g, molecular weight about 440
e. Poly(ethylene oxide)diamine (PEODA-11, Jeffamine ED 600)	Texaco Chemical Co.	Liquid at 27°C, viscosity 0.072 Pa-s at 20°C, total amine 97.5 wt % or 3.19 meq/g, molecular weight about 600
Poly(propylene glycol)diamine (PPGDA-3, Jeffamine D230)	Texaco Chemical Co.	Liquid at 27°C, molecular weight about 230, total amine 8.4 meq/g
f. Poly(propylene glycol)diurea (PPGDU-33, Jeffamine BuD-2000)	Texaco Chemical Co.	Urea condensate of poly(propylene glycol)diamine, light yellow, viscosity 22 Pa-s at 77°F, total amine 0.01 meq/g, molecular weight about 2075
c. Dodecanediamine (DDDA)	DuPont Petrochemicals	White crystalline solid, melting point 71°C, molecular weight 200, amine value 553
Paraformaldehyde	Aldrich Chemical Co. Milwaukee, WI	95%, melting point 163–165°C
Urea	Aldrich Chemical Co.	Melting point 134°C
Ammonium chloride	Aldrich Chemical Co.	Moist white crystals, 97%, melting point 119–121°C
Ammonium oxalate	Aldrich Chemical Co.	White crystals, monohydrate 99%+, ACS grade

by measuring rates of acid liberation caused by the reaction of the curing agents (ammonium chloride and amine hydrochlorides) with formaldehyde; (b) extractable content (sols) of cured resins; (c) mechanical properties of both solid-wood joints and particleboards during moist heat aging; (d) fracture energy of bonded-wood joints; and (e) formaldehyde emission of particleboards. All research to date has concerned modified resins with an effective 1.6 mol ratio of formaldehyde to urea.

EXPERIMENTAL

Materials and Synthesis

The chemicals employed are described in Table I. As in Parts I and II, we used code names; for example, hexamethylenediamine is HMDA, and crude BHMTA is C-BHMTA (Table II). For urea-capped amines, the final A in the code name is replaced by U; for example, HMDA becomes HMDU and C-BHMTA becomes C-BHMTU. The hydrochloride salts of the amines are designated, for example, as HMDA · 2HCl and TEATA · 3HCl. The preparation of concentrated aqueous formaldehyde has been described.[1]

Urea Derivatives of Amines

The amines were liquids or a low-melting solid (HMDA), except for DDDA—a solid with a melting point of 71°C, which required a different procedure for making the urea-capped amine. Crude bishexamethylenetriamine (C-BHMTA) was an impure mixture. For the reaction of C-BHMTA with urea, we assumed that only primary amine functions in the mixture were reactive and that composition was an average of the weight percent range. This led to an average effective equivalent weight of 95 (Table II).

As in Part II, all urea derivatives were made in the presence of the total urea to be used in the subsequent resin synthesis.[2] Except for poly(ethyleneoxide)diamine (PEODA-11) and poly(propyleneglycol)diurea (PPGDU-33), the amines constituted about 8 mol % of the total urea (free urea plus urea in the derivative). Because of their higher molecular weights, PEODA-11 and PPGDU-33 were added at about 2 and 0.5 mol % of the urea, respectively, to restrict the weight substitution of amine. The weight substitutions ranged from 15 to 38% (Table III).

Liquid or Low-Melting Solid Amines. The process for making the urea-capped amine deriva-

Table II   Composition of Crude Bishexamethylenetriamine

Compound	Wt %
Bishexamethylenetriamine (BHMTA)	30–50
Oligomeric amines	10–35
C_{10} amines	10–15
Hexamethylenediamine	7–9
Caprolactam	5–8
6-Aminocapronitrile	1–7
Water	0.5–1.0
Other organics	2–5

tives differed somewhat from the process described previously.[1,2] The appropriate amounts of amine and urea (for a total amount of 2000 g urea-capped amine plus urea) were charged into a reaction kettle equipped with a mechanical stirrer, 150 g of water was added, and the mixture was heated slowly. In most cases, vigorous reflux was observed between 110 and 120°C, and the product began to precipitate soon thereafter. At that point—instead of refluxing for 4–5 h as in previous work—the mixture was poured into a Teflon-coated pan and cooled to room temperature. The precipitate was broken into smaller pieces and dried to a constant weight at 50–60°C in a vacuum oven at about 0.1 MPa.

Solid Dodecanediamine. In this case, about 1000 g urea, 300 g DDDA, and 500 g H_2O were charged into the reaction kettle and heated slowly. When the mixture went into solution, the remaining urea and DDDA (for a total of 2000 g urea-capped amine plus urea) were added gradually while maintaining the fluidity of the mixture. When all the urea and DDDA were added, the solution was heated and maintained at the reflux temperature (110°C) until the product started to precipitate; then the solution was poured into a Teflon-coated pan and cooled.

Hydrochloride Derivatives of Amines

The hydrochloride derivatives of hexamethylenediamine (HMDA 2HCl) and triethylaminetriamine (TEATA · 3HCl) were prepared according to Farlow[3] by adding concentrated HCl to the amine in methanol and precipitating the solid derivative in acetone. For PPOTA and TEODA, preliminary trials using the same procedure showed that no precipitate was formed on adding acetone. Therefore, concentrated HCl was added directly to the liquid amine and the excess acid subsequently removed under vacuum and heat (50–65°C).

Table III Composition of Urea and Urea-derivative Mixtures

| | Urea Substitution[a] | |
Amine	Mol %	Wt %
Hexamethylenediamine (HMDA)	8.33	14.9
Bishexamethylenetriamine (C-BHMTA)	8.33	22.3
Dodecanediamine (DDDA)	4.55	13.7
Poly(propylene oxide) triamine (PPOTA)	7.69	37.9
Poly(ethylene oxide)diamine (PEODA-11)	2.38	19.6
Poly(propylene glycol)diurea[b] (PPGDU-33)	0.50	15.0

[a] Percentage of total urea expressed as amine.
[b] Obtained as a urea derivative from the manufacturer.

Resins

All laboratory resins were synthesized by adding the urea (or the combined urea and urea-capped amine) in two steps (Table IV). The first step yielded an effective formaldehyde-to-urea mole ratio (F/U) of 2.0, and the second step yielded a final F/U of 1.6. Procedures for synthesis and characterization were reported previously.[1,2]

In DDDU-modified resins, the DDDU/urea mixture did not dissolve completely during the first or second addition. We avoided this problem by reducing the DDDA substitution for urea from the usual 8 mol % to 4.6 mol % (Table III), adding all the DDDU/urea mixture in the first addition at F/U 2.0 and adding only urea in the second addition.

Four unmodified resins were used for comparison: a laboratory-prepared UF resin at F/U 1.6 (denoted control), two Neste commercial UF resins (denoted Neste 1.2 and Neste 1.6), and a commercial Borden PF. Initial pH, viscosity, solids content, and free formaldehyde values of the unmodified and modified resins are given in Table V.

Chemical Properties of Adhesives

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermograms were obtained on various resin-curing agent combinations using a Perkin-Elmer DSC-2[†] at a

[†] 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.

heating rate of 20 K/min from 300 to 480 K in hermetically sealed capsules.

Rate of pH Change

Resin (20 g) was weighed into a test tube that was then placed in a constant temperature water bath and allowed to equilibrate for about 20 min. A five weight percent curing agent was added to the resin, and the mixture was stirred vigorously for 3–5 min. The pH of the mixture was measured at intervals until gelation occurred. Measurements were made at 25, 35, 45, and 60°C for several resin-curing agent combinations.

Extraction of Cured Resin

Resin (10 g) was mixed with 5 wt % of the curing agent. The adhesive was spread thinly in a 380 by 200 mm Teflon-coated aluminum pan. After about 10 min exposure in a hood, the pan was placed in an oven with the temperature preset at the DSC exotherm peak of the adhesive (Table VI). The adhesive was cured for 10 min, ground, and sieved (U.S. Standard Sieve Series No. 40, 35 mesh).

Extractions were performed with tetrahydrofuran (THF) because it is a good solvent for uncured UF resins, and urea-capped amines and amine hydrochlorides are easily soluble in THF. The cured, sieved resin (5 g) was weighed into a bottle, and 25 mL of THF was added. The bottle was capped, placed on a shaker, and agitated for 48 h. The extract was carefully decanted, 25 mL of fresh THF was added, and the agitation was repeated for another 48 h. The second extract was carefully decanted and added to the first, and the solution was centrifuged at 333 rad/s for 15 min to remove any suspended particles. The solvent was allowed to evaporate in a laboratory hood, and the residue (sol) was then dried at room temperature under vacuum. The extracted, cured resin (gel) was washed several times in a vacuum funnel with acetone and vacuum-dried at room temperature to constant weight.

Preparation of Bonded Joints and Particleboard

To demonstrate the improved performance resulting from amine modification of resins, solid-wood joints and particleboards were made with both modified and unmodified resins and subjected to various accelerated aging treatments.

Solid-Wood Specimens

Hard maple (*Acer saccharum*, Marsh.) lumber was selected for straightness of grain and freedom from

Table IV   Composition of Resins

Component	Control	PEODU-11	PPOTU	HMDU	C-BHMTU	PPGDU-33[b]	DDDU[c]
				Wt %[a]			
Formaldehyde[d]	44.93	39.30	30.62	39.75	37.47	41.87	40.71
Urea + derivative 1st addition	44.93[e]	49.50	56.60	49.15	51.01	48.67	50.10
Urea + derivative 2nd addition	11.20	12.78	11.10	11.52	9.46	9.46	9.19

[a] Based on total resin solids.
[b] Urea/PPGDU-33 = 41.67/7.00; 2nd addition = urea only.
[c] Urea/DDDU = 34.36/15.74; 2nd addition = urea only.
[d] CH_2O solution = 47.81%.
[e] Urea only.

growth defects. The grain direction and straightness were determined with a scratching device that follows the wood fiber direction. The lumber was conditioned to an equilibrium moisture content (EMC) of 6% at 27°C and 30% relative humidity (RH).

Shear Block Substrates. Hard maple pieces (8 by 64 by 300 mm) were cut with grain parallel to the 64 by 300 mm surface, and shear block substrates were made by edge gluing four of these pieces. Just before bonding, one surface of each substrate was carefully jointed on a sharp three-blade, hand-fed jointer. Then, the substrate was abrasively planed on the opposite surface to a uniform 6.5 mm thickness. Two such substrates were prepared for each adhesive (resin-curing agent combination).

Fracture Toughness Substrates. Two hard maple substrates (8 by 127 by 356 mm) were carefully cut so that the grain was at a 5°–7° angle with the 127 by 356 mm surface. Bonding two such substrates at that surface yields a V-shaped grain configuration bisected by the bondline and pointing in the direction of crack travel. This specimen configuration ensures that the growing crack remains in or near the bondline rather than deviating into the wood.

Just before bonding, one surface of each substrate was carefully jointed with the grain on a sharp three-blade, hand-fed jointer. The opposite side of the substrate was then abrasively planed to achieve a uniform 6.5 mm thickness. Two fracture toughness substrates were prepared for each adhesive (resin-curing agent combination).

Adhesive Preparation and Bonding. The adhesive mixtures were prepared by thoroughly stirring 5.0 wt % of the curing agent (ammonium chloride or amine hydrochloride) into an appropriate amount of resin. The adhesive was applied at the rate of 200–250 g/m². Ten minutes of open assembly and 2 min of closed assembly time were allowed. The adhesive assemblies were placed in a press heated by circulating hot oil and bonded under 0.7 MPa pressure. The platen temperature for assem-

Table V   Initial Resin Properties

Resin	pH	Viscosity[a] (Pa-s)	Solids Content (%)	Free Formaldehyde (%)
Control	7.78	0.25	56	0.44
PEODU-11	7.88	0.33	59	0.63
PPOTU	8.06	2.25	66	0.26
HMDU	7.93	0.56	59	0.41
C-BHMTU	7.86	0.42	60	0.33
PPGDU-33	7.95	0.70	57	0.45
DDDU	7.89	1.67	58	0.35
Neste (1.6)	7.80	0.22	67	0.40
Neste (1.2)	8.50	—	65	0.10

[a] Viscosity at 25°C.

Table VI Exotherm Parameters from Differential Scanning Calorimetry

Modified Resin	DSC Parameter	Curing Agent[a]		
		NH$_4$Cl	TEATA · 3HCl	HMDA · 2HCl
Control	H_c[b]	35	37	27
PEODU-11		33	35	21
PPOTU		63	64	63
HMDU		48	43	35
C-BHMTU		44	43	35
PPGDU-33		26	30	18
DDDU		42	40	29
Neste 1.6		95	91	80
Control	R_c[c]	0.35	0.28	0.29
PEODU-11		0.28	0.26	0.24
PPOTU		0.65	0.43	0.52
HMDU		0.54	0.40	0.38
C-BHMTU		0.41	0.33	0.34
PPGDU-33		0.31	0.31	0.27
DDDU		0.45	0.29	0.36
Neste 1.6		0.85	0.69	1.07
Control	T_p[d]	374	375	383
PEODU-11		375	377	384
PPOTU		375	374	382
HMDU		374	374	382
C-BHMTU		378	378	386
PPGDU-33		378	377	384
DDDU		378	378	380
Neste 1.6		369	367	375

[a] 5% of total resin.
[b] H_c = exotherm heat (J/g resin solids).
[c] R_c (J/g/min) = H_c/time span of exotherm.
[d] T_p = exotherm peak temperature (K).

blies made with a given adhesive was set to produce a bondline temperature approximately equal to that of the adhesive DSC exotherm peak temperature (Table VI) within 4–6 min. The total pressing time was fixed at 10 min; therefore, the bondline was maintained at or greater than the DSC peak exotherm temperature for 6 to 4 min before removing the bonded assemblies from the press.

The PF adhesive was applied to the substrates at the same rate as was the UF adhesive. The PF adhesive was allowed 0 min open assembly and 25 min closed assembly time before bonding. The PF assemblies were bonded under 0.7 MPa pressure and 130°C platen temperature for 15 min.

In all cases, bonding was performed within 24 h of surfacing the substrates. The bonded assemblies were reconditioned to EMC at 27°C and 30% RH before cutting the individual specimens.

Particleboard

Particles of Southern Pine (*Pinus* spp.) were screened to remove fines and large chunks and then dried to 2.0–2.4% moisture content (MC). Adhesive was sprayed on this furnish in a small laboratory blender to a level of 7% by weight (resin solids basis). Sufficient water was also sprayed on the furnish to increase the moisture content to about 10% (oven-dry basis). Half the sprayed furnish was transferred through a vibrating screen (6 mm mesh) to a 0.5 by 0.5 m forming box, ensuring a uniform distribution of the particles. A thermocouple was positioned at the center of the mat, and the remaining half of the furnish was then added. The mat was pressed in a circulating oil-heated hot press. The space between the platens was controlled by computer to achieve a final board thickness of 12 mm. The platens were

heated to a temperature that would allow the mat core to reach the DSC exotherm peak temperature (Table VI) in 4–6 min. Total heating time was 10 min. After bonding, the particleboard panels stood in vertical racks for 3 days in a well-ventilated room at about 25°C and 65% RH. Panels were then cut into specimens for the various tests.

The conditions for making the PF-bonded particleboards were the same as that for the UF-bonded particleboards except that the platen temperature was elevated to 177°C.

Specimen Preparation

The procedure for cutting specimens differed for the shear block and fracture toughness tests.

Shear Block. Approximately 35 mm were trimmed from all bonded assemblies to avoid edge effects. Each assembly yielded 30 small shear block specimens with a 25.4 by 25.4 mm bond area. This specimen was developed by Strickler[4] for durability testing and is modeled after the standard shear block specimen.[5]

Fracture Toughness. Each bonded assembly was ripped into six strips 16 mm wide and 356 mm long. Subsequently, each strip was bonded with epoxy resin between two contoured members made from 16 mm-thick oriented strandboard (OSB). The fracture toughness specimen formed a contoured double cantilever beam (CDCB) (Fig. 1) developed at the USDA Forest Service, Forest Products Laboratory.[6]

Internal Bond Strength and Thickness Swell. The outer 50 mm of each particleboard panel was trimmed before cutting specimens. A por-

tion of each trimmed panel was cut into 50 by 50 by 13 mm-thick specimens according to the ASTM standard for testing the internal bond (IB) strength of particleboard.[7] The same specimens served for thickness swelling measurements. The remainder of each panel was cut into specimens for determining the bending properties and formaldehyde emission.

Formaldehyde Emission. The standard desiccator test for formaldehyde emission (FMT-1)[8] requires eight 70 by 127 mm specimens having a total face area of 0.142 m². The amount of experimental material available limited us to three 70 by 127 mm plus two 61 by 146 mm specimens (0.088 m² face area). Immediately after cutting, the specimens were wrapped in plastic and shipped to the National Particleboard Association (NPA) for formaldehyde emission testing.

Treatment and Aging of Bonded Specimens

Vacuum-Pressure Soak–Dry Treatment

Slightly different vacuum-pressure soak–dry (VPSD) treatments, VPSD-1 and VPSD-2, were used for solid-wood and for particleboard specimens, respectively.

Each VPSD-1 cycle consisted of submerging specimens in cold water for 30 min at about 0.1 MPa vacuum, then for 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 specimens of each adhesive were allocated to each of one, two, five (or six), or 10 treatment 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 specimens of each adhesive type were allocated to each of one, two, six, and 10 treatment cycles. An additional set of four specimens was left untreated to serve as controls.

Moist Heat Aging

Moist heat aging was used only for solid-wood shear block specimens. This accelerated aging treatment consisted of exposure to constant 70°C and 80% RH conditions for up to 40 days. The treatment was conducted in an environmental chamber equipped with a rotating rack to ensure evenly aged specimens. Groups of four specimens of each adhesive type were allocated to each of 2, 10, 20, or 40 days of moist heat aging.
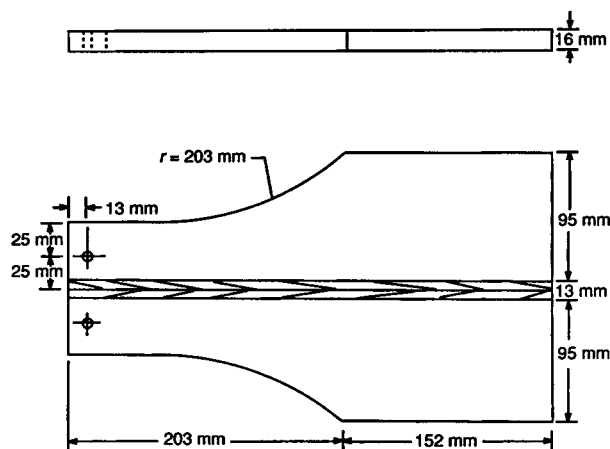

Figure 1 Contoured double-cantilever beam fracture specimen.

Specimen Tests

After treatment or aging, all types of specimens were equilibrated again to 6% MC before testing. All mechanical testing was performed on a Riehle/Ametek universal testing machine.

Shear Block

The solid-wood shear block specimens were tested according to standard test method D 905.[5]

Fracture Toughness

The solid-wood CDCB specimens were loaded by a tensile force applied at 0.5 mm/min to the narrow ends of the two contoured members so that they acted as short cantilever beams (Fig. 1). The result of this force was a tensile or cleavage stress (Mode I fracture) at the bondline crack in the maple test strip causing intermittent growth of the crack. Therefore, we measured a series of crack initiation loads and the related loads at which the crack arrested. Detailed procedures for the test and calculations are described elsewhere.[6,9,10]

Internal Bond Strength and Thickness Swell

The strength of the particleboard perpendicular to the plane of the panel was determined by the standard test method D 1037.[7] Bending strength and stiffness were also measured but are not reported because they mirrored the IB results. The residual thickness swelling of the particleboard after swelling and redrying was also measured on the specimens used for the IB test.

Formaldehyde Emission

Specimens were sent to the NPA to determine the formaldehyde emission value by the standard 2 h desiccator test (FMT-1).[8] Before determining the emission, each specimen was edge-coated with wax and conditioned for 24 h in a room at $24 \pm 3°C$, 50 $\pm$ 5% RH with an ambient formaldehyde concentration ≤ 0.1 part per million. After the initial emission value was obtained, the specimens were reconditioned for 30 days, and the emission value was determined again.

RESULTS AND DISCUSSION

Chemical Properties

Differential Scanning Calorimetry

Differential scanning calorimetry thermograms were run routinely on all resin-curing agent combinations to measure relative reactivity and to identify any adhesive systems that might be difficult to cure. The DSC exotherms were similar in shape to those reported previously,[1] so we present here only some general observations of the behavior of several resin-curing agent combinations (Table VI). We defined the cure rate as the rate of heat evolution during cure (R_c), that is, the ratio of the exotherm heat (H_c) to exotherm time span (t_c). Based on these definitions, we made the following observations:

1. The cure rate for a given resin mixed with NH_4Cl was greater than that with $TEATA \cdot 3HCl$, and the latter was usually similar to the cure rate with $HMDA \cdot 2HCl$. On the basis of higher exotherm peak temperature (T_p), however, $HMDA \cdot 2HCl$ was clearly less active than the other two curing agents.
2. For a given curing agent, the order of resin reactivity based on rate of heat evolution was Neste 1.6 $\gg$ PPOTU > HMDU $\gg$ C-BHMTU > DDDU > control > PEODU-11 > PPGDU-33. On the basis of exotherm peak temperature (T_p), the distinctions were not as great, but cure activity for all three curing agents fell in a different order: Neste 1.6 $\gg$ (HMDU, PPOTU, control) > (PEODU, PPGDU, C-BHMTU, DDDU).

Rate of pH Change

We postulated previously[1,2] that the improved performance of some modified adhesives was partially due to a more controlled cure rate and consequent achievement of a less stressed, more random network. In these adhesives, the resin cure is catalyzed by the low pH resulting from the HCl liberated by two processes: (1) formaldehyde reaction with the ammonium chloride or amine hydrochloride curing agents and (2) curing agent dissociation. Therefore, the rate of cure is affected by the amount of free formaldehyde in a resin and the structure of both curing agent and resin. To further clarify the relative effectiveness of these adhesives, we measured rates of pH decrease for ammonium chloride and $HMDA \cdot 2HCl$ combined with several resins in water.

Figure 2 illustrates the observed changes in pH with time for different adhesives at 25°C. At all temperatures studied (25, 35, 45, and 60°C), we fitted the linear portion of each curve to a straight line by linear regression. The resultant slopes were treated as constant rates of pH decrease at a given

temperature. Arrhenius plots of these rate constants led to apparent activation energies and preexponential factors for the process. Table VII gives the measured rates; Table VIII gives the Arrhenius parameters and the rates of pH decrease calculated at the respective DSC exotherm peak temperatures for each adhesive.

At lower temperatures, measured rates for resins containing HMDA · 2HCl were lower than for those containing NH$_4$Cl. However, the rates for HMDA · 2HCl-cured adhesives had a greater temperature sensitivity (higher activation energies) than did the rates for NH$_4$Cl-cured adhesives.

Therefore, when we extrapolated the rates to actual resin cure temperatures (DSC peak exotherm temperature), we found a more rapid pH decrease for HMDA · 2HCl-cured adhesives than for the NH$_4$Cl-cured adhesives. This last finding clearly disagrees with the order of the cure rates established by the DSC-derived parameters. For example, the cure rates (R_c) were lower and the peak exotherm temperatures (T_p) were higher for control, PEODU, and PPOTU when cured with HMDA · 2HCl than when cured with NH$_4$Cl (Table VI). Moreover, for a given curing agent, the DSC-derived cure rates for the three different resins did not follow the same order as that of the extrapolated rates from the pH change. Assuming that the extrapolations are valid, these differences indicate that the cure rate is controlled not just by the rate of pH decrease but also by the resin and curing agent structure.

Soluble Fraction of Cured Resin

Room-temperature THF extraction of cured adhesives dissolved only small amounts of the resins, from 1.0 to 4.4% (Table IX). Even the more aggressive Soxhlet extraction resulted in soluble fractions that were insignificantly higher. This suggests that the amines are almost completely incorporated into the resin structure and that a high degree of cure is achieved under the curing conditions used.

Physical Properties

Because resin quantities were limited and these experiments were regarded as screening efforts, only three specimens were tested to arrive at each data point in the figures. For solid-wood joints, standard deviations from the three 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 testing, 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 the other groups, using a two-standard-deviation spread as an approximate criterion.
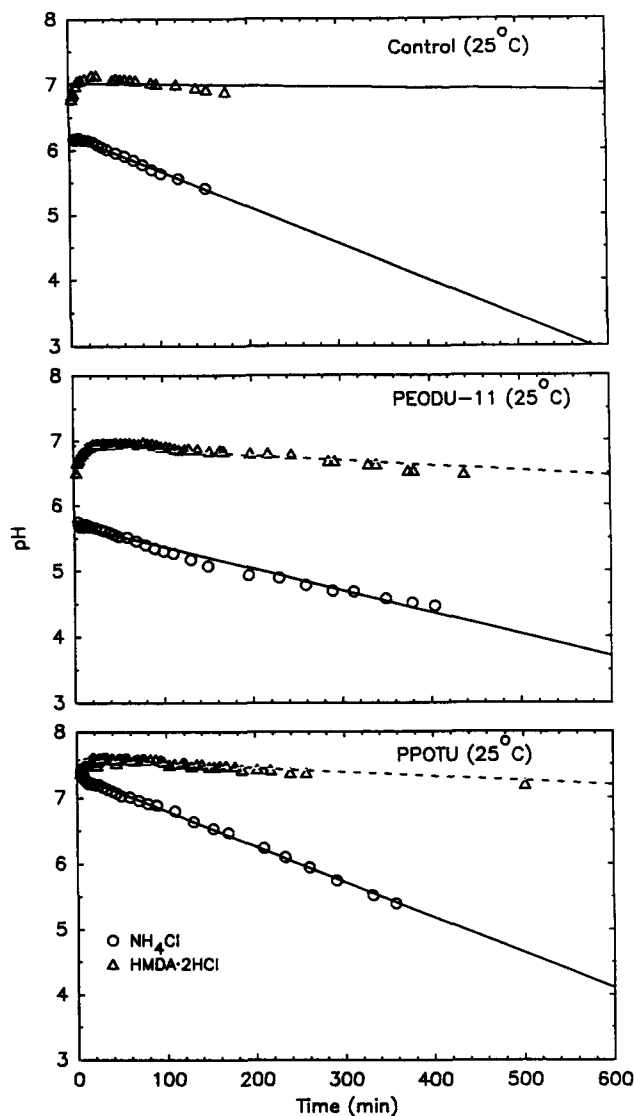

Figure 2 Rate of pH decrease with time at 25°C for unmodified and modified UF resins with ammonium chloride and amine hydrochloride curing agents.

Cyclic Soak–Dry Effects on Solid-Wood Joints

Figures 3 and 4 summarize our new observations on the effects of cyclic VPSD-1 treatment on the shear

Table VII Rate of pH Decrease during Cure for UF Adhesive Systems

| | pH Decrease Rate $\times$ 10^5 (s^{-1}) | | | | | |
| | Control | | PEODU | | PPOTU | |
Temperature (°C)	NH$_4$Cl	HMDA $\cdot$ 2HCl	NH$_4$Cl	HMDA $\cdot$ 2HCl	NH$_4$Cl	HMDA $\cdot$ 2HCl
25	9.3	0.4	5.4	1.3	9	1.1
35	22	5.1	12	3.4	28	5.8
45	52	40	52	40	79	24
60	223	234	186	173	307	155

strength of solid-wood joints. In general, the results are consistent with those reported previously.[1,2] The unmodified (control and Neste 1.6) resins cured with NH$_4$Cl (Fig. 4, bottom) suffered extensive strength loss in the soak–dry treatment as they did in previous experiments. Several adhesives modified with the new amines were very resistant to the soak–dry treatment, some even equaling the performance of PF-adhesive-bonded joints. More specifically, we note the following:

1. With NH$_4$Cl as the curing agent, joints bonded with C-BHMTU-modified adhesive were marginally improved compared to unmodified (control and Neste 1.6) adhesive in resistance to cyclic stress (Fig. 3, top). Joints

Table VIII Arrhenius Parameters for Rate of pH Decrease and Estimated Rate at DSC Peak Exotherm Temperature

| Resin and Curing Agent | Parameter | | |
	E^a	ln A^b	S^c
Control			
NH$_4$Cl	62	16.0	0.02
HMDA $\cdot$ 2HCl	92	21.9	0.10
PEODU			
NH$_4$Cl	74	19.9	0.03
HMDA $\cdot$ 2HCl	103	30.6	0.18
PPOTU			
NH$_4$Cl	71	19.7	0.04
HMDA $\cdot$ 2HCl	100	29.3	0.09

[a] Apparent activation energy (kJ/mol) from Arrhenius equation fitted to data in Table VII.

[b] Preexponential constant (s^{-1}) from Arrhenius equation fitted to data in Table VII.

[c] S = estimated rate (s^{-1}) at DSC peak temperature, calculated from E and ln A.

bonded with DDDU- and PPGDU-modified resin cured with NH$_4$Cl were severely degraded during the VPSD treatment (Fig. 3, top; DDDU not shown). The relatively poor performance of the PPGDU-modified resin adhesive was probably caused by the small molar amount of amine modifier used. As a result of its high molecular weight (compare in Table I), PPGDU was present in the resin at only 0.5 mol % relative to urea. In contrast, 2–8 mol % was used with the other modifiers, which have much lower molecular weights.

2. With the exception of PPGDU/TEATA $\cdot$ 3HCl, curing with either HMDA $\cdot$ 2HCl or TEATA $\cdot$ 3HCl enhanced the resistance of joints bonded with UF adhesives, whether the resin was modified or not modified. Joints bonded with these adhesives retained 70–100% of their original strength (Fig. 3, middle and bottom).

3. Joints bonded with modified resins cured with amine hydrochloride curing agents (Fig. 4, bottom) and joints of unmodified commercial resin cured with C-BHMTA $\cdot$ 2HCl (Fig. 4, top) approached the performance of joints bonded with PF adhesive.

4. Curing with adipic acid or ammonium salts of formic and oxalic acids produced good cyclic stress resistance with some resins. However, the fracture surfaces of adhesive layers cured with ammonium formate were heavily laced with bubbles, which certainly would detract from the strength. The cured adhesive also emitted an offensive odor, presumably arising from decomposition products of the heat-sensitive ammonium salt. Moreover, adipic acid and ammonium oxalate dissolved poorly in some of the resins. Therefore, these systems were not studied further.

Table IX   Soluble Fraction of Cured Resins

Curing Agent	Soluble Fraction (wt %)[a]						
	Control	PEODU-11	PPOTU	HMDU	C-BHMTU	PPGDU-33	DDDU
NH₄Cl	1.2	1.4	1.6	3.0	2.4	4.4	1.4
	(2.0)		(1.7)				
TEATA·3HCl	1.2	1.2	1.4	2.2	2.2	2.8	2.4
HMDA·3HCl	1.2	1.4	1.0	1.4	1.2	1.2	1.2
PPOTA·3HCl	2.8	2.8	2.0	2.2	2.6	3.4	2.4

[a] Extraction with THF at room temperature; values in parentheses from Soxhlet extraction with THF.

Fracture Behavior of Solid-Wood Joints

The strain energy release rate (fracture energy) at crack initiation (G_{I_c}) and arrest (G_{I_a}) were calculated from the observed loads at crack initiation and arrest. The brittleness index (I) is further calculated from the expression $(G_{I_c} - G_{I_a})/G_{I_c}$. Table X summarizes these fracture parameters for several adhesives cured at their respective DSC exotherm peak temperatures. For each of the two curing agents, fracture energy of specimens bonded with modified UF resins (except for HMDU-modified resin) was greater than that of specimens bonded with the unmodified UF resins (control and Neste 1.6) and the PF resin. Moreover, for a given resin, the fracture energy was greater with TEATA·3HCl curing agent than with NH₄Cl. Except for DDDU, the brittleness indices (I) were also greater with the TEATA·3HCl curing agent.

High fracture energy means that a large amount of energy is required to initiate crack growth, and this suggests the existence of a good joint. The formation of a good joint depends upon obtaining adequate penetration of the wood and good adhesion between the adhesive and adherends—in other words, a strong continuous interphase between the bulk adherend and the bulk adhesive. A good joint is also characterized by a continuous film of solid adhesive between the two interphases. As noted elsewhere,[9-11] when the adhesive bond is such that wood failure, even though shallow, is induced, the resulting fracture energy is always high. Microscopic examination of the fracture surfaces from these joints revealed the following:

1. The control and Neste 1.6 resins cured with NH₄Cl had large populations of preexisting cracks in both the adhesive and the interphase, resulting from adhesive shrinkage
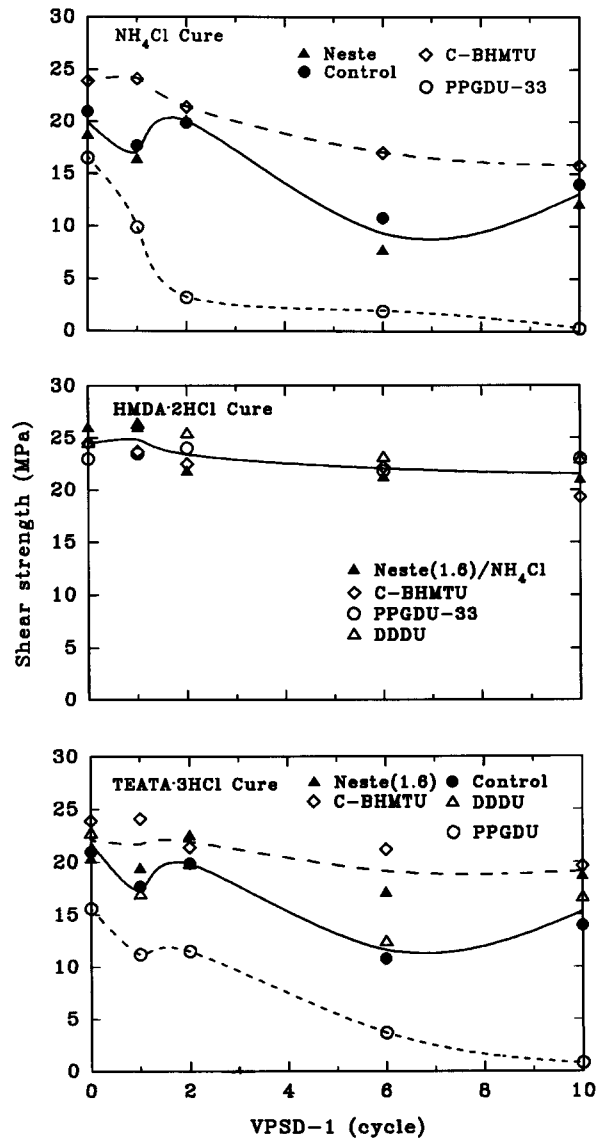

Figure 3   Effect of cyclic vacuum-pressure soak–dry treatment (VPSD-1) on strength of maple shear blocks bonded with selected adhesives.
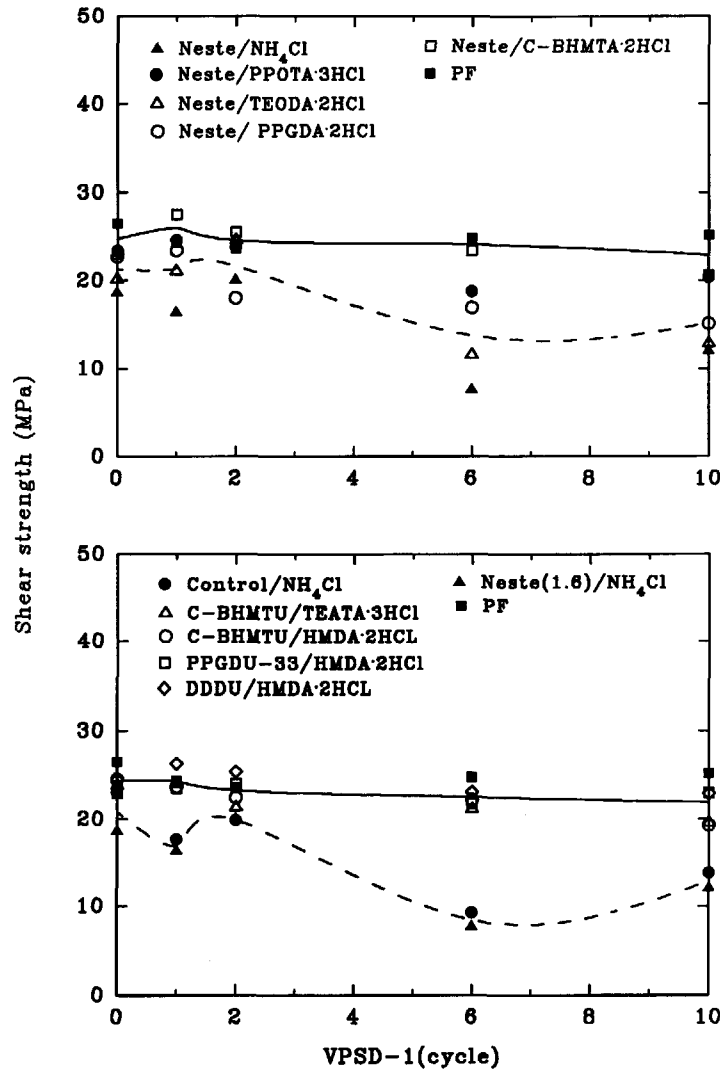
Figure 4 Comparison of amine-modified and unmodified UF adhesives in maple shear blocks under cyclic soak–dry treatment (VPSD-1) to PF-adhesive-bonded blocks.

during cure. Joints bonded with these adhesives failed in a weak boundary layer of the adhesive or in weakened surface cells, and the main crack frequently jumped from one interphase to the other through the preexisting shrinkage cracks in the adhesive layer.

2. Shrinkage cracks were much fewer in modified adhesive layers than in unmodified adhesive layers. Failure of joints bonded with the modified resins cured with NH_4Cl was still largely within the interphase, but the crack jumped from interphase to interphase less frequently because the relative absence of preexisting cracks in the adhesive layer hindered the jump.

3. In joints derived from resins cured with TEATA·3HCl, the main crack was frequently in the wood near the interphase and crossed between adherends in the manner of item 2 above.

The NH_4Cl-cured control and Neste 1.6 resin produced a discontinuous adhesive layer resulting from the cracks that occurred as the adhesive cured and shrank. Under load, these discontinuities may be of a critical size, leading to crack initiation. They may also act as crack diverters. In either case, these discontinuities provide an easy path for the growing crack to oscillate back and forth from one interphase

Table X   Fracture Characteristics for Adhesive Systems Cured at DSC Exotherm Peak Temperatures

Resin	NH$_4$Cl			TEATA · 3HCl		
	G_{I_c}[a]	G_{I_a}[a]	I[b]	G_{I_c}[a]	G_{I_a}[a]	I[b]
HMDU	133	104	0.22	175	101	0.43
C-BHMTU	234	179	0.23	223	137	0.40
PPGDU-33	231	197	0.15	247	160	0.36
DDDU	281	155	0.45	378	247	0.35
Control	139	114	0.16	196	127	0.35
Neste (1.6)	156	122	0.22	188	115	0.39
PF	169	111	0.34	—	—	—

[a] Strain energy release rate (J/m^2). G_{I_c} is crack initiation; G_{I_a} is crack arrest.
[b] I is brittleness index $(G_{I_c} - G_{I_a})/G_{I_c}$.

to the other in search of the weakest zone through which to propagate, thus encouraging crack growth. The fracture energies of joints made with these adhesives were therefore relatively low, and crack growth was stable (low I values).

In contrast to joints made with NH$_4$Cl-cured adhesives, the relatively continuous nature of TEATA · 3HCl-cured adhesive layers, coupled with apparently adequate penetration and bonding (strong, undamaged interphase), required increased energy to initiate cracks and led to wood failure. The larger I values of joints made with TEATA · 3HCl-cured adhesives means that the cracks propagate further before being arrested, but this difference may simply be a result of more stored

energy in the bonded system before crack growth initiates.

Thus, we conclude that modification with amines prevents or reduces cure shrinkage stress cracking, thereby eliminating or reducing the number of preexisting flaws that facilitate crack-growth initiation. Modification also inhibits the tendency of a growing crack to jump from one interphase to the other in search of the weakest zone through which to propagate.

Moist Heat Aging Effects on Solid-Wood Joints

Figure 5 shows the moist heat aging behavior of several modified UF adhesives compared to joints of
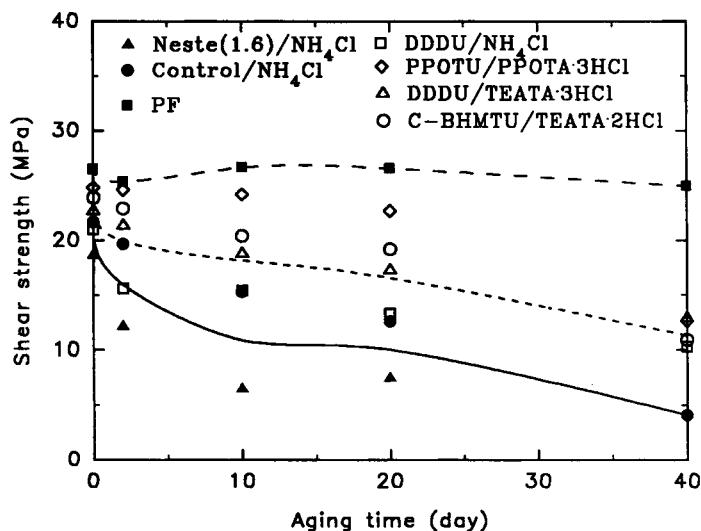

Figure 5   Effect of moist heat aging at 70°C and 80% RH on the strength of maple shear blocks bonded with C-BHMTU- and DDDU-modified UF adhesives.

PF and unmodified UF adhesives. All UF adhesives showed significant reductions in strength after 40 days at 70°C and 80% RH in contrast to the PF-bonded joints. Nevertheless, joints of several modified UF adhesives possessed superior resistance to extended moist heat exposure compared to those of the control and Neste 1.6 resins cured with NH₄Cl.

Some adhesives with good cyclic stress resistance, such as PPGDU-33/HMDA·2HCl, DDDU/HMDA·2HCl, and C-BHMTU/HMDA·2HCl (Fig. 4), fared poorly in moist heat aging (data not shown). Thus, for the modifications reported here, no general relationship is apparent between cured resin resistance to cyclic stress (resin flexibility) and resistance to moist heat (resin hydrolytic stability).

Cyclic Soak–Dry Effects on Particleboard

Bending strength, IB strength, and bending stiffness for a given adhesive followed very similar patterns in cyclic VPSD-2 treatment. Therefore, we report only the IB results to illustrate the effects of modification on cyclic stress resistance (Fig. 6).

The initial IB values for particleboards made with these urea-capped amine resin/amine hydrochloride adhesives were either greater than or nearly equivalent to that of the PF-bonded particleboard (Fig. 6). In contrast, the initial IB values of particleboards made from the control resin with NH₄Cl or from the Neste 1.6 resin with NH₄Cl or amine hydrochloride curing agents (data not shown for last group) were much lower than that of the PF particleboard (Fig. 6). After VPSD exposure, the IB strength values of all UF-bonded particleboards fell

below that of the PF particleboard. However, the boards bonded with modified adhesives, particularly the DDDU-modified resin, retained more IB strength than did boards bonded with the unmodified adhesives. In general, the resistance to cyclic stress appeared to be more dependent on resin differences than on variations in curing agent. Results for boards made with HMDU-, BHMTU-, and PPOTU-modified resins cured with ammonium chloride were reported previously.[2] Boards made with those adhesives equaled or approached the performance of boards made with PF resin. The thickness swell in cyclic VPSD-2 treatment closely paralleled that for IB (Fig. 7).

Note that the results reported here differ from those reported in Part II[2] in that IB strength values in the current experiments were much lower, even though the same resin content was used. The difference may be due to the difference in the modifiers or it may be due to the species of wood and the geometry of the particles. Hemlock particles with a fairly large aspect ratio were used in the previous experiments. Considerably smaller particles of Southern Pine were used in the current experiments. Southern Pine is a more difficult wood to bond than is hemlock, and the smaller pine particles also increase the surface area that must be effectively coated with adhesive to provide adequate bonding.

Formaldehyde Emission from Particleboard

Results on formaldehyde emission from particleboard are summarized in Table XI. Because we were
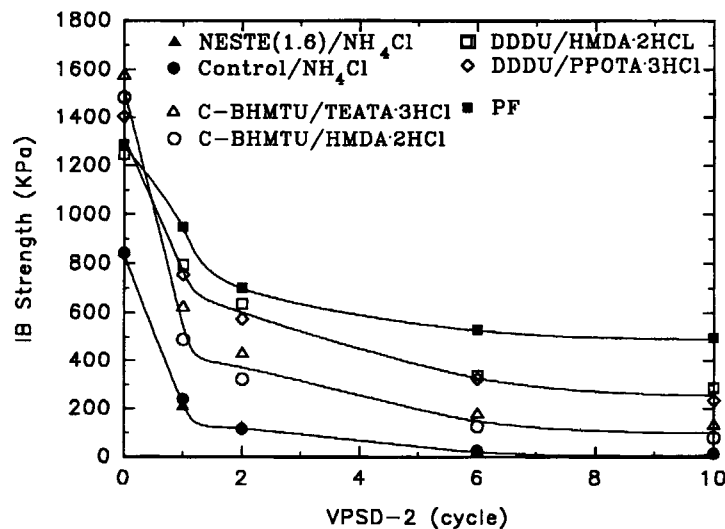

Figure 6 Variation of internal bond strength of Southern Pine particleboards under cyclic soak–dry treatment (VPSD-2).
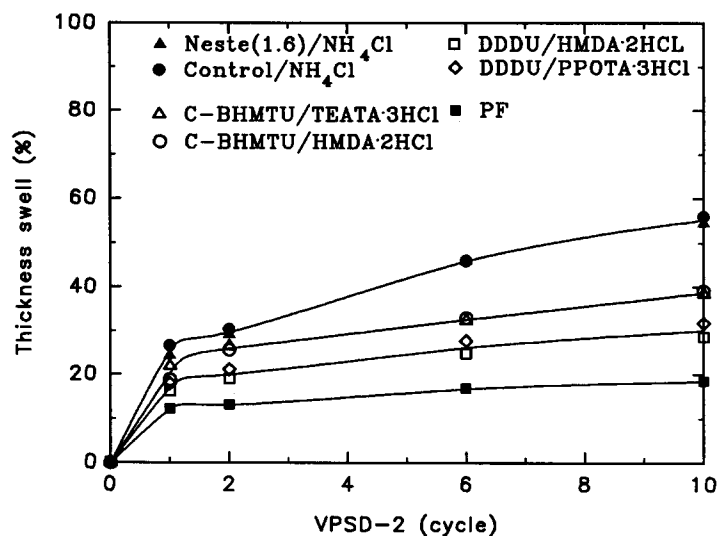
Figure 7   Nonrecoverable thickness swelling of Southern Pine particleboard under cyclic soak–dry treatment (VPSD-2).

unable to use the number and size of specimens required by the standard desiccator test,[8] we cannot directly compare our results with national standards for formaldehyde emission from particleboard. However, we can compare emissions from boards bonded with various modified resins to the emission from boards made with two resins that would probably meet the national standard—a commercial unmodified UF adhesive with F/U ratio 1.2 (Neste 1.2) and a commercial PF adhesive. We are also able to see the effects of aging (exposure to freely circulating air) upon the rate of formaldehyde emission.

Resin Modification with Urea-Capped Amine.   For a given curing agent, the emissions from adhesives based on modified resins were initially lower than those of the control, the lowest being DDDU/NH₄Cl at 50% of control/NH₄Cl. However, the modified adhesives in many cases decreased less with aging than did the control resin with the respective curing agent. Both of these effects may be partially attributable to lower free formaldehyde contents in most of the modified resins compared to the control (Table V).

Adhesive Modification with Amine Hydrochloride.   For a given resin, the emission was greater for the amine hydrochloride-cured adhesive than for the ammonium chloride-cured adhesive. This may reflect greater formaldehyde scavenging capability of the ammonium chloride because at constant weight composition ammonium chloride provides more moles of NH₂ functionality than do most amines.

Aging.   In some cases, aging reduced the formaldehyde emission to as little as one-fourth the amount before aging. The emission from boards made with resins at F/U 1.6 was reduced more by aging than was the emission for boards made with the Neste F/U 1.2 resin. The initially lower-emitting F/U 1.2 resin should be expected to change less on aging than will the F/U 1.6 resins.

In Part I of this series,[1] we presented data demonstrating that the formaldehyde liberated by hydrolysis of neat resins (no wood) cured with ammonium chloride was clearly greater in amount and rate than that from neat resins cured with the amine hydrochlorides. This reduction in neat resin formaldehyde liberation by amine hydrochlorides is opposite to that reported here for particleboards. Moreover, C-BHMTU/TEATA·3HCl and DDDU/TEATA·3HCl adhesives that imparted better resistance to moist heat aging (hydrolysis) in bonded joints (Fig. 5) also led to particleboard having relatively higher initial formaldehyde emissions (Table XI). These observations are consistent with the argument that formaldehyde emission from particleboard is controlled more by free formaldehyde in the board rather than by hydrolysis of the resin. The large reduction in emission with aging further supports this argument.

Despite our inability to directly compare with the national standard for formaldehyde emission, we conclude that higher cure temperatures and lower mole ratio resins, both of which are more commercially realistic, would probably sufficiently decrease the emission of formaldehyde from particleboard

Table XI Particleboard Formaldehyde Emission for Various Resins and Curing Agents

| Resin | Emission (μg/mL)[a] | | | | | | | |
| | NH$_4$Cl | | HMDA·2HCl | | TEATA·3HCl | | PPOTA·3HCl | |
	Initial	Aged	Initial	Aged	Initial	Aged	Initial	Aged
Control	4.8	1.2	6.2	1.4	5.4	1.8	5.5	1.9
HMDU	3.5	1.0	5.0	1.2	—	—	—	—
C-BHMTU	3.3	1.0	3.4	1.0	4.4	1.2	—	—
PPOTU	3.1	1.4	—	—	—	—	4.3	1.4
DDDU	2.3	1.0	5.4	1.3	5.2	1.6	—	—
PPGDU-33	—	—	5.3	1.4	—	—	—	—
Neste (1.6)	5.0	1.3	9.4	1.8	5.6	1.7	10.7	2.2
Neste (1.2)	0.9	0.6	1.3	0.5	1.1	0.5	1.7	0.6
PF	0.5	0.2	—	—	—	—	—	—

[a] From 2 h modified desiccator test; "aged" is aged 30 days at 24°C, 49–52% RH, ambient HCHO concentration < 0.1 part per min.

made with amine-modified resins to meet that standard.

CONCLUSIONS

Based on all the results from this program to date, it is clear that incorporating certain di- or trifunctional amines into UF resins at F/U 1.6 leads to significant improvements in the durability and stability of bonded wood products. Specifically, the most promising modifiers are as follows:

1. Urea-terminated amines with NH$_4$Cl curing agent:
   - Linear, difunctional, aliphatic materials such as C-BHMTU and HMDU
   - Branched, trifunctional, aliphatic TEATU
   - Branched, trifunctional, aliphatic ether (PPOTU)

2. Hydrochloride salts of amines:
   - Aliphatic amine hydrochlorides, linear or branched, such as HMDA·2HCl and TEATA·3HCl
   - Branched, aliphatic ether amine hydrochloride PPOTA·3HCl.

We originally postulated that improved behavior should come about by incorporating modifiers into the UF chains to bring about increased flexibility,

decreased intermolecular association, and greater cross-linking efficiency. The more effective amines appear to be those of low to moderate molecular weight that possess inherent flexibility or trifunctionality or both. Depending on the backbone structure of the amine, higher molecular weight amines may be less effective because they become incompatible with the aqueous UF system (DDDA) and/or because we are unable to incorporate a sufficient number of modifier molecules (PPGDA).

Subsequent efforts will employ the most promising amines in lower mole ratio resins to determine whether formaldehyde emission limits can be met while maintaining improved durability.

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