Polyamine-Modified Urea-Formaldehyde Resins. II. Resistance to Stress Induced by Moisture Cycling of Solid Wood Joints and Particleboard

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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 resin cure and by improving the ability of the cured system to withstand cyclic stresses. Urea-formaldehyde resins were modified by (i) incorporating urea-terminated di- and trifunctional flexible amines into the resin structure, (ii) curing the resins with the hydrochloride derivatives of some of these amines (in place of ammonium chloride), or (iii) using both processes. The cyclic stress resistance of solid wood joints and the internal bond strength and thickness swell of particleboards made with these resins were compared with these properties in joints and particleboards made with an unmodified resin and a commercial urea-formaldehyde resin. The strength of joints and the internal bond strength of particleboards made with resins modified with urea-terminated hexamethylenediamine, bishexamethylenetriamine, and poly(propylene oxide)triamine at modifier contents of 13, 16, and 28 wt %, respectively, showed excellent stability even after repeated wet–dry cycles. Similar stress resistance was shown by wood joints and particleboards bonded with the unmodified resin cured with the hydrochloride salts of hexamethylenediamine and triethyleneaminetriamine. In contrast, solid wood joints and particleboards bonded with the unmodified resin cured with ammonium chloride showed lower resistance to cyclic stress. Particleboards that possessed good cyclic stress resistance also showed less thickness swell.

INTRODUCTION

Urea-formaldehyde (UF) resins form strong bonds under a wider variety of conditions and cost less than phenol-formaldehyde (PF) resins. However, the lower durability of UF-bonded wood products, particularly under humid and warm or cyclic moisture conditions, limits their use to interior applications. A significant improvement in the stability and durability of UF-bonded wood products would enlarge their scope of application and broaden their marketability into areas currently dominated by products made with the more expensive, less versatile, and more supply-sensitive PF resins.

The lower stability and durability of UF resins is attributable to hydrolytic degradation and stress rupture. The structural factors responsible for these processes suggest that the stability and durability of a UF resin can be enhanced by modifying its structure to allow production of a cured resin with a more flexible structure and a more random distribution of cross links. In part I of this series, we discussed our approach to meeting these requirements by incorporating flexible amines into the resin structure, and presented initial results that supported our approach.[1] We incorporated several di- or trifunctional amines into a UF resin by adding the amines as urea-capped derivatives during resin synthesis, by using amine hydrochloride salts as acid curing agents, or by using both processes. In each

case, we observed cure rates comparable to those of a control system and found significantly improved short-term resistance of solid wood joints to cyclic stresses induced by cyclic wet–dry exposures.

The experiments in part I were essentially screening tests. For example, resin synthesis methods evolved during the study, and testing of the stability and durability of the bonded product was limited to 10 wet–dry cycles of solid wood joints.[1] This article substantiates the earlier claims of improved stability and durability by employing a consistent synthesis procedure for all the resins, extending the solid wood joint testing to more cycles, and testing the resistance of particleboard to cyclic moisture exposure.

Throughout this article, we employ the following terminology. The term resin refers to an aqueous, synthesized polymer without curing agent. The polymer was an unmodified UF resin (control or commercial) or a UF resin modified by synthesis with urea-capped amine. The term adhesive refers to a resin to which curing agent was added. Curing agents included formic acid, ammonium chloride, and the hydrochloride salts of hexamethylenediamine and triethylaminetriamine. As in part I, we use either the commercial names of the amines or acronyms, e.g., hexamethylenediamine is HMDA

and triethylaminetriamine is TEATA. To designate urea-capped amines, the final A is replaced by U, e.g., HMDU and TEATU. The hydrochloride salts of the amines are designated, for example, as HMDA·2HCl and TEATA·3HCl.

EXPERIMENTAL

Materials and Synthesis

The chemicals employed are described in Table I. The preparation of concentrated aqueous formaldehyde has been described.[1]

Amine Derivatives

In part I of this study,[1] most urea derivatives of the amines were synthesized in a separate step and subsequently added to the appropriate urea and formaldehyde composition during resin synthesis. In the work reported here, all urea derivatives were made in the presence of the total urea to be used in a particular resin synthesis. Except for poly(ethyleneoxide)diamine (PEODA-11), the amines constituted about 8 mol % urea (Table II). Because of its higher molecular weight, PEODA-11 was added at only about 2 mol % urea to restrict the weight

Table I   Test Chemicals

Chemical	Source[a]	Remarks
Hexamethylenediamine (HMDA)	DuPont Petrochemicals, Wilmington, DE	85% aqueous solution
Bishexamethylenetriamine (BHMTA)	Aldrich Chemical Co., Inc., Milwaukee, WI	Technical grade, 90%, MP 34–36°C
Triethylaminetriamine (TEATA) (Tren)	Organic Chemicals Division, W. R. Grace & Co., Lexington, MA	High purity grade with < 2% ethylene amine
Poly(ethyleneoxide)diamine (PEODA-11) (Jeffamine ED-600)	Texaco Chemical Co., Austin, TX	Liquid, viscosity 0.072 Pa·s at 20°C; total amine 3.19 meq/g
Poly(propyleneoxide)triamine (PPOTA) (Jeffamine T-403)	Texaco Chemical Co., Austin, TX	Pale yellow liquid, viscosity 0.070 Pa·s at 25°C
Paraformaldehyde	Aldrich Chemical Co., Inc., Milwaukee, WI	95%, MP 163–165°C
Urea	J. T. Baker Chemical Co., Philadelphia, PA	MP 134°C
Ammonium chloride	Columbus Chemical Industries, Inc., Columbus, WI	Reagent grade
Formic acid	J. T. Baker Chemical Co., Phillipsburg, NJ	88% aqueous solution

[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.

Table II   Composition of Urea-Terminated Amines

Amine[a]	Urea Substitution[b] (%)	
	Mole	Weight
HMDA	8.00	14.9
PEODA-11	2.38	20.4
BHMTA	8.33	24.5
PPOTA	7.69	37.9
TEATA	7.69	16.9

[a] See Table I for full names of amines.
[b] Percentage of urea substitution by amine as amine.

substitution of that amine. A total of 10 mol of the appropriate amounts of amine and urea (Table II) were charged into a reaction kettle equipped with a mechanical stirrer. Fifty grams of water were added, and the mixture was refluxed at 135–145°C until the level of refluxing dropped conspicuously (about 4–5 h). The mixture was cooled to room temperature and dried to a constant weight at 50–60°C in a vacuum oven (about 0.1 MPa vacuum).

The hydrochloride derivatives of hexamethylenediamine (HMDA · 2HCl) and triethylaminetriamine (TEATA · 3HCl) were prepared according to Farlow.[2]

Resins

All resins were synthesized by adding the urea (or the combined urea and urea-capped amine) in two steps: The first step had an effective formaldehyde to urea mole ratio (F/U) of 2.0, and the second step yielded a final F/U of 1.6. The total weight fractions of amine in the final modified resins varied from about 0.09–0.26 (Table III). Procedures for synthe-

sis and characterization were reported previously.[1] Table IV gives some initial resin properties.

Preparation and Testing of Solid Wood Joints

The adhesive mixtures were prepared by thoroughly stirring 0.5 g curing agent (ammonium chloride, formic acid, HMDA · 2HCl, or TEATA · 3HCl) into 10 g UF resin (unmodified or modified with urea-capped amine). Adhesive was then brushed on each adherend. For each adhesive, two hard maple (*Acer saccharum*) panels (180 × 230 × 6 mm) were bonded under the following conditions: 200–250 g/m^2 adhesive spread, 10 min open assembly time (2 min for formic acid curing), 2 min closed assembly time, 10 min press time, 1.0 MPa bonding pressure, and bonding temperatures as shown in Table V.

After bonding, the panels were reconditioned to 6% moisture content. Each panel was cut into 16 reduced-size (645 mm^2) ASTM D-905-type compression shear specimens.[3] The resultant 32 specimens were divided into 8 groups of 4 specimens each. One group was tested dry (6% moisture content), and the other groups were subjected to 1, 5, 10, 15, 20, 25, or 30 vacuum-pressure-soak-dry (VPSD) cycles. Each cycle consisted of submerging the specimens in cold tap water for 30 min at about 0.1 MPa vacuum followed by 30 min at 0.4 MPa pressure, and then drying for 20 h in a forced-draft oven at 43–45°C. The cycled specimens were equilibrated to 6% moisture content before testing on a universal testing machine at a crosshead speed of 5 mm/min.

Preparation and Testing of Particleboards

Particles of eastern hemlock (*Tsuga canodensis*) were reduced in a hammermill fitted with a 6-mm screen and subsequently further screened to remove fines. Before blending the furnish with 7% by weight

Table III   Composition of Control and Urea-capped Amine-modified Resins[a]

Component	Weight Fraction[b]				
	Control	PPOTU	HMDU	PEODU-11	BHMTU
Formaldehyde	0.449	0.306	0.400	0.391	0.368
Urea/amine[c]					
First addition	0.449/0	0.352/0.215	0.418/0.073	0.396/0.101	0.389/0.126
Second addition	0.101/0	0.079/0.048	0.095/0.017	0.089/0.023	0.088/0.029

[a] Final F/U mole ratio = 1.6.
[b] Solids basis.
[c] Weight fraction of amine as amine.

Table IV Initial Resin Properties

Resin	F/U Ratio	pH	Viscosity[a] (Pa·s)	Solids Content (%)	Free CH₂O (%)
Control	1.6	7.84	—	60	0.38
HMDU	1.6	7.40	0.496	61	0.35
PEODU-11	1.6	7.92	0.316	60	0.61
BHMTU	1.6	7.66	0.718	61	0.57
PPOTU	1.6	7.80	—	67	0.39
Commercial	—	—	2.508	63	1.37

[a] Resin viscosity was measured after the resin was stored about 6 months in a refrigerator.

of adhesive (dry solids basis), water was added to give a target wood moisture content of 10.5–11.5%. After blending, the particles were transferred to a 300 × 300 mm board former (mold) through a 6-mm screen to ensure uniform distribution, and a thermocouple was positioned at the center of the mat. The mat was placed carefully on an electrically heated oil press, pressed to a thickness of 12 mm, and cured for a total of 10 min. The press platen temperature was preadjusted to a value that would allow the mat core to reach the differential scanning calorimetry (DSC) exotherm peak temperature (Table V) in 4–6 min.

Initial bending tests were carried out on dry specimens (conditioned at 27°C and 30% RH) and on wet specimens after one vacuum-pressure-soak. Specimens were 50 × 275 × 12 mm and were tested flatwise with a 250-mm span at a crosshead speed of 0.5 mm/min.

Measurements of tensile strength perpendicular to the face of the board (internal bond) and thickness swell were carried out on specimens 50 × 50 × 12 mm. For each board, these properties were measured after 0, 1, 3, 5, and 10 VPSD cycles. In this case, each VPSD cycle consisted of submerging the specimens in cold tap water for 30 min at about 0.1 MPa, followed by 30 min at 0.4 MPa pressure,

and then drying for 23 h in a forced-draft oven at 80°C. All measurements were made after reequilibrating the specimens to 27°C and 30% RH. Internal bond was measured at 1 mm/min crosshead speed.

RESULTS

Solid Wood Joints

The effects of cyclic stress (VPSD) on the shear strength of joints bonded with selected adhesive systems, i.e., various resin and curing agent combinations, are shown in Figures 1–3. These figures illustrate the general behavior of the joints. The joints clearly fall into two categories: those that demonstrated a high degree of resistance to cyclic stress and those with lower resistance. Systems with good resistance include the control resin cured with HMDA · 2HCl or TEATA · 3HCl (Fig. 1), as well as resins modified with HMDU, BHMTU, or PPOTU and cured with any of the curing agents (illustrated in Fig. 2 for HMDU resin with different curing agents and in Fig. 3 for several resins cured with TEATA · 3HCl). Thus, modifying the UF system with some urea-capped amines or with some amine hydrochloride curing agents improved resistance to

Table V Bonding Temperatures[a]

Curing Agent	Bonding Temperature for Various Resins (°C)					
	Control	HMDU	PEODU-11	BHMTU	PPOTU	Commercial
NH₄Cl	95	95	100	95	95	95
HMDA · 2HCl	105	105	105	105	105	100
TEATA · 3HCl	95	95	100	95	95	95
Formic acid	160	160	160	160	160	160

[a] The bonding temperature was approximately the exotherm peak temperature determined from DSC measurements.
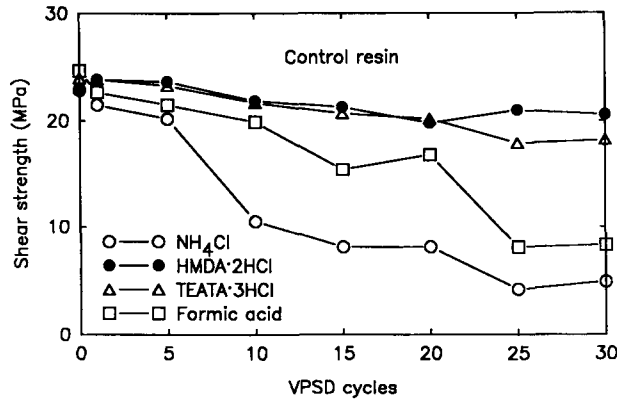
Figure 1 Effect of cyclic stress on shear strength of solid wood joints bonded with control UF resin cured with four different curing agents.

cyclic stress. In contrast, joints with lower resistance included those made with control resin cured with ammonium chloride or formic acid (Fig. 1), i.e., control resin without any amine modifier. Other low-resistance systems included those made with PEODU-11-modified resin or the commercial UF resin (Fig. 3). Figure 3 demonstrates the clear demarcation between the two categories of joints; it also shows that the modified UF systems with good resistance are much superior to the laboratory PF system used to bond Southern Pine.

Particleboards

Initial Dry and Wet Bending Properties

Table VI summarizes the initial dry and wet bending strength and stiffness of particleboards made with four resins and three curing agents. The board made
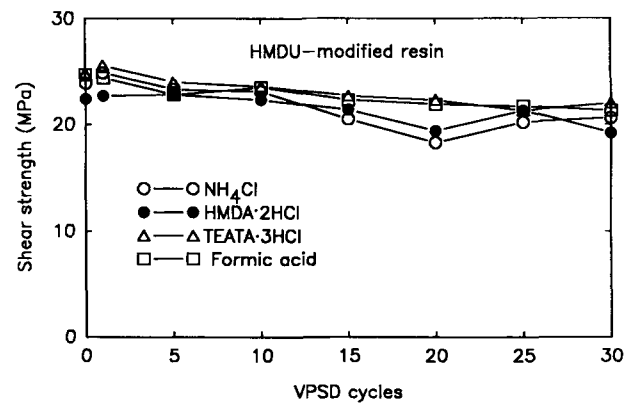

Figure 2 Effect of cyclic stress on shear strength of solid wood joints bonded with HMDU-modified UF resin cured with four different curing agents.
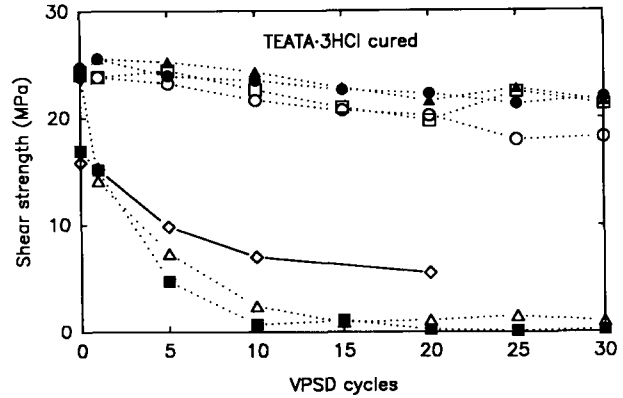

Figure 3 Effect of cyclic stress on shear strength of solid wood joints bonded with various UF resins cured with TEATA · 3HCl compared with that of Southern Pine bonded with PF resin. O, control UF; ●, HMDU-modified UF; △, PEODU-11-modified UF; ▲, PPOTU-modified UF; □, BHMTU-modified UF; ■, commercial UF; ◊, PF-Southern Pine.

with the control resin–ammonium chloride adhesive possessed notably lower wet and dry strength and stiffness than boards made with the control resin–HMDA · 2HCl adhesive. Likewise, the board made with the control resin–ammonium chloride adhesive was also inferior to boards made with amine-modified resins and any of the curing agents examined. However, the relative losses in strength and stiffness caused by soaking were quite consistent among all boards. All boards, except for the control resin–ammonium chloride board, were in the range required for materials manufactured according to the ANSI-A208.1-1989 Commercial Standard for 1M1 particleboard (UF or equivalent).[4] The board made with PPOTU-modified resin and cured with TEATA · 3HCl stood out in all the tests and surpassed the dry strength requirements of ANSI-A208.1 for type 2M2 particleboard (PF or equivalent).[4]

Cyclic Stress Resistance

Figure 4 presents the internal bond (IB) strength data for boards made with several UF resins—control, HMDU, BHMTU, PPOTU, and commercial—all cured with ammonium chloride. Effects of different curing agents are illustrated in Figure 5. Initial strength of the UF boards ranged from 1,700 kPa for the PPOTU-modified adhesive to 900 kPa for the commercial unmodified UF adhesive. The IB values decreased rapidly in the first few VPSD cycles, following the behavior observed for most wood-based, reconstituted materials. Despite the losses in

Table VI   Particleboard Bending Properties[a]

Modifier	Curing Agent	Dry Values[b] (MPa)		Residual Values after One VPS Cycle (MPa)		Property Loss (%)	
		MOR	MOE	MOR	MOE	MOR	MOE
Control[c]	NH₄Cl	9.3	1,572	5.4	365	42	77
	HMDA · 2HCl	12.6	1,944	7.7	486	39	75
HMDA	NH₄Cl	13.0	2,006	6.8	434	48	78
	HMDA · 2HCl	14.0	1,958	8.4	502	40	76
	TEATA · 3HCl	13.0	1,931	7.8	473	40	75
BHMTU	NH₄Cl	14.1	2,262	6.9	534	51	76
PPOTU	NH₄Cl	14.5	2,110	8.9	541	39	74
	HMDA · 2HCl	15.1	2,103	6.8	432	55	80
	TEATA · 3HCl	17.3	2,399	10.0	597	42	75

[a] Bending strength (MOR) and modulus (MOE).
[b] Equilibrated at 27°C and 30% RH.
[c] Laboratory-made, unmodified UF resin.

strength during the first few VPSD cycles, the adhesives maintained their approximate rank. The three modified UF-bonded boards had superior IB strength values after VPSD cycling compared to both the laboratory and commercial unmodified UF-bonded boards.

Data for two flakeboards bonded with phenolic adhesive from an earlier study[5,6] are included for comparison in Figure 4. Board A was made in the laboratory with 0.38-mm thick, 25-mm long, random-width Douglas-fir flakes and 6% resin; Board C was a commercial product made with aspen flakes. The UF-bonded boards started with generally higher
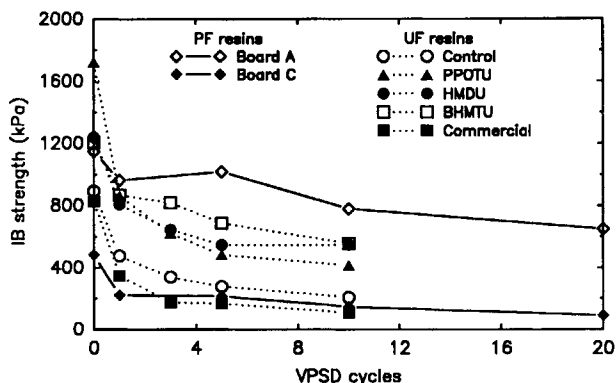

Figure 4   Effect of cyclic stress on internal bond (IB) strength of particleboard bonded with various UF resins cured with ammonium chloride compared with particleboard bonded with phenol-formaldehyde (PF) resin.
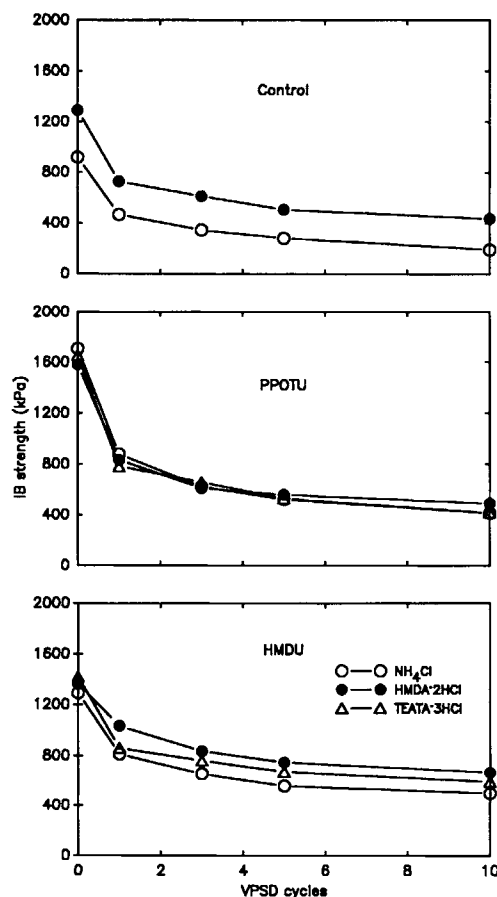

Figure 5   Effect of cyclic stress on internal bond (IB) strength of particleboard bonded with three UF resins and various curing agents.

strength values than did the PF-bonded boards but lost a greater percentage of their original strength in the first VPSD cycle. However, after the first cycle, the rate of IB strength loss by the UF-bonded boards leveled off just as it had with the PF-bonded boards. Despite the greater initial strength loss, modified UF-bonded boards compared favorably in this exposure to the laboratory-made PF-bonded board (Board A), and they obviously performed better than did the commercial PF-bonded board (Board C). In fact, the performance of the board made with HMDU and cured with HMDA · 2HCl (Fig. 5) equaled the performance of Board A.

Thickness swelling after VPSD cycling is shown in Figure 6 for PF-bonded boards and boards made with several UF resins cured with ammonium chloride. The effects of curing agent type are illustrated in Figure 7 for the control resin. The boards bonded with the commercial resin–ammonium chloride adhesive and boards bonded with the control UF resin–ammonium chloride adhesive swelled roughly 43 and 33%, respectively, after 10 VPSD cycles (Fig. 6). Using urea-capped amine resin–ammonium chloride adhesives or curing with amine hydrochlorides reduced thickness swelling to 20–25% after 10 VPSD cycles.

Boards made with HMDU, BHMTU, or PPOTU cured with ammonium chloride and boards made with control resin cured with amine hydrochloride swelled more than the laboratory PF-bonded board (Board A) but were comparable in swelling to the commercial PF-bonded board (Board C). (For point
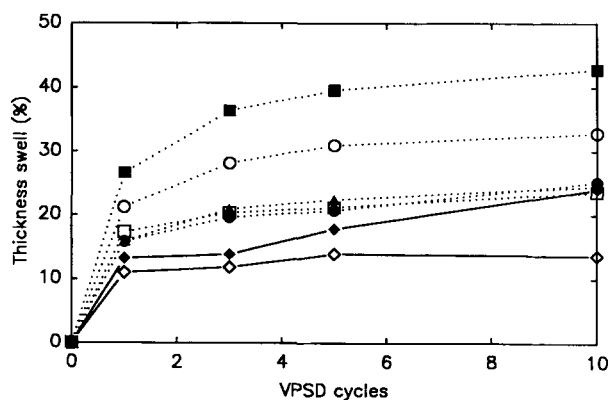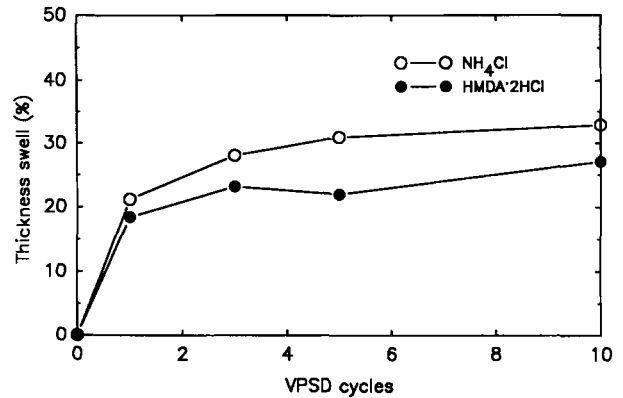

Figure 7 Effect of cyclic stress on thickness swell of particleboard bonded with control UF resin cured with ammonium chloride and HMDA · 2HCl.

of reference, the commercial PF-bonded board survived 11 years of full outdoor exposure, but not without considerable loss of thickness and mechanical properties. The laboratory PF-bonded board survived the same exposure with only surface roughening and very little loss of properties.)

DISCUSSION

We present here a preliminary rationale for the observed behavior of joints and particleboards bonded with unmodified and modified resin–curing agent systems. Other studies to clarify the present interpretation are in progress or preparation; these studies include fracture mechanics testing and microscopic examination of failed surfaces.

The results on solid wood joints reported here confirm the less extensive data reported earlier.[1] Those findings were interpreted in terms of two favorable effects of the amine modifiers. First, the modifiers resulted in resins with inherently greater flexibility and toughness compared to conventional UF resins and thus greater ability to withstand the stresses imposed on the resin or resin–wood bonds. Second, some urea-capped amine-modified resins and/or amine hydrochloride curing agents slowed the rate of cure. This resulted in the production of a more randomly crosslinked, stress-free network, especially when the polymer chains were more flexible. Specimens bonded with PEODU-11-modified resin did not perform as well as those bonded with the other modified UF resins. This may have been due to the relatively low mole percent substitution of PEODU-11 in comparison to the other modifiers

Figure 6 Effect of cyclic stress on thickness swell of particleboard bonded with various resins cured with ammonium chloride. O, control UF; ●, HMDU-modified UF; ▲, PPOTU-modified UF; □, BHMTU-modified UF; ■, commercial UF; ◆, commercial PF (Board C); ◇, laboratory PF (Board A).

for an equivalent weight percent substitution (Table II). The large molecular weight of the PEODU-11 molecule and its low functionality mean that modification with PEODU-11 offers relatively fewer opportunities for crosslinking than with the other modifiers.

The failure process is more complex in particleboard than it is in solid wood joints. Particleboard contains many preexisting flaws where failure can initiate under stresses imposed by mechanical loading or by wood particle swelling and shrinking. The performance of the board depends on the resistance to crack growth of the material adjoining these flaws; that material includes, of course, the cohesive resin bonds, the resin–wood bonds, and the wood itself. Because the UF-bonded boards studied here were made with the same furnish and the same resin content, the improved behavior of boards made with some of the modified systems suggests that those resins are tougher. Therefore, the resin and resin–wood bonds made with these modified systems were more resistant to crack growth than were the bonds made with the unmodified systems. This could account for the superior initial bending strength and stiffness and initial IB strength of particleboards made with the modified systems.

The tougher, more ductile nature of the modified systems could also contribute to the lower thickness swelling in the first VPSD cycle, although other factors, such as board density and drying temperature, also affect thickness swelling in the VPSD treatment.[7,8] However, during the first VPSD cycle, we can assume that sharp-tipped cracks formed from the growth of preexisting flaws in the wood or at the wood–adhesive interface. The fact that subsequent rates of IB strength loss and thickness swelling were relatively independent of adhesive type suggests that once sharp-tipped cracks are formed, continued crack growth is influenced more by the furnish and board density than the adhesive.

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