Evaluation of Block Shear Properties of Selected Extreme-pH Structural Adhesives by Short-Term Exposure Test

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ABSTRACT: Nine structural adhesives with varying pH were selected to examine the effect of adhesive pH on wood–adhesive bond quality. The adhesives evaluated included four highly alkaline phenol–formaldehyde, one intermediate pH phenol–resorcinol–formaldehyde, two acidic melamine–urea–formaldehyde, and two acidic melamine–formaldehyde resins. Block shear specimens were prepared using Douglas-fir and black spruce wood. The adhesive performance was evaluated by measuring the shear properties (strength and wood failure) of the specimens tested at the dry and vacuum–pressure–redry (VPD) conditions. Adhesive pH, test condition, and wood species showed significant effects on shear properties. The different adhesives performed differently at the dry and VPD conditions. The high-pH adhesives (phenol–formaldehyde and phenol–resorcinol–formaldehyde) showed similar high wood failures at both test conditions and performed better than the low-pH adhesives (melamine–formaldehyde and melamine–urea–formaldehyde), especially after the VPD conditioning. The low-pH adhesives showed high wood failure at the dry condition, but wood failure decreased significantly after VPD conditioning for both species, indicating that the low-pH adhesives were less durable than the high-pH adhesives. High-pH adhesives did not have a negative impact on the strength of the bonded specimens. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 657–665, 2011

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INTRODUCTION

There are three types of linkages involved in a wood–adhesive bond, namely adhesive layer, wood–adhesive interface, and wood layer adjacent to the adhesive layer. The latter is probably more susceptible to the negative effects of extreme pH for long-term exposure. The wood substance in wood cell walls is composed of holocellulose (40–44% cellulose and 15–35% hemicellulose) and 18–35% lignin. Usually, a low pH predominantly affects the holocellulose, whereas a high pH mainly affects the lignin.[1,2] Thus, a low pH may have a more detrimental effect on wood strength than a high pH.

Gillespie and River[3] reported that yellow birch and Douglas-fir plywood shear specimens stored for 4 years at 27°C and 30% relative humidity (RH) lost little, if any, strength when bonded with nonacidic adhesives, but showed appreciable strength loss when bonded with acidic adhesives. Similarly, in an evaluation of the durability of various structural wood adhesives by indoor and roofed outdoor exposure, Raknes[4,5] reported that acidic phenol–formaldehyde (PF) adhesives started showing signs of failure after 10–15 years, probably due to acid damage to the wood. In comparison, alkali resorcinol–formaldehyde (RF) adhesives still retained satisfactory strength.

Some adhesives become more acidic during curing. The acid-induced gelling reactions can cause severe deterioration of the wood substance.[6] Kline et al.[7] observed strength losses in plywood with aging at pH values less than about 4 for urea–formaldehyde adhesives and 3.5 for PF adhesives. Wangaard[8] also found that with acid-catalyzed intermediate-temperature-setting PF at moderate humidity exposure conditions, the more acidic adhesives seemed to cause deterioration of the wood adjacent to the bond line. The alkaline-catalyzed adhesives did not show this effect. Similar observations were made by Eickner[9] on bonding compreg-to-compreg with three types of adhesives (alkaline intermediate-temperature-setting PF, room-temperature-setting RF, and acidic PF) exposed to 93°C and 20% RH.

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The author found that the alkaline intermediate-temperature-setting PF and the room-temperature-setting RF retained relatively high strengths after 1 year of exposure, whereas those glued with the acidic PF lost strength. Moreover, a Weyerhaeuser application guide on Microllam® laminated veneer lumber (LVL) scaffold plank[10] indicates that the most hazardous acidic chemical solutions to wood are those that have pH ≤ 3.

Green et al.[11] studied the durability of structural solid-sawn lumber (Douglas-fir, southern pine, spruce-pine-fir, and yellow poplar), LVL (Douglas-fir, southern pine, and yellow poplar) bonded with PF, and laminated strand lumber (LSL) (aspen and yellow poplar) with an isocyanate-based adhesive exposed at 82°C and 80% RH for up to 24 months. After exposure, the products were reconditioned to room temperature at 25% RH before testing in edgewise bending. Reductions in bending strength were observed for all three types of products after 12–24 months of exposure. They concluded that acid hydrolysis of hemicellulose, especially of arabinose, seemed to be the fundamental cause of strength loss resulting from thermal degradation. The products became more acidic with exposure time, and arabinose showed the largest and most consistent decrease with time of exposure. The average pH of the solid wood control dropped from 4.2 (unexposed) to 3.6 for specimens exposed to the above environment for 12–24 months; the average pH of the LVL dropped from 6.2 to 4.7 after 12 months, and the pH of LSL dropped from 4.8 to 3.8. The difference in pH between the LVL and LSL was probably due to the type of adhesive used in the products, where the PF used in LVL had higher pH than the isocyanate adhesive used in LSL.

Kline et al.[7] observed a correlation between strength loss on aging of plywood bonded with alkali-catalyzed PF and the increase in alkalinity of the panel and found that the critical plywood pH value above which deterioration on aging became appreciable was around 8 for PF adhesives. Blomquist[12] investigated the effect of varying the alkalinity of a hot-pressed PF (film pH 10.0–11.5), an intermediate-temperature-setting PF (freshly mixed pH 8.0–10.2 and corresponding film pH 8.1–11.2), and a room-temperature-setting RF (freshly mixed pH 7.1–8.4 and corresponding film pH 7.4–8.8), by varying the amount of caustic soda added to the adhesive formulation, on the wood-adhesive bond in yellow birch and Douglas-fir plywood specimens. The specimens were exposed continuously at different conditions (about 27°C/65% RH, 70°C/20% RH, about 27°C/97% RH), or repeated cyclic high and low humidity (2 weeks at 27°C/97% RH followed by 2 weeks at 27°C/30% RH), over a 2- to 3-year period. Exposure at room conditions had no significant effect on the durability of the specimens regardless of the alkalinity of the adhesive formulations. Exposure at elevated temperature/low humidity for 3 years showed evidence of damage to the wood in birch specimens bonded with the most alkaline hot-pressed PF formulations when tested wet. Exposure at high humidity/room temperature was found to be the most damaging condition to the most alkaline hot-pressed PF used in the tests. Exposure at the cyclic high/low humidity for 3 years resulted in significant losses in strength and wood failure in birch plywood bonded with the two most alkaline hot-pressed PF.

Hse[13] examined the effects of several PF adhesive properties, including pH, on the bond quality of southern pine plywood. The pH of the liquid adhesive ranged from 10.5 to 12.1. However, the corresponding cured adhesive film pH would likely be higher based on the observations by Blomquist[12] and Kline et al.[7] The relationships of pH to wet shear strength and wood failure were found to be parabolic. It is interesting to note that from the regression equations generated, the maximum values of wood failure and shear strength were found to correspond to liquid adhesive pH 11.0 and pH 10.7, respectively. The author indicated that it was unlikely that pH altered the wood substrate sufficiently to influence the quality of bonding. Santos et al.[14] examined the effects of pH and synthesis temperature on the performance of thermosetting adhesive formulations based on demethylated wood creosote–formaldehyde when used in bonding *Araucaria angustifolia* sheets. The pH's of the adhesive formulations were 12.00, 12.25, 12.50, 12.75, 13.00, 13.25, and 13.50. The dry and wet shear strengths were observed to be positively and linearly correlated with increasing pH. However, no trend was observed between pH and wood failure. These results indicated that within the pH range studied, the adhesive probably did not have an adverse effect on the wood. Zimmermann et al.[15] showed that 5-hr exposure of spruce wood to 10% NaOH, 18% NaOH, or 24% KOH at room temperature resulted in slight reductions in hemicellulose components and, in most cases, significant reductions in bending strength and stiffness.

This project was conducted to better understand the role and need for pH limits on the cured adhesive film with respect to the development of adhesive standards that ensure good long-term performance and, at the same time, permit innovative adhesive systems to be developed and used in the most appropriate applications. The goal of this study was to provide background information that will assist wood adhesive standard committees in refining the newly published CSA O112.9[16] and O112.10[17] standards. The main objective was to evaluate the effect of extreme pH of acidic and basic adhesives on bond durability and performance after exposure to different environmental conditions. The

TABLE I
Wood Adhesives Used in the Study and pH of the Cured Adhesives

Resin ID	Resin type	pH of cured adhesive films[a]				Remarks[b]
		Method 1	Method 2	Method 3	Method 4	
R-I	PF	12.79 (0.04)	13.15 (0.05)		13.11 (0.04)	n/a
R-II	PF	12.76 (0.05)	12.81 (0.07)		12.15 (0.07)	n/a
R-III	PF	12.44 (0.04)	12.87 (0.09)		12.00 (0.04)	n/a
R-IV	PF	12.11 (0.05)	12.69 (0.05)		11.95 (0.08)	n/a
R-V	PRF	10.58 (0.03)	10.84 (0.03)	10.09 (0.05)	10.51 (0.05)	2.2 : 1.0 (6.0 : 1.0)[c]
R-VI	MUF	2.92 (0.07)	6.91 (0.09)	2.94 (0.05)	4.98 (0.02)	100 : 25
R-VII	MUF	2.78 (0.11)	7.00 (0.50)	2.78 (0.11)	4.99 (0.06)	100 : 30
R-XI	MF	3.72 (0.04)	3.63 (0.22)	3.93 (0.03)	3.98 (0.02)	100 : 10
R-XII	MF	3.60 (0.03)	2.39 (0.06)	3.71 (0.01)	3.84 (0.01)	100 : 20

[a] The result is the average of three replicates, and the values in parentheses are standard deviations.
[b] The actual weight ratio of resin to hardener.
[c] The weight ratio of resin and hardener based on solids content. The values in parentheses are solids weight ratio of resin to hardener.

study examined the impact of wood species, high- and low-pH adhesives, and exposure conditions on block shear properties (strength and wood failure).

MATERIALS AND METHODS

Adhesives

Four commercially used high-pH PF adhesives (R-I, R-II, R-III, and R-IV) and one intermediate pH phenol–resorcinol–formaldehyde (PRF) adhesive (R-V; liquid resin pH around 10.0) were supplied by adhesive manufacturers (Tembec [Elko, BC, Canada], Hexion [Quebec, QC, Canada], Arclin [Springfield, OR]). The hardener for R-V was 20–25% powder slurry of which the major components were *para*-formaldehyde and walnut shell flour. In addition, one commercial low-pH melamine–urea–formaldehyde (MUF) adhesive was made into two different pH formulations (R-VI and R-VII) by adding different levels of hardener. The hardener was a slurry composed of several chemicals, mainly formic acid and resorcinol. The slurry had a pH of around 1.5, and its volatile content was about 40 wt %. A commercial low-pH melamine–formaldehyde (MF) (methylated melamine) adhesive was also made into two different pH formulations (R-XI and R-XII) by varying the weight ratios of resin to hardener. The main component of the hardener was aluminum chloride, and the nonvolatile content was between 20 and 30 wt %. For the MUF and MF, the ratios of resin to hardener were within the range recommended by the adhesive manufacturers. Information on the adhesives used in the study is given in Table I. The four high-pH PF adhesives, the intermediate pH PRF adhesive, and one of the low-pH MF adhesives have been certified and are currently used for engineering wood applications in North America. The low-pH MUF adhesive was used to be used for structural application, but it is no longer on the market. The manufacturer kindly prepared this type of MUF adhesive for this study.

Wood substrate

The wood species used were black spruce (*Picea mariana* [Mill.] BSP) supplied by a local sawmill (i.e., in Quebec) and Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco) obtained from Tembec. They were stored at 65% RH and temperature of 21°C for 6 months to reach equilibrium moisture content (EMC). The billets were cut with the following dimensions: black spruce, 820 × 138 × 31 mm (length × width × thickness) and Douglas-fir, 820 (or 600) × 88 × 32 mm. Only the billets that met the visual wood quality requirements of CSA O112.9 standard were selected. They were planed on both surfaces to about 21 mm in thickness, measured for weight and density, and stored at 65% RH/21°C before use in less than 24 hr. Densities of wood were measured before assembling by weighing the billets after conditioning and measuring the length, width, and thickness. The densities of the Douglas-fir billets selected were 0.65–0.75 g/cm^3 and those of black spruce were 0.45–0.55 g/cm^3 based on actual weight and volume at 65% RH and 21°C.

Design of experiment

Nine adhesives with different pHs, two wood species (Douglas-fir and black spruce), and two test conditions (dry and vacuum–pressure–redry [VPD]) were used. For each treatment combination, at least 20 block shear specimens were prepared. Block shear specimens of solid wood were also prepared as controls.

Preparation of cured adhesive films and pH measurement

Four methods were adopted to prepare cured adhesive films for pH measurement: Method 1, adhesives were cured at 102–105°C for 1 hr based on CSA O112.6-1977[18] for hot-setting resins; Method 2, adhesives were cured at 66°C for 4 hr, followed by 1 hr at 150°C based on ASTM D 1583-01[19] for hot-setting resins; Method 3, adhesives were cured at room temperature overnight based on ASTM D 1583-01 for room-temperature-setting resins and or CSA O112.7[20]; and Method 4, the cured resin squeezed out of glue lines during hot pressing was collected from block shear assemblies. Information on the pH of the cured films of the adhesives is given in Table I. More detailed information is available in the study of Zhang et al.[21]

Block shear specimen preparation

The preparation of two-ply test assemblies followed the procedures recommended by the adhesive manufacturers. The spread rates were different from resin to resin, ranging from 190 to 300 g/m^2. The open assembly time was 2–8 min and the closed assembly time was 10–20 min. The platen temperature was 150–180°C, and the press time was 1–3 min after the glue-line temperature reached 100°C. The block shear assembly and shear specimens were prepared according to ASTM D 905-03.[22] For comparison, solid wood block shear specimens were also prepared. To minimize the variability because of wood, the shear specimens cut from each assembly were assigned alternately to the two test conditions by sequence, i.e., the specimens were matched.

Conditioning and testing

Block shear specimens were conditioned by one of the two methods before test: dry and VPD. For the dry condition, the block shear specimens were conditioned at 65% RH and 21°C to reach EMC of about 12%. For the VPD condition, the specimens were placed in an impregnation tank, and a metal screen sheet placed over the specimens and weighted down. Tap water (~ 20°C) was introduced into the tank to immerse the specimens. A vacuum of 635 mmHg (85 kPa) was applied for 30 min, followed by a pressure of 550 kPa for 120 min. After impregnation, the pressure was released, excess water was wiped from the specimen surfaces, and the specimens were then placed in an oven at 60°C to dry to their original weight. The redried specimens were conditioned at 65% RH and 21°C to reach EMC prior to test.

The specimens were tested in shear by compression loading using a shear test device described in ASTM D 905-03. The load rate was 10 mm/min. After testing, the specimens were dried at 105°C for at least 24 hr before MC measurement and wood failure assessment. Wood failure was determined using guidelines described in ASTM D 5266.[23]

Moisture content (MC) of the specimens was determined by determining the weight of specimens before and after oven drying. The MC is calculated as weight difference before and after 24-hr oven-drying divided by oven-dry weight.

Data analysis

Statistical analyses were performed to examine the effects of the factors on the response variables. Analysis of covariance was also performed to examine the covariate impact on the response variables, and one-way fixed-effects treatment structure with simple linear regression models was used to make adjustments to the values.[24] Analysis of variance (ANOVA) was also applied to examine the variance of a dependent variable. The ANOVA table shows the statistics used to test hypotheses about the population means, in which the mean squares are formed by dividing the sum of squares by the associated degrees of freedom. The F value is the test statistic used to decide whether the sample means are within sampling variability of each other. The P value indicates the probability of getting a mean difference between the groups as high as what is observed by chance.

RESULTS AND DISCUSSION

The pH of cured films and squeezed-out cured adhesives

High-pH adhesives

The pH values of the cured films of the high-pH adhesives took a few days to reach equilibrium. The pH values at the different curing conditions are summarized in Table I. Of the five adhesives, only R-V could be cured at room temperature. The pH values of the cured films obtained with Method 2 were higher than those obtained with Method 1. This was probably attributed to the higher curing temperature used in the former method. The results obtained from Method 4 were also different from those obtained from Methods 1 and 2. This was probably due to the differences in the assembly procedures recommended by the adhesive manufactures. Curing conditions had a significant effect on pH (Table I). The pH obtained from Method 4 (i.e., using the squeezed-out adhesive from the glue line of the block shear assemblies) was different from that obtained from the adhesive in the glue line because the resin did not experience the same curing conditions. It should be pointed out that it was very difficult to collect a pure cured adhesive sample from the glue line without any wood component being attached because the glue line was very thin. However, the pH measured from Method 4 could provide a clue for estimating the pH of the glue line. The trend in pH of the cured films using Method 4 was estimated to be: R-I > R-II > R-III ≥ R-IV > R-V, which varied from 13.11 to 10.51.

Low-pH adhesives

The pH values of the cured films of the low-pH adhesives measured with the four methods also took a few days to stabilize. This indicates that the cured adhesives either underwent hydrolysis in the aqueous solution or the acid components in the ground particles took time to dissolve in the water. The pH values obtained at different curing conditions are summarized in Table I. The pH changed markedly with different curing conditions. For adhesives R-VI and R-VII, the pH increased from 2.92 to 6.91 and from 2.78 to 7.00 when measured with Methods 1 and 2, respectively. However, for R-XI and R-XII, the pH decreased from 3.72 to 3.63 and from 3.60 to 2.39 when measured with Methods 1 and 2, respectively. The pH of the cured films was lower than 3.0 when measured with Methods 1, 2, or 3 and was always higher than 3.0 (around 4 or 5) when measured with Method 4.

Block shear properties

Solid wood

The published shear strengths parallel to the grain of Douglas-fir and black spruce are shown in Table II. Table II shows that the specific gravity and shear strength of solid wood vary with the location of growth and MC. As indicated above, the wood samples used in this study were sourced in Canada. The density of the Douglas-fir used was 0.62–0.72 g/cm^3 based on actual weight at $\sim$ 12% MC and volume at $\sim$ 12% MC, which would be equivalent to specific gravity of 0.54–0.64 based on weight when oven dry and volume at 12% MC. This was higher than the published value, indicating the effect of growth location on this property. The density of the black spruce used was 0.50–0.56 g/cm^3 based on actual weight at $\sim$ 12% MC and volume at $\sim$ 12% MC, which would be equivalent to specific gravity of 0.45–0.50 based on weight when oven dry and volume at 12% MC. This was similar to the published value. Other factors that affect shear strength are test method and specimen type. ASTM D 2559[26] indicates that bonded shear specimens tested in accordance with ASTM D 905-03, on the average, yield higher shear strength values than solid wood shear specimens tested in accordance with ASTM D 143.[27] In this study, ASTM D 905-03 was used in testing both the bonded and solid wood shear specimens.

TABLE II
Block Shear Strength of Douglas-Fir and Black Spruce in North America

Wood species	MC (%)	Specific gravity[a]	Shear parallel to grain (MPa)	Remarks
Douglas-fir (United States)				[b]
Coast	12	0.48	7.8	
Interior west	12	0.50	8.9	
Interior north	12	0.48	9.7	
Interior south	12	0.46	10.4	
Douglas-fir	8	0.43	7.6	[c]
	12		7.0	
	16		6.5	
Black spruce	12	0.46	8.5	[b]

[a] Based on weight when oven dry and volume at 12% MC.
[b] Forest Products Laboratory, 1999.[25]
[c] ASTM D 2559–04.[26]

Bonded wood

The effects of adhesive type and test condition on the shear strength and wood failure of Douglas-fir are shown in Table III. The shear strength after the VPD conditioning was lower than that at the dry condition for all the adhesives, including that of the solid wood specimens. These results indicate that the VPD treatment not only reduced the solid wood shear strength, but also the bonded shear strength and also reduced the amount of wood failure.

The shear strength and wood failure of black spruce, as influenced by adhesive type and test condition, are shown in Table IV. Test condition had less effect on the shear strength of black spruce, in contrast to that of Douglas-fir, which was more negatively affected by the VPD treatment, suggesting that Douglas-fir was less durable than spruce under the wet conditions.

Normalized shear strength

The shear strength values were normalized by dividing the wood-adhesive bond shear strength by the solid wood shear strength (Table V). At the dry condition, the normalized bond strengths for both Douglas-fir and black spruce for all of the adhesives were generally less than 1, indicating that the strength of the solid wood was greater than that of the bond strength.

On the other hand, in the VPD condition, for the high-pH adhesives, the normalized strengths for both Douglas-fir and black spruce were generally greater than 1. This indicates that the short-term VPD exposure did not negatively affect the bond strength of the high-pH adhesives, confirming their

TABLE III
Block Shear Strength and Wood Failure of Douglas-Fir[a]

Resin ID	Treatment	Shear strength (MPa)	Tukey's means comparison grouping[b]	Wood failure (%)	Tukey's means comparison grouping[b]	No. of specimens	Moisture content (%)	Density[c] (g/cm^3)
Solid wood	Dry	13.2 (1.5)	A1		–	16	13.7 (0.4)	0.69 (0.04)
R-I	Dry	11.0 (2.3)	A2, A3, A4	97.4 (4.1)	B1	31	9.9 (0.4)	0.66 (0.02)
R-II	Dry	11.8 (1.3)	A1, A2	99.8 (1.0)	B1	25	12.0 (0.4)	0.66 (0.02)
R-III	Dry	11.3 (1.5)	A2, A3	100 (0.0)	B1	23	12.2 (0.4)	0.66 (0.02)
R-IV	Dry	11.6 (2.0)	A1, A2, A3	100 (0.0)	B1	23	12.2 (0.4)	0.66 (0.02)
R-V	Dry	11.3 (0.9)	A2, A3	97.6 (4.0)	B1	23	12.9 (0.3)	0.66 (0.02)
R-VI	Dry	10.7 (1.3)	A2, A3, A4	97.7 (4.0)	B1	22	11.8 (0.3)	0.66 (0.02)
R-VII	Dry	10.7 (1.3)	A2, A3, A4	97.5 (6.7)	B1	22	12.3 (0.3)	0.67 (0.02)
R-XI	Dry	11.3 (1.8)	A2, A3	99.1 (3.3)	B1	23	12.7 (0.3)	0.67 (0.03)
R-XII	Dry	11.5 (1.4)	A1, A2, A3	91.3 (15.0)	B1, B2, B3	23	11.5 (0.4)	0.66 (0.02)
Solid wood	VPD	8.1 (1.7)	A5, A6		–	31	12.9 (0.5)	0.69 (0.04)
R-I	VPD	9.4 (1.1)	A4, A5	98.6 (4.3)	B1	31	13.0 (0.6)	0.66 (0.02)
R-II	VPD	9.6 (1.2)	A4, A5	96.7 (6.2)	B1, B2	24	13.9 (0.6)	0.66 (0.02)
R-III	VPD	9.4 (1.3)	A4, A5	93.9 (12.3)	B1, B2, B3	23	13.5 (0.6)	0.66 (0.02)
R-IV	VPD	10.1 (0.7)	A3, A4	99.8 (1.0)	B1	23	13.6 (0.5)	0.66 (0.02)
R-V	VPD	9.5 (2.0)	A4, A5	97.5 (4.3)	B1	23	11.6 (0.2)	0.66 (0.02)
R-VI	VPD	8.3 (1.5)	A5, A6	85.9 (14.7)	B3, B4, B5	22	11.8 (1.3)	0.66 (0.02)
R-VII	VPD	8.2 (1.5)	A5, A6	80.2 (16.1)	B4, B5	22	12.7 (0.3)	0.67 (0.02)
R-XI	VPD	7.0 (2.2)	A6	88.3 (13.4)	B2, B3, B4	23	11.6 (0.3)	0.67 (0.03)
R-XII	VPD	7.5 (2.2)	A6	77.0 (19.6)	B5	23	12.3 (0.6)	0.66 (0.02)

[a] Means ± standard deviations of 20+ replicates.

[b] Tukey's grouping: "honestly significant difference" test was conducted for pairwise comparison, significant at 0.05 level of probability. A1, A2, etc. are groups of strength. B1, B2, etc. are groups of wood failure. If the means are in the same group, they are not significantly different.

[c] Based on volume and weight at 12% MC.

TABLE IV
Block Shear Strength and Wood Failure of Black Spruce[a]

Resin ID	Treatment	Shear strength (MPa)	Tukey's means comparison grouping[b]	Wood failure (%)	Tukey's means comparison grouping[b]	No. of specimens	Moisture content (%)	Density[c] (g/cm^3)
Solid wood	Dry	10.8 (1.2)	C1, C2, C3		–	31	14.1 (0.4)	0.52 (0.01)
R-I	Dry	10.2 (1.3)	C2, C3, C4, C5, C6	95.2 (9.5)	D1	36	10.0 (1.2)	0.53 (0.01)
R-II	Dry	10.9 (1.2)	C1, C2, C3	98.4 (2.8)	D1	22	11.5 (0.8)	0.52 (0.01)
R-III	Dry	10.1 (1.8)	C2, C3, C4, C5	95.8 (9.0)	D1	22	11.9 (0.3)	0.52 (0.01)
R-IV	Dry	10.5 (1.0)	C1, C2, C3, C4, C5	95.0 (11.0)	D1	22	11.8 (0.3)	0.52 (0.01)
R-V	Dry	11.4 (1.1)	C1, C2	98.8 (2.2)	D1	24	13.4 (0.3)	0.53 (0.01)
R-VI	Dry	10.5 (1.7)	C1, C2, C3, C4, C5	98.8 (3.6)	D1	25	11.3 (0.2)	0.54 (0.01)
R-VII	Dry	9.6 (1.3)	C3, C4, C5, C6, C7	95.0 (3.6)	D1, D2	20	12.3 (0.2)	0.53 (0.01)
R-XI	Dry	10.0 (1.7)	C2, C3, C4, C5, C6	94.6 (7.6)	D1, D2, D3	25	11.7 (0.3)	0.53 (0.01)
R-XII	Dry	9.3 (1.4)	C4, C5, C6, C7	84.7 (15.0)	D3	24	11.5 (0.4)	0.52 (0.02)
Solid wood	VPD	10.1 (1.6)	C2, C3, C4, C5, C6		–	31	13.6 (0.4)	0.52 (0.01)
R-I	VPD	9.9 (1.3)	C3, C4, C5, C6	95.2 (9.5)	D1	36	12.7 (0.7)	0.53 (0.01)
R-II	VPD	11.8 (1.0)	C1	97.1 (4.9)	D1	21	12.8 (0.3)	0.52 (0.01)
R-III	VPD	10.7 (1.4)	C1, C2, C3, C4	93.4 (8.2)	D1, D2, D3	22	12.4 (0.3)	0.52 (0.01)
R-IV	VPD	10.5 (0.8)	C1, C2, C3, C4, C5	94.6 (10.7)	D1, D2, D3	22	13.1 (0.4)	0.52 (0.01)
R-V	VPD	11.0 (1.3)	C1, C2, C3	95.4 (6.1)	D1	24	13.0 (0.3)	0.53 (0.01)
R-VI	VPD	8.8 (2.2)	C6, C7	92.8 (6.8)	D1, D2, D3	25	13.1 (0.4)	0.54 (0.01)
R-VII	VPD	10.8 (1.3)	C1, C2, C3	93.5 (5.4)	D1, D2, D3	20	13.1 (0.2)	0.53 (0.01)
R-XI	VPD	9.1 (1.2)	C5, C6, C7	85.0 (14.1)	D2, D3	25	12.6 (0.3)	0.53 (0.01)
R-XII	VPD	8.2 (1.2)	C7	66.1 (16.4)	D4	23	11.9 (0.3)	0.52 (0.01)

[a] Means ± standard deviations of 20+ replicates.

[b] Tukey's grouping: "honestly significant difference" test was conducted for the pairwise comparison, significant at 0.05 level of probability. C1, C2, etc. are groups of strength. D1, D2, etc. are groups of wood failure. If the means are in the same group, they are not significantly different.

[c] Based on volume and weight at 12% MC.

TABLE V
Normalized Block Shear Strength for Douglas-Fir and Black Spruce Specimens

Resin ID	Test condition	Douglas-fir	Black spruce
Solid wood	Dry	1.00	1.00
R-I	Dry	0.83	0.95
R-II	Dry	0.90	1.01
R-III	Dry	0.86	0.94
R-IV	Dry	0.88	0.97
R-V	Dry	0.86	1.06
R-VI	Dry	0.81	0.97
R-VII	Dry	0.81	0.89
R-XI	Dry	0.86	0.92
R-XII	Dry	0.87	0.86
Solid wood	VPD	1.00	1.00
R-I	VPD	1.16	0.97
R-II	VPD	1.18	1.17
R-III	VPD	1.16	1.06
R-IV	VPD	1.25	1.03
R-V	VPD	1.18	1.09
R-VI	VPD	1.03	0.87
R-VII	VPD	1.02	1.07
R-XI	VPD	0.86	0.90
R-XII	VPD	0.93	0.81

known good durability. In addition, some penetration of the adhesive into the wood probably occurred, thus reinforcing the wood layer adjacent to the bond line against the effect of the VPD exposure. For the low-pH adhesives, the normalized shear strengths for both Douglas-fir and black spruce were predominantly less than 1, with some values slightly greater than 1. In combination with the wood failure results, indications are that the bond quality of the low-pH adhesives was probably impaired by the VPD treatment.

Statistical analysis of block shear properties

The ANOVA performed on the block shear properties data for the five high-pH adhesives (R-I, R-II, R-III, R-IV, and R-V) is shown in Table VI. The results indicate that wood species did not have a significant effect on block shear strength, but had a significant effect on wood failure. Adhesive had a significant influence on block shear strength, but not on wood failure. Test condition had a significant effect on both block shear strength and wood failure.

The ANOVA values for the block shear properties data for the four low-pH adhesives (R-VI, R-VII, R-XI, and R-XII) are given in Table VII. Wood species did not have a significant effect on either strength or wood failure. Adhesive did not have a significant effect on block shear strength at the 95% level of probability, but had a significant effect on wood failure. Again, test condition had a significant effect on both wood failure and block shear strength. Tukey's "honestly significant difference" test was conducted for the pairwise means comparison at 0.05 level of probability, and the results are shown in Tables III and IV.

For the high-pH adhesives, the block shear strengths of the Douglas-fir specimens were in the same group in dry condition (A2) and also in the VPD condition (A4) as shown in Table II. Likewise, the wood failures were all in the same group (B1). The block shear strengths of the black spruce specimens for all the adhesives were in the same group at the dry condition (C2) and at the VPD condition (C3), except that R-II had a higher value. The wood failures of the black spruce specimens were similar at the dry and at the VDP conditions (D1). The above results suggest that the adhesives with pH between 10.51 and 13.11, as determined by Method 4, had similar impact on the block shear strength and wood failure regardless of wood species. The present results were consistent with the findings of Santos et al.[14] that high-pH phenolic resins did not have a negative effect on shear strength.

For the low-pH adhesives, the block shear strengths of the Douglas-fir specimens were similar in the dry condition (A2 and A3 in Table III), and

TABLE VI
ANOVA of Block Shear Strength and Wood Failure of High-pH Adhesives

Source	DF	SS	Type III SS	Mean square	F-value	$P > F$
Dependent variable: strength						
Model	6	152.17		25.36	11.39	<0.0001
Error	493	1,097.45		2.23		
Corrected total	499	1,249.62				
Wood species	1		4.12	4.12	1.85	0.175
Adhesive	4		57.58	14.40	6.47	<0.0001
Test condition	1		90.79	90.79	40.78	<0.0001
Dependent variable: wood failure						
Model	6	1,179.36		196.56	4.23	<0.0001
Error	493	22,903.30		46.46		
Corrected total	499	24,082.66				
Wood species	1		637.97	637.97	13.73	0.0002
Adhesive	4		262.11	65.53	1.41	0.23
Test condition	1		257.87	257.87	5.55	0.02

TABLE VII
ANOVA of Block Shear Strength and Wood Failure of Low-pH Adhesives

Source	DF	SS	Type III SS	Mean square	*F*-value	$P > F$
Dependent variable: strength						
Model	5	384.58		76.92	21.74	<0.0001
Error	361	1,277.11		3.54		
Corrected total	366	1,661.69				
Wood species	1		1.41	1.41	0.40	0.53
Adhesive	3		22.67	7.56	2.14	0.095
Test condition	1		361.20	361.20	102.10	<0.0001
Dependent variable: wood failure						
Model	5	23,094.5		4,618.9	24.54	<0.0001
Error	361	67,954.15		188.24		
Corrected total	366	91,048.65				
Wood species	1		85.52	85.52	0.45	0.50
Adhesive	3		11,421.61	38,07.20	20.23	<0.0001
Test condition	1		11,717.07	11,717.07	62.25	<0.0001

also in the VPD condition (A6). However, the shear strength was much lower in the VPD condition compared with the dry condition. The wood failures were similar among the adhesives and were even comparable with those of the high-pH adhesives (i.e., all in the same group B1) at the dry condition. However, the wood failures were reduced significantly at the VPD condition. Similarly, the block shear strength and wood failure of the black spruce specimens were higher at the dry condition compared with the VPD condition.

CONCLUSIONS

Adhesive type of varying pH and test condition significantly affected the block shear properties (strength and wood failure) of Douglas-fir and black spruce. The high-pH adhesives (PF and PRF) performed better than the low-pH adhesives (MF and MUF), especially after the VPD conditioning, indicating differences in durability between these two types of adhesives. High-pH adhesives did not have a negative impact on the strength of the bonded specimens.

Because the low-pH adhesives used in this study were not very durable, it is suggested that more-durable low-pH adhesives, if available, be studied to examine their impact on bond durability and properties of the wood layer adjacent to the bond line.

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