

Bacterially derived biopolymers as wood adhesives

Anthony P. Haag^{a,b,*}, Raina M. Maier^c, Joan Combie^d, Gill G. Geesey^{a,b}

^a Department of Microbiology, Montana State University, 109 Lewis Hall, Bozeman, MT 59717, USA

^b Specialty Biopolymers Corp., 524 Professional Dr., Suite E, Bozeman, MT 59718, USA

^c Department of Soil, Water, and Environmental Science, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, USA

^d Montana Biotech Corporation, 1910-107 Lavington Court, Rock Hill, SC 29732, USA

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Abstract

The wood adhesive market is very large and problems due to volatile organic compounds and toxic chemicals in many adhesives and their production are significant. In addition, most of the adhesives are derived from depleting petrochemical resources. An environmentally friendly wood adhesive based on renewable resources and produced by microbial fermentation has been explored. Using the shear block test method, a microbially produced polysaccharide has been tested and the effects of wood type, humidity, set time, partial acetylation, and surface wetting agents were determined. Shear strength of the microbial polysaccharide adhesive was compared to that of a commercial wood adhesive and other polysaccharides. Shear strengths of up to 20 MPa (3000 psi) for bonding maple have been obtained at 53% relative humidity and 22°C.

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1. Introduction

Currently, adhesives used in the wood products industry are petrochemically based (phenol-formaldehyde, polyurethane, polyvinyl acetate). In the United States, greater than 1 billion pounds/year of these resins are utilized for wood products manufacturing. Many of these adhesives contain volatile organic compounds (VOCs) and toxic chemicals and are produced by processes that employ VOC and toxic raw materials. Reduction of the uses of these materials is a stated goal of the United States Environmental Protection Agency's Pollution Prevention program. This, in addition to the fact that petroleum reserves are a disappearing resource, is driving the development of adhesives composed of alternative materials, including natural product-based adhesives.

Polysaccharides are a chemically and structurally diverse class of natural products, some of which possess adhesive properties [1]. Starch, a plant polysaccharide, is

widely used as an adhesive for bonding paper products [2]. It has been combined with polyvinyl alcohol (PVOH), a melamine-formaldehyde derived crosslinking agent, and acrylic latex as a wood adhesive. In three-layered birch veneer plywood, shear strengths of 15 MPa were obtained with the starch/PVOH blend alone and 41 MPa with the starch/PVOH/crosslinker/latex mixture [3]. The latter produced a bond that was stronger than the wood substrate and is comparable to commercial wood adhesives. Even though starch is a renewable resource, the other three components are petrochemical based. Konjac glucomannan, a plant polysaccharide, and chitosan, a polysaccharide derived from chitin obtained from crustacean exoskeletons, were recently evaluated as wood adhesives [4]. Shear strengths of 1–3 MPa were reported for three-ply plywood. For reference, shear strengths of adhesives normally used at room temperature range from 1 to 50 MPa depending on the adherend material, joint design, and rate of loading [5]. In wood bonding applications, shear strengths of adhesives, such as those based on polyvinyl acetate (PVA), are generally expected to surpass that of the wood itself. Thus, the polysaccharides in these studies have produced adhesive strengths which are generally lower than commercial wood adhesives but

*Corresponding author. Department of Microbiology, Montana State University, 109 Lewis Hall, Bozeman, MT 59717, USA. Fax: +1-406-994-1774.

E-mail address: ahaag@montana.edu (A.P. Haag).

may be suitable for some applications. This performance in combination with the fact that there currently are limited adhesives on the market that are free of VOCs and/or petroleum derivatives, or use biological products as their primary component, encourage further research on polysaccharide based wood adhesives.

In general, microbial extracellular polysaccharides do not contain VOCs or toxic chemicals, and can be synthesized through fermentation of renewable resources including organic waste products. These microbiological products are also environmentally compatible and biodegradable. Efficient technology for large-scale production of microbial extracellular polysaccharides currently exists. Xanthan gum, synthesized by the bacterium *Xanthomonas campestris*, is produced by a high-yield process at a rate of 40 MM lb/yr [6] and sells for \$4.5/lb [7]. Microbial extracellular polysaccharides thus possess features that make them worthy of consideration as an alternative to current synthetic chemical adhesives.

Several extracellular polysaccharides of microorganisms have been evaluated as commercial adhesives. Pullulan, an extracellular polysaccharide produced by the fungus *Aureobasidium pullulans*, as well as derivatives of natural pullulan, have been described as a paper adhesive [8,9] and as a wood adhesive [10]. In the latter application, a shear strength of 5 MPa was observed for bonds formed with pine. Dextran has been utilized as a remoistenable adhesive for wallpaper [11] but has not been reported as a wood adhesive. The adhesive properties of an extracellular polysaccharide produced by the marine bacterium *Alteromonas colwelliana* LST have been evaluated [12]. Single lap shear strengths of the adhesive polysaccharide after setting for 7 days in air were reported to be up to 331 KPa on cold rolled steel, 276 KPa on aluminum, and 545 KPa on wood. None of the microbial polysaccharides evaluated to date exhibit properties that demand their use as the primary component of wood adhesives that are free of VOCs. Nevertheless, it is likely that other polysaccharides produced by bacteria possess unique adhesive properties of commercial value. It is also likely that some of these adhesive polysaccharides could be produced using the same large scale production methods as xanthan or dextran, yielding a VOC-free adhesive derived from completely renewable components that, on an economic basis, competes with current petroleum based adhesives.

Previously, we have evaluated a microbial extracellular polysaccharide (MB adhesive) produced by a bacterium from the culture collection of Montana Biotech Corporation as a VOC-free adhesive for aluminum and plastic bonding applications. MB adhesive displayed tensile and shear strengths of 5.6–6.2 MPa on aluminum [13]. The setting mechanism requires drying by evaporation of the water solvent. MB

adhesive does not become crosslinked in this process and the integrity of the adhesive bond is compromised by rehydration. Less hydrophilic derivatives, prepared through chemical modification of the natural product, improved tensile and shear strength during submersion in water and under humid atmospheric conditions [13].

In the following study, we investigate the use of MB adhesive in wood applications. The porous nature of a wood surface is suited to the setting mechanism of the MB adhesive. The shear strength of MB adhesive was evaluated using four wood substrates: maple, a hardwood; Douglas fir, a softwood; and two wood composites, particleboard and medium density fiberboard. Performance of MB adhesive was also compared to that of a commercial PVA-based wood adhesive and other, commercially available polysaccharides. The performance of MB adhesive was also evaluated after chemical derivatization with a less hydrophilic acetate group to improve moisture resistance and as formulations containing surfactants to improve surface wettability.

2. Experimental

2.1. Production and recovery of MB adhesive

The bacterium, which synthesized the MB adhesive, was obtained from the culture collection of Montana Biotech Corp. The bacterium was cultivated in a liquid medium at 35°C as previously described [13]. Cells from 2-day cultures were pelleted by centrifugation. Extracellular polymer was precipitated from the culture menstruum by addition of cold ethanol at a 1:1 (vol/vol) ratio. Precipitated polymeric material was recovered by centrifugation and decantation of the supernatant liquid. The remaining viscous liquid was diluted with water to a concentration of 31% solids. This product (MB adhesive) consisted of 95% carbohydrate [14] and 2% protein [15] by dry weight and was used directly in adhesion experiments.

2.2. Partially acetylated MB adhesive (MB-OAc)

Dried MB adhesive (2.000 g) was dissolved in 4.0 ml of water and then diluted with 40 ml of pyridine. Acetic anhydride (12.1 g, 11.2 ml, 9.5 eqv) was added over a 35-min period with stirring using a cold water bath to maintain the temperature below 30°C. After stirring an additional 20 h at ambient temperature, the partially acetylated MB adhesive (MB-OAc) was precipitated by mixing the reaction mixture with 700 ml of water. After the precipitate was allowed to settle, the supernatant was decanted and the remaining precipitated material was mixed with 10 ml of water over a 15-min period. The MB-OAc was separated and the water wash was

repeated. The MB-OAc was then soaked in 20 ml of water for 2 days. After separation of the aqueous supernatant, the MB-OAc was recovered as a viscous liquid which upon air-drying yielded 2.36 g of solid. Incorporation of acetate ester groups was confirmed by infrared (1750 cm^{-1} , KBr, Nicolet 740 FT-IR spectrometer) and nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$ (500 MHz, DMSO-d_6) δ 1.99 ppm ($-\text{COCH}_3$); $^{13}\text{C-NMR}$ (75 MHz, DMSO-d_6) δ 170.1 ($-\text{COCH}_3$), 20.7 ($-\text{COCH}_3$) ppm; Bruker DRX500 spectrometer). The concentration of acetate groups was determined to be 6.2 milliequivalents/g by the method of Hestrin [16].

2.3. Molecular weight analysis of MB adhesive

The molecular weights of MB and MB-OAc adhesives were examined by size exclusion chromatography on Waters Ultrahydrogel 500 and 2000 columns ($7.8 \times 300\text{ mm}$) on a Dionex DX-300 high-performance liquid chromatograph with a Hewlett-Packard 1037 refractive index detector. Dried MB adhesive was dissolved in 0.1 M aqueous sodium nitrate at a concentration of 5 mg/ml. Solutions (100 μl) of the adhesive were then injected onto the columns and eluted with 0.1 M aqueous sodium nitrate at 22°C at a flow rate of 0.8 ml/min. Since MB-OAc adhesive was not soluble in water, it was deacetylated with ethanolic NaOH prior to application to the column and then analyzed. The molecular weights of the MB and MB-OAc adhesives were determined by comparison of retention time with those of dextran standards.

2.4. Production and recovery of rhamnolipids

Two rhamnolipid materials were used in the study of the effects of surfactants. The monorhamnolipid (α -L-rhamnopyranosyl- β -hydroxydecanoyl- β -hydroxydecanoate) was obtained from *Pseudomonas aeruginosa* ATCC 9027. The rhamnolipid mixture containing both monorhamnolipid and dirhamnolipid (2-O- α -L-rhamnopyranosyl- α -L-rhamnopyranosyl- β -hydroxydecanoyl- β -hydroxydecanoate) was obtained from *P. aeruginosa* IGB83. The growth media, harvesting and purification protocols used for the rhamnolipid preparations have been described previously [17], and were used with the following exceptions. For ATCC 9027 monorhamnolipid production, the glucose in the mineral salts growth medium was increased from 1% to 2%. For IGB83 mono-, dirhamnolipid production, the glucose was increased from 1% to 3%. The molecular weight of the monorhamnolipid preparation is 504 and of the rhamnolipid mixture is 577. The critical micelle concentration of both preparations is 0.1 mM. Desired amounts of the rhamnolipid products were added directly into the adhesive mixtures.

2.5. Commercial products

Titebond™ Original Wood Glue (Franklin International; Columbus, OH) was obtained from a commercial supplier. Sodium alginate (product no. A-2158, “low viscosity”), pullulan (product no. P 4516), sodium carboxymethyl cellulose (Na-CMC, product no. C-8758, “low viscosity”), and starch (from corn, practical, product no. S-4180) were obtained from Sigma-Aldrich (St. Louis, MO). Soluble starch (product no. S516) and Tween™ 80 (polyoxyethylene [20] sorbitan monooleate) were obtained from Fischer Scientific (Pittsburgh, PA). Dextrin (product no. 0161-17) was obtained from Difco Co. (Detroit, MI). UCAR™ 443 was a gift from the Dow Chemical Company.

2.6. Preparation of adhesive mixtures

The MB adhesive was used as prepared above at a 31% concentration (wt/wt). The MB-OAc adhesive was prepared by dissolving 1 part by weight of MB-OAc in 1 part of 95% ethanol and 1.5 parts of water (28% solids). Pullulan was dissolved in water at a 33% concentration. Dextrin, prepared as a 50% aqueous solution, unmodified corn starch, prepared as a 20% aqueous solution, and soluble starch, prepared as a 25% solution, required heating to 80°C to form a homogeneous paste and then they were applied to the wood surface before cooling. Sodium alginate and sodium carboxymethyl cellulose, due to their higher viscosities, were dissolved in water at concentrations of 17% and 20%, respectively. For some experiments, the adhesive was mixed with or applied in conjunction with a surface wetting agent. Surface wetting agents were added at a concentration of 1% or 5% (wt/wt) relative to the adhesive solids content. Surface wetting agents were mixed into the adhesive material by agitation with a spatula until visibly homogeneous. In one study, the monorhamnolipid surface wetting agent was applied as a surface primer, at concentrations of 1% and 9% (wt/wt) in aqueous ethanol, to the wood surface using a brush just prior to the application of adhesive.

2.7. Wood materials

Sugar maple, Douglas fir, particleboard (3/4 in floor underlayment, conforms to ANSI A208.1-99, Potlatch Corp., Post Falls, ID) and medium density fiberboard (3/4 in Super Refined MDF², Plum Creek Timber Co., Columbia Falls, MT) were purchased from commercial lumber suppliers and cut to $30.5 \times 6.4 \times 1.9\text{ cm}$ ($12 \times 2.5 \times 0.75\text{ in}$) dimensions. Maple and fir boards were selected that had the grain follow the long dimension of the board. The face to which the adhesive was to be applied was freshly surfaced with a planer.

2.8. Adhesive strength testing method

ASTM D 905-94 (“Standard Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading”), a general adhesive performance test in wood applications, was used in this study [18]. This method is also used to test water-based PVA adhesives, which set by water evaporation at room temperature, similar in behavior to our adhesive. In this method, two rectangular blocks of wood are bonded together along their largest faces (Fig. 1), and after a set period, the shear strength is measured in the direction along the plane of the bond. In some instances, the shear strength of the adhesive was greater than the shear strength of the wood substrate, so the measurement reflects the integrity of the wood matrix rather than the adhesive.

2.9. Substrate preparation

Four pairs of 0.86-cm diameter holes were drilled at intervals along the length of 30.5-cm-long boards so that five 5.1-cm-long pieces could be cut from each board after bonding and setting. With the exception of the adhesive mixtures prepared from sodium alginate and Na-CMC, which were applied by spreading with a spatula, the adhesives were applied with a brush. Adhesive was applied to achieve a density of 0.013–0.020 g/cm² on each face. The time for adhesive application before joining the two surfaces was typically 5 min. Ten to 20 min after joining, the surfaces were compressed and held in place with eight bolts at 30 Kg-cm of torque. After setting overnight, the bolts were removed and setting continued for a total of 7 days at 53% relative humidity (RH) and 22°C. During the sixth day of setting, the boards were cut to 5.1-cm squares, and 0.64-cm rabbit grooves were cut along each end on

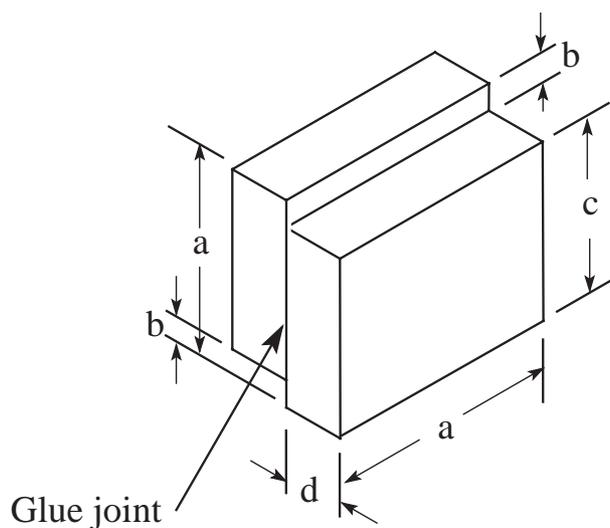


Fig. 1. Wood block dimensions and joining configuration ($a = 5.08$ cm, $b = 0.64$ cm, $c = 4.44$ cm, $d = 1.90$ cm).

opposite sides to the depth of the glue line following ASTM D 905-94. In the study to evaluate set rate, wood specimens were cut to final size prior to application of the adhesive in order to avoid failure during cutting of weakly bonded surfaces at short set times and to achieve more uniform exposure of the bonded surfaces to the desired humidity. Thus, the individual test specimens were glued and then clamped with bar clamps and transferred to an environment in which RH was controlled. The bonded surface area on each specimen was 19.4 cm². The test specimens were stored in plastic bags during transport to cutting and testing locations to minimize changes in moisture content. Shear strength under compression was determined according to ASTM D 905-94 using an Instron testing machine (model 4206) with load cell A509-5 rated at 14,000 kg capacity at a load rate of 0.51 cm/min. Typically 5–10 replicates were performed for each experiment. Shear strength is defined as the load required to break the specimen divided by the area of the bond.

Moisture resistance of the adhesive bond was evaluated as follows: after adhesive application, test specimens were set for 1 week at 53% RH followed by an additional week at (a) 53% RH (control) or (b) 94% RH (elevated RH), all at 22°C. RH of 53% and 94% during the set period was achieved by storing test specimens in a sealed container holding a saturated solution of magnesium nitrate or potassium nitrate, respectively [19].

3. Results and discussion

3.1. Molecular weight of MB and MB-OAc adhesives

The peak molecular weights of the MB adhesive and MB-OAc derivative, as determined by size exclusion chromatography, were approximately 40 kDa (Fig. 2).

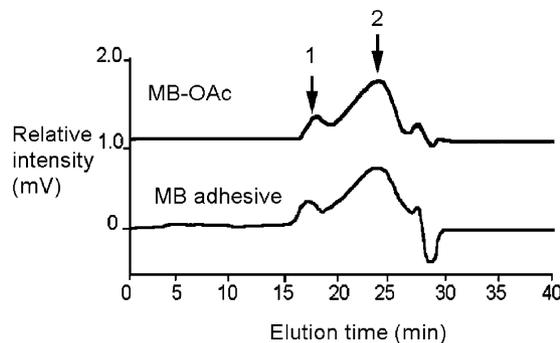


Fig. 2. Size exclusion chromatograms of MB-OAc after deacetylation (top) and MB adhesive (bottom). Peak retention times of molecular weight standards are: dextran ($M_w = 505,000$ Da), 19.8 min; dextran ($M_w = 207,000$ Da), 21.5 min; dextran ($M_w = 41,000$ Da), 23.2 min. Arrow 1 shows exclusion limit of column. Arrow 2 shows elution peak of MB and MB-OAc adhesives.

Table 1
Shear strengths (MPa) of four different wood substrates bonded with MB adhesive and Titebond™

	Maple	Douglas fir	MDF ^a	PB ^b
MB	12.5 (8, 15%) (cohesive failure)	12.2 (5, 13%) (mostly wood failure)	2.1 (3, 12%) (wood failure)	2.5 (3, 6%) (wood failure)
Titebond™	17.2 (10, 6%) (adhesive failure ^c)	13.4 (5, 10%) (mostly wood failure)	2.0 (3, 12%) (wood failure)	2.9 (3, 6%) (wood failure)

Number of replicates and coefficient of variation (standard deviation/mean × 100) are shown in parenthesis.

^aMedium density fiberboard.

^bParticleboard.

^cWith 10–15% wood failure.

The minor, high molecular weight peak corresponds to the exclusion limit of the column (approximately 7000 kDa).

3.2. Performance of MB adhesive relative to commercially available synthetic adhesive on four wood types

The shear strength of MB adhesive was compared to that of Titebond™ Original Wood Glue, an aqueous PVA-based commercial adhesive that also sets at room temperature by water removal (Table 1). The composition of PVA-based adhesives has been described [20]. MB adhesive displayed a shear strength that was 73% of that achieved by Titebond™ on maple. The bond established between maple and MB adhesive generally failed in the cohesive mode. That is, since the wood surface appeared to contain a uniform distribution of MB adhesive on both faces after failure, the strength of the bond was defined primarily by interactions within the MB adhesive matrix rather than by interactions between the wood surface and the MB adhesive. In contrast, the Titebond™ bond with maple showed some failure in the wood substrate and some failure of the adhesive bond, which was primarily in the adhesive mode. That is, the adhesive failed at the wood–adhesive interface, not within the adhesive matrix itself. With the other, softer wood materials, Douglas fir, medium density fiberboard, and particleboard, the wood failed before the adhesive bond for both Titebond™ and MB adhesive.

3.3. Shear strength vs. set time

The relationship between the shear strength of MB adhesive and set time was evaluated on maple substrates. Surfaces exposed to 53% RH achieved nearly 50% of maximum shear strength within an 8 h period, while full strength at this RH was achieved within 48 h (Table 2). The reason for the observed increase in coefficient of variation (CV) of bond strength at the longer set times is not currently understood. No color changes in the adhesive were observed, suggesting the increase in CV was not a result of oxidation.

Table 2
Shear strength vs. set time for MB adhesive bonded to maple at 53% RH

Set time (h)	Mean shear strength(MPa)	No. replicates	CV (%)
2	3.8	4	25
8	6.2	3	6
24	9.8	4	8
48	12.2	3	9
168	13.2	4	20
336	11.4	4	31

Table 3
Shear strength of MB adhesive relative to other polysaccharides bonded to maple following a 7-day set at 53% RH

Adhesive	% Solids (wt/wt)	Mean strength (MPa)	No. replicates	CV (%)	<i>p</i> -value at 95% confidence level ^a
MB	31	14.5	10	20	
Titebond™	45	19.7	10	11	0.0003
Na-CMC	20	17.0	5	22	0.21
Dextrin	50	4.1	5	58	
Na-alginate	17	9.0	4	21	0.002
Pullulan	33	13.6	5	28	0.80

^aProbability based on 2-tail student's *t*-test that shear strength of candidate adhesive is significantly different from that of MB adhesive.

3.4. Comparison of shear strength of MB adhesive with commercially available polysaccharides

The shear strength of the MB adhesive was compared to that of several commercially available polysaccharides as well as Titebond™ after a set time of 7 days at 53% RH. The shear strength of Titebond™ was significantly greater (at 95% confidence level) than that of the MB adhesive under these conditions (Table 3). Whereas, Na CMC and pullulan exhibited shear strengths that were not significantly different from MB adhesive, the shear strengths of Na alginate and dextrin were significantly less than that of MB adhesive (Table 3). Unmodified corn starch and soluble starch, which are chemically similar to dextrin, exhibited weaker shear strengths and more replicate variability than dextrin (data not shown).

3.5. Surfactant effects

Surface wetting agents or surfactants can decrease the surface tension of the substratum allowing better surface coverage of the adhesive to improve their interaction. Two types of naturally occurring, bacterially derived surfactants, a mono-rhamnolipid (RL) and a mono-RL/di-RL mixture (Fig. 3), and Tween™ 80 were evaluated for their ability to improve the shear strength of the MB adhesive on wood. When the mono-RL surfactant was added to the MB adhesive at a concentration of 1% (wt/wt), relative to MB solids, and the mixture used to bond maple surfaces and set at 53% RH at room temperature for 7 days before testing, the shear strength increased 24% relative to that achieved with the MB adhesive alone (Table 4). The difference, however, was not statistically significant at the 95% confidence level. The primary bond failure mode was cohesive with a considerable amount (80%) of wood failure. Increasing the mono-RL concentration to 5% (wt/wt) total solids also improved the shear strength relative to MB alone, but not to the extent achieved at the 1% concentration (Table 4). The primary bond failure mode was again

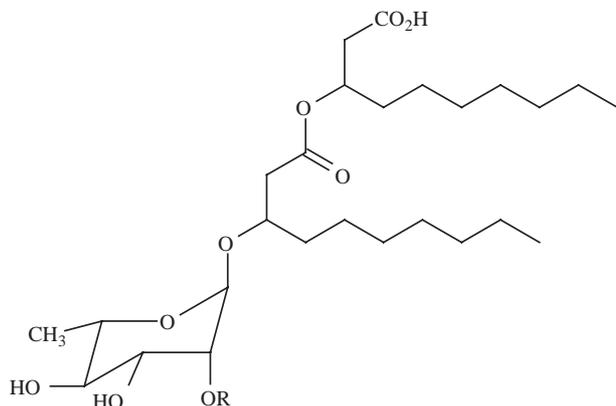


Fig. 3. General structure of rhamnolipid: monorhamnolipid, R = H; dirhamnolipid, R = L-rhamnosyl.

cohesive with a considerable amount of wood failure. Application of the mono-RL as a surface primer with 1 or 9% solid content before application of the MB adhesive resulted in a 50% decrease in shear strength relative to that of the MB adhesive without added primer (Table 4). When the mono/di-RL surfactant was added to the MB adhesive at a concentration of 1% (wt/wt) of total solids, the shear strength of the mixture was 9% greater than that of the MB adhesive alone (Table 4). The primary bond failure mode was again cohesive with a considerable amount of wood failure. Increasing the concentration of the surfactant in the mixture to 5% (wt/wt) of total solids resulted in a 45% decrease in shear strength relative to that produced by the MB adhesive alone. The primary bond failure mode was cohesive with only a small amount (5%) of wood failure. The surfactant Tween™ 80, when added to the MB adhesive at a concentration of 1% (wt/wt) of total solids, increased the shear strength by 16% over that achieved by the MB adhesive without added surfactant (Table 4). However, the difference was not significant at the 95% confidence level. Increasing the Tween™ 80 concentration to 5% (wt/wt) total solids decreased shear strength to 61% of that achieved by MB adhesive without added surfactant. In summary, the shear strength of the MB adhesive bond increased, although not significantly at the 95% confidence level, with the addition of 1% surfactant in the order mono-RL > Tween 80 > mono/diRL. Finally in this series of experiments, note that although the shear strength of MB adhesive without added surfactant was 19% greater than in the previous series (Table 3), this difference was not statistically significant at the 95% confidence level in the Student's *t*-test.

In the group of experiments shown in Table 5, set times were extended to 14 days (either a continuous 14 days at 53% RH, or 7 days at 53% RH followed by 7 days at 94% RH). When set for 14 days at 53% RH, shear strengths of MB adhesive formulations containing the mono-RL surfactant or UCAR™ 443, a styrene-

Table 4
Effect of surfactant on shear strength of MB adhesive bonded to maple following a 7-day set at 53% RH

Adhesive	Surfactant conc.[% (wt/wt) of total solids]	Mean strength (MPa)	% change relative to control	No. replicates	CV (%)	<i>p</i> -value at 95% confidence level ^b
MB (control)	0	17.2		4	15	
MB + mono-RL	1	21.4	+24	4	21	0.08
MB + mono-RL	5	19.8	+16	5	19	
MB + mono/di-RL	1	18.8	+9	4	11	
MB + mono/di-RL	5	9.4	-45	5	40	
MB + Tween 80	1	20.0	+16	5	8	0.06
MB + Tween 80	5	6.6	-61	5	68	
MB with mono-RL primer	1 ^a	8.5	-50	4	34	
MB with mono-RL primer	9 ^a	8.2	-52	4	84	

^aConcentration of surfactant in primer.

^bProbability based on 1-tail student's *t*-test that shear strength of MB adhesive with surfactant is significantly greater than that of MB adhesive without added surfactant.

Table 5
Effect of exposure to elevated humidity on shear strength of MB adhesive/surfactant formulation

Adhesive	Relative humidity (%)	Mean shear strength (MPa)	% Change relative to control	p-Value at 95% confidence level ^a	% of strength achieved at 53% RH	No. replicates	CV(%)
MB (control)	53	13.0				4	29
MB+1% mono-RL	53	18.4	+41	0.02		5	7
MB+1% mono-RL	53 →94	0.1			1	5	46
MB+5% mono-RL	53 →94	0.1			1	5	43
MB+5% UCAR 443	53	21.2	+63	0.01		3	13
MB+5% UCAR 443	53 →94	0.2			1	5	42
MB+15% UCAR 443	53	21.9	+68	0.004		5	10
MB+15% UCAR 443	53 →94	0.1			1	5	36

^aProbability based on 1-tail student's *t*-test that shear strength of MB adhesive with surfactant is significantly greater than that of MB adhesive without added surfactant (control) after a 7-day set time at 53% RH.

Table 6
Influence of relative humidity on shear strength of MB adhesive and its partially acetylated derivative

Adhesive	Relative humidity(%)	Mean strength (MPa)	% of strength achieved at 53% RH	No. replicates	CV (%)	p-value at 95% confidence level ^a
Titebond™	53	24.0		8	19	0.0004
Titebond	53→94	17.2	72	10	6	
MB	53	16.3		8	23	
MB	53→94	0.2	1	3	12	
MB-OAc	53	14.4		8	24	0.29
MB-OAc	53→94	5.1	35	9	34	

^aProbability based on 2-tail student *t*-test that shear strength of candidate adhesive is significantly different from that of MB adhesive.

acrylic latex were significantly greater (95% confidence level) than that of MB adhesive without added surfactant set under the same conditions. Previously, when shear strength was evaluated after a 7-day set time, shear strength of the MB adhesive formulation containing mono-RL was not significantly greater than the MB adhesive without added surfactant (Table 4). These results suggest that surfactants improve shear strength of the adhesive at moderate humidity when set time is increased from 1 to 2 weeks. At this time, we do not have an explanation for the time-dependent effect that these surfactants have on shear strength of the adhesive at moderate RH. Although UCAR 443 provided a greater effect on shear strength than mono-RL, the latter provides an advantage by its production from renewable resources and biodegradability.

3.6. Adhesive performance at elevated RH

Long-term performance of adhesive joints is affected by climatic conditions such as humidity and temperature. Adhesives that resist these effects have more applications and are of greater value. MB adhesive, when applied to maple, set for 7 days at moderate (53%) RH, and then exposed to elevated (94%) RH, retained only 1% of the shear strength achieved after a 14-day set at moderate RH (Table 6). In contrast, Titebond™, when exposed for 7 days to elevated RH following a

7-day set at moderate RH, retained 72% of the shear strength achieved after a 14-day set at moderate RH (Table 6). As observed previously (Table 3), the shear strength of Titebond™ was significantly greater than that of the MB adhesive when set for 14 days at moderate RH.

As shown in Table 5, the addition of surfactant did not improve shear strength of the MB adhesive at elevated RH relative to that displayed by MB adhesive without added surfactant. MB adhesive containing mono-RL at either 1% or 5% (wt/wt) total solids, like the MB adhesive without added surfactant, lost essentially all shear strength when exposed to elevated RH for 7 days following a 7-day set at moderate RH (Table 5). UCAR™ 443, which has been observed to improve the water resistance of cross-linked, starch-based wood adhesives [3], when added at either 5% or 15% (wt/wt) of total solids, also failed to improve shear strength at elevated RH relative to that achieved by the MB adhesive without added surfactant (Table 5).

As shown in Table 6, a partially acetylated derivative of the MB adhesive (MB-OAc), when applied to maple and exposed to elevated RH for 7 days following a 7-day set time at moderate (53%) RH retained 35% of the shear strength it exhibited after a 14-day set time at moderate RH. The shear strength of MB-OAc after the 14-day set time at moderate RH was 88% of and not significantly different from that displayed by the native

MB adhesive subjected to the same conditions (Table 6). The results demonstrate that partial substitution of hydroxyl groups with acetate groups resulted in an improvement in shear strength at elevated RH from 0.1 to 5.1 MPa. However, this derivative still displayed a shear strength that was only 30% of that achieved by Titebond™ exposed to the same conditions. Nevertheless, the results suggest that moisture resistance can be significantly improved through manipulation of polysaccharide chemistry.

4. Conclusions

The microbially derived MB adhesive is a strong wood adhesive under conditions of moderate humidity. This performance results from its polysaccharide structure. The adhesive strength at high humidity may be increased by covalent derivatization of the polysaccharide hydroxyl groups with less hydrophilic acetyl groups. As has been shown for other adhesives, addition of surface wetting agents also improves the strength of the MB adhesive on wood. The combination of good adhesive strength at moderate humidity and environmentally friendly features makes formulations of the MB polysaccharide a potentially useful wood adhesive in applications where bonding agents containing toxic, non-biodegradable VOCs or petroleum-based products are undesirable. Since facilities already exist for large-scale production of microbial polysaccharides, the MB adhesive should be economical to produce and price competitive with current wood adhesives on the market which contain components that pose a risk to human and environmental health.

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