

Bacterially derived wood adhesive

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Accepted 16 March 2005

Available online 11 July 2005

Abstract

Wood adhesives play an essential role in industry, however, many contain significant amounts of toxic components and volatile organic compounds (VOCs) and most are produced from depleting petrochemical resources. We are currently investigating adhesives derived from microbial extracellular polysaccharides for use in the wood products market. Polysaccharides are generally non-toxic, biodegradable, and produced from renewable resources. This study focuses on a new extracellular polysaccharide-based adhesive with performance that may be useful in some wood product applications. The adhesive exhibits improved performance over a previously described bacterial polysaccharide and produces shear strengths on maple substrates of up to 20 MPa at 53% relative humidity and 22 °C. Full strength was achieved in two days with half strength in 2 h. Although shear strength was sensitive to relative humidity, moisture resistance was substantially increased by partial acetylation of the polysaccharide.

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Keywords: Adhesives for wood; Novel adhesives; Water based; Environmentally friendly

1. Introduction

Wood and wood-based composites offer a sustainable resource for the building, furniture, and construction industries. Adhesives are an integral component of wood products and the market is very large (>\$1 billion/year in the United States). However, most wood adhesives, for example, phenol/formaldehyde, polyurethane, and polyvinyl acetate (PVA), are based on non-renewable, depleting petrochemical resources. In addition, many adhesives contain residual toxic chemicals, such as formaldehyde, and VOCs. Reduction in the use of these materials is a goal of the United States Environmental Protection Agency's Pollution Prevention program. Current approaches to reduce VOCs include aqueous emulsion and hot melt technologies.

Although greatly reducing VOC emissions, these adhesives still rely on petrochemical-based polymers.

An alternate approach that addresses environmental concerns is biologically based adhesives. Included are adhesives based on animal protein (hide, casein), plant protein (soy), and plant polysaccharide (starch). Biologically based adhesives are generally useful but have limited applications due to moisture sensitivity, thermal instability, or processing difficulties.

Polysaccharides are a structurally diverse class of natural polymers with repeat units containing one or more monosaccharides which are joined by acetal linkages (Fig. 1). Characteristic functional groups are ethers and hydroxyls which, due to their polar nature and hydrogen-bonding ability, impart strong adhesion to high energy surfaces like wood. In addition, the high molecular weight of polysaccharides imparts substantial cohesive strength necessary in a useful adhesive. In general, as a result of the high density of polar functionalities, polysaccharides are also hydrophilic. The strength of adhesives prepared from them is

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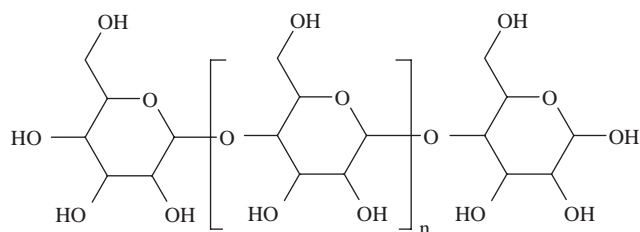


Fig. 1. A general, representative polysaccharide structure, poly(1,4-glucopyranose).

affected by the presence of water which can be undesirable in some adhesive applications. The hydroxyl groups of polysaccharides can be converted to more hydrophobic ester or ether derivatives which affords a net reduction in the hydrophilicity of the polysaccharide. Partial acetylation has been employed to improve melt processing behavior of starch [1], reduce swelling by water, and reduce biodegradation rate [2,3].

Polysaccharides that have been evaluated as wood adhesives include starch, which in combination with petrochemical-based components, produced a strong, moisture resistant plywood adhesive [4]. Konjac glucomannan, a plant polysaccharide, and chitosan, a polysaccharide derived from chitin which is obtained from crustacean exoskeletons, have been evaluated as wood adhesives [5]. In general, the adhesives based solely on polysaccharides have adhesive strengths lower than commercial wood adhesives but may be suitable for non-structural applications. This performance in combination with the fact that there are limited adhesives on the market that are free of VOCs or petrochemical derivatives, or use biological products as their primary component, encourage further research on polysaccharide-based wood adhesives.

Extracellular polysaccharides derived from microorganisms are an attractive source of adhesive materials. They generally do not contain VOCs or toxic chemicals and can be synthesized by fermentation of renewable resources. Biofilm-forming microbes utilize extracellular polysaccharides in aqueous environments for surface attachment [6]. Extracellular polysaccharides also occur with chemically diverse structures which may be selected for specific applications. Economical production of extracellular polysaccharides on an industrial scale has been demonstrated. For example, xanthan gum is efficiently produced at an annual rate of 40 million pounds [7] and sells for \$4.5/lb [8].

Microbial polysaccharides that have been evaluated as wood adhesives include pullulan [9] and “polysaccharide adhesive viscous exopolymer (PAVE)” [10]. Shear strength of the former using pine wood substrates was comparable to a commercial PVA-based adhesive (5 MPa). However, no shear strength data was presented for pullulan when used to bond hardwood substrates,

and no moisture resistance data was presented. PAVE showed shear strengths of up to 0.55 MPa. In the single-lap, tensile shear test method (6.2 cm² bond area) which was used, neither the type of wood substrate nor the relative humidity (RH) used for the test were described. More recently, an adhesive derived from another bacterial polysaccharide which was produced by Montana Biotech Corporation (MB adhesive) exhibited shear strengths approaching that of a commercial PVA-based adhesive on maple substrates at moderate (53%) RH [11]. Upon exposure to high (94%) RH, the bond lost virtually all of its strength. Derivatization of the polysaccharide hydroxyl groups with a more hydrophobic acetate group imparted a small but significant improvement in moisture resistance.

In the following study, we describe another microbially derived extracellular polysaccharide (termed SB adhesive for Specialty Biopolymers adhesive) and its partially acetylated derivative that display higher shear strength with maple substrates than the corresponding MB adhesives at high humidity.

2. Experimental

2.1. General

Proton (500 MHz) and carbon-13 (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer. Samples were dissolved in dimethyl sulfoxide (DMSO)-d₆ and chemical shifts reported relative to residual DMSO-d₅ at $\delta = 2.50$ (¹H) and 39.51 ppm (¹³C). Infrared spectra were recorded on a Nicolet 740 FT-IR spectrometer. Samples were prepared as KBr pellets.

2.2. SB adhesive

This adhesive is a proprietary composition developed by Specialty Biopolymers Corporation, Bozeman, MT, which contains, as its sole component, a polysaccharide with a peak molecular weight of 500 kDa. The adhesive was prepared at a 33% concentration (wt/wt) of polysaccharide in water.

2.3. MB and MB-OAc adhesive

The preparation of these materials has been previously described [11,12]. MB adhesive was synthesized by a bacterium from the culture collection of Montana Biotech Corp. Extracellular polymer was precipitated from the culture menstruum by addition of ethanol. The precipitate was isolated 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 and 2% protein by dry weight. MB-OAc with a degree of acetylation of 57% was prepared by acetylation of dried MB adhesive with acetic anhydride. Peak molecular weights of both MB and MB-OAc adhesives were 40 kDa.

2.4. Commercial adhesive

Titebond™ Original Wood Glue (Franklin International; Columbus, OH) was obtained from a commercial supplier.

2.5. Preparation of partially acetylated SB adhesive (SB-OAc)

Dried SB adhesive (5.10 g, containing 4.5% water) was dissolved in 9.59 g of water. Pyridine (82 mL) was added and then, with efficient stirring, acetic anhydride (41.50 g, 13.5 eqv) was added over a 1-h period. During the addition, temperature was maintained at $<30^{\circ}\text{C}$ with a cooling bath. After stirring at ambient temperature for an additional 21 h, SB-OAc was precipitated by diluting the reaction mixture with 1.4 L of cold water. This mixture was allowed to cool at 5°C for 3 h and then centrifuged to aid phase separation. The white, sticky precipitate was separated by decantation of the supernatant liquid. The precipitate was washed twice with 50 mL of water and then allowed to stand overnight in 50 mL of water. After decantation of the water, the soft, white gummy material (15.91 g) was air-dried, reweighed (7.51 g), and IR and NMR spectra obtained: IR 1758 cm^{-1} ; $^1\text{H-NMR}$ δ 2.02 ppm ($-\text{COCH}_3$); $^{13}\text{C-NMR}$ δ 169.3–170.0 ($-\text{COCH}_3$) and 20.4–21.2 ppm ($-\text{COCH}_3$). The degree of substitution of acetyl groups was determined by the method of Hestrin [13] with glucose pentaacetate as standard. The SB-OAc adhesive was prepared at a 36% solids concentration (wt/wt) of acetylated polysaccharide in 44% aqueous ethanol.

2.6. Wood materials

Sugar maple (*Acer saccharum*), Douglas fir (*Pseudotsuga menziesii*), particleboard (3/4" floor underlayment, conforms to ANSI A208.1-99, Potlatch Corp., Post Falls, ID) and medium density fiberboard (MDF, 3/4" Super Refined MDF², Plum Creek Timber Co., Columbia Falls, MT) were purchased from commercial suppliers and cut to $30.5 \times 6.4 \times 1.9\text{ cm}$ ($12 \times 2.5 \times 0.75$ inch) 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. The wood materials were conditioned to equilibrium moisture content (constant weight) by storage in sealed containers over saturated aqueous solutions of potassium acetate, magnesium nitrate, or potassium nitrate (23, 53, or

94% RH, respectively) at 22°C [14]. A period of 2 weeks typically was required to reach equilibrium moisture content.

2.7. 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 [15]. 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 or composites are bonded together along their largest, tangential faces (Fig. 2), and after a set period, the shear strength is measured along the plane of the bond and in the direction of the grain. In some instances, the shear strength of the adhesive was greater than the shear strength of the wood or composite substrate, so the measurement reflects the integrity of the wood or composite matrix rather than the adhesive. The percentage of the bond area that shows wood failure is recorded and reported as an average for each set of replicates.

2.8. Substrate preparation and testing

Four pairs of 0.86-cm diameter holes were drilled at intervals along the length of the 30.5-cm-long boards so that five 5.1-cm-long pieces could be cut from each board after bonding and setting. Adhesive was applied with a brush to achieve a density of $0.015\text{--}0.020\text{ g/cm}^2$ on each face. The time between application of the adhesive and joining the two surfaces was typically 5 min. Ten to 20 min after they were joined, the surfaces

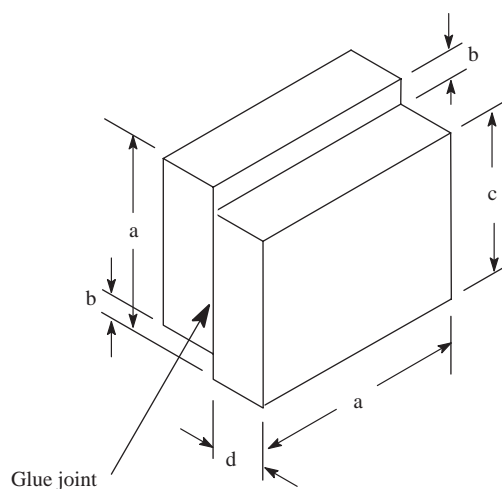


Fig. 2. Wood block dimensions and joining configuration ($a = 5.08\text{ cm}$, $b = 0.64\text{ cm}$, $c = 4.44\text{ cm}$, $d = 1.90\text{ cm}$).

were compressed and held in place with eight bolts at 30 kg-cm of torque. After the adhesive was allowed to set overnight, the bolts were removed, and setting was allowed to continue for a total of seven days at 53% RH, unless specified otherwise, and 22 °C. During the sixth day of setting, the boards were cut to 5.1-cm squares and 0.64-cm rabbet grooves were cut along each end on 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 in the specified configuration and transferred to an RH-controlled environment. 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 4206 testing machine 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. Error is reported in terms of coefficient of variation (CV) which is defined as the standard deviation divided by the mean. Percentage of wood failure was also measured. All tests were done using maple substrates except for the initial survey with two wood species and two composites.

Moisture resistance of the adhesive bond was evaluated as follows: after conditioning of the wood at either 53 or 23% RH and adhesive application, test specimens were set for one week at 53 or 23% RH

followed by exposure to a) 53% (moderate) RH or b) 94% (high) RH at 22 °C for additional periods of time.

3. Results and discussion

3.1. Comparison of SB adhesive with a commercial, PVA-based adhesive benchmark on two wood types and two wood composites

In a preliminary survey, SB adhesive formed a bond that was nearly as strong as the commercial benchmark, TitebondTM Original Wood Glue, on maple (79% of Titebond's shear strength) and Douglas fir (93% of Titebond's shear strength) when set at 53% RH for 14 or 8 days, respectively, at 22 °C (Table 1). Statistical analysis showed, however, that the shear strengths with SB adhesive were not significantly different than Titebond at the 95% confidence level (student t-test, 2-tail, Table 1). SB adhesive had 88% of the shear strength of Titebond for bonding particleboard (PB) and 55% of Titebond's strength for bonding medium density fiberboard (MDF) after setting at 53% RH for 14 days. The shear strengths of both SB adhesive-bonded composites were significantly different than those of Titebond at the 95% confidence level (Table 1).

Titebond-bonded maple specimens failed primarily in the adhesive mode (83%), i.e., at the adhesive-wood interface, with 17% wood failure. SB adhesive-bonded specimens failed primarily in the cohesive mode (82%) with a similar amount of wood failure (18%). Both Titebond and SB adhesive-bonded fir specimens failed predominantly in the wood matrix (85% and 79%, respectively). Titebond-bonded particleboard and MDF showed 100% composite failure. The SB adhesive-bonded particleboard showed cohesive failure with only low amounts of composite failure (27%). The SB

Table 1
Shear strengths of two wood and two composite substrates bonded with SB adhesive and TitebondTM original wood glue

Adhesive	Substrate	Shear strength (MPa)	Number of replicates	CV%	Average % wood failure	<i>p</i> ^a
SB	Maple	14.6	5	15	18	0.07
	Douglas fir	12.5	5	10	79	0.29
	PB	3.7	5	9	27	0.03
	PB, sanded	3.8	5	4	100	
	MDF	2.2	4	30	1	0.005
	MDF, sanded	3.6	5	28	24	0.04 ^b
Titebond	Maple	18.5	5	18	17	
	Douglas fir	13.4	5	10	85	
	PB	4.2	5	6	100	
	MDF	4.0	5	10	100	

Bonded specimens were allowed to set at 53% RH for 14 days (maple, particleboard, and MDF) or 8 days (fir).

^a*p* is the probability that the shear strength of the SB bonded substrate is not significantly different than that of the corresponding Titebond bonded substrates as calculated with the student *t*-test (two-tail) at a 95% confidence level. A significant difference is indicated by *p* < 0.05.

^bCompared with the corresponding unsanded MDF bonded with SB adhesive.

adhesive-bonded MDF also showed cohesive failure with even lower amounts of composite failure (1%). These results with particleboard and MDF are in contrast to the results obtained previously with another microbial polysaccharide-derived adhesive, MB adhesive, which gave the same strength as Titebond with 100% composite failure [11]. Subsequent experiments showed that a light surface sanding improved the performance of SB adhesive on particleboard and MDF. Although the bonded particleboard showed only a slightly higher shear strength (3.8 MPa, Table 1), the specimens now showed 100% composite failure. The bonded MDF showed a significant improvement in shear strength (3.6 MPa), however, it still exhibited a low degree of composite failure.

3.2. Set rate

The effect of set time on shear strength was examined using SB adhesive and maple substrates at 23% and 53% RH. At 53% RH, half (7.0 MPa) of the maximum shear strength was obtained in just 2 h (Fig. 3). The maximum (14.1 MPa) was obtained in two days and then shear strengths decreased at extended times. The shear strength at the final time point was significantly different than the 48-h value but not significantly different than the 168-h value based on the 95% confidence level in the student t-test (2-tail). It was also notably lower than results in other experiments using a 336-h (2 wk) set time; a difference that cannot be explained at this time. Note that edge effects may be more pronounced in this experiment in which the blocks were bonded individually relative to all other experiments in which the blocks were cut from the larger bonded assemblies. The greater edge effects may account for the lower shear strengths observed at the longer set times.

At 23% RH, half (10.2 MPa) of the maximum shear strength was also attained within 2 h of joining and the

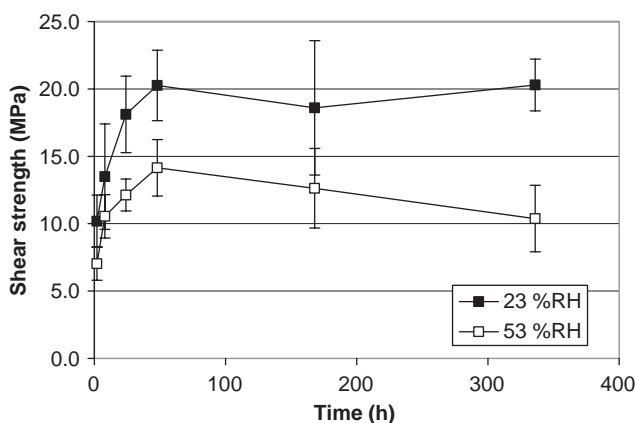


Fig. 3. The effect of set time on shear strength at 23% and 53% RH. Error bars represent \pm one standard deviation.

maximum (20.2 MPa) was obtained in 48 h. Note that the 23% RH setting conditions produced a shear strength that was 50% higher than that at 53% RH. The maximum shear strength of SB adhesive at 23% RH was also approximately equal to that obtained with Titebond at 53% RH (Table 1).

3.3. Moisture resistance

Characterization of adhesive performance under a range of environmental conditions is important in determining the potential applications and market value of an adhesive. The effect of RH on shear strength was determined after the bonded maple specimens were allowed to set for one week at moderate (53%) RH followed by exposure to high (94%) RH for increased times. Bonds formed with maple substrates and Titebond™ Original Wood Glue, the benchmark to which SB adhesive was compared, exhibited an average shear strength of 23.9 MPa (CV 8%) over a five-week period at 53% RH (Fig. 4). Bonds formed with the SB adhesive under the same conditions exhibited an average shear strength of 18.0 MPa (CV 13%). The shear strength of the SB adhesive bond formed after one week at 53% RH was not significantly different from that measured after

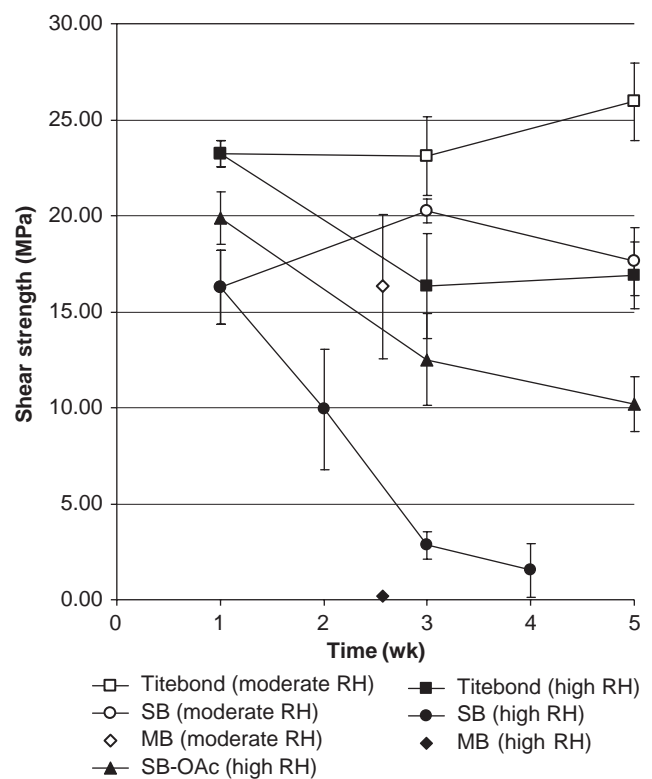


Fig. 4. The effect on shear strength of prolonged exposure of bonded maple substrates to high or moderate RH after an initial one-week set period at moderate RH. Error bars represent \pm one standard deviation. To facilitate comparison, MB data from Ref. [11] is included.

a five-week period (probability, $p = 0.28$). Note that the shear strength of SB adhesive in this experiment was significantly different than the corresponding data shown in Table 1 ($p = 0.01$). We cannot explain this variability at this time.

When exposed to 94% RH for two weeks after the initial one-week set period at 53% RH, the bond formed by TitebondTM retained 69% of the strength observed after one week at 53% RH (Fig. 4). Exposure to 94% RH for two additional weeks produced no further loss in shear strength. The strength of the bond formed by the SB adhesive after one, two and three weeks exposure to 94% RH after the initial one-week set at 53% RH was 61, 17, and 9%, respectively, of that observed after the initial one-week set at 53% RH (Fig. 4). Thus, the bond formed with SB adhesive exhibited greater sensitivity to elevated humidity than that formed with TitebondTM.

The sensitivity of the bond formed by SB adhesive to elevated humidity was also determined after an initial set period at 23% RH for one week. The bond formed after one week at 23% RH exhibited a shear strength of 25.3 MPa (CV 6%) that was 55% greater than that formed after one week at 53% RH, but dropped to 13.7 MPa (CV 14%) after one week at 94% RH (54% of strength after one week at 23% RH), to 3.9 MPa (CV 31%) after two weeks (15% of initial strength), and to 1.3 MPa (CV 77%) after three weeks (5% of initial strength). Thus, the loss in bond strength upon exposure to high humidity could not be avoided by performing the initial set at a lower humidity.

The results are consistent with a reversible setting mechanism in which the shear strength is dependent on the concentration of water in the adhesive. The adhesive hardens as the water solvent evaporates or is absorbed into the wood substrate and reaches a final shear strength dependent on the equilibrium moisture content in the adhesive at the ambient RH. Setting rate increases under conditions that favor more rapid loss of water, lower RH and drier wood. After setting to full strength, bond weakening occurs under conditions of elevated humidity by reabsorption of moisture into the adhesive. The rate of moisture reabsorption, and hence rate of loss of shear strength, when humidity conditions change will be determined by the relative change in atmospheric RH as well as the mass and dimensions of the wood that is bonded since wood also absorbs moisture and slows the mass transfer of moisture into the bond.

3.4. Improvement in moisture resistance by derivatization

Based on the evidence that bond strength is compromised by water absorption at high humidity, the SB adhesive was chemically modified to impart a more hydrophobic character. The polysaccharide was par-

tially acetylated with a controlled amount of acetic anhydride to yield a water insoluble product (SB-OAc) in which 58% of the available hydroxyl groups were acetylated. When SB-OAc was prepared as a 36% solution in aqueous ethanol and used to bond maple substrates, a significant improvement in moisture resistance of the bond was observed. Bonds formed after one week at 53% RH exhibited a significantly higher shear strength ($p = 0.01$) that was 122% of that formed by nonderivatized SB adhesive. SB-OAc also exhibited a shear strength that was 86% of that formed by TitebondTM set under the same conditions (Fig. 4). After a two-week exposure at 94% RH, SB-OAc adhesive maintained a shear strength of 63% of its initial value. By comparison, bonds formed with nonderivatized SB adhesive and TitebondTM maintained 15 and 69%, respectively, of the strength displayed under the same conditions (Fig. 4). After a four-week exposure at 94% RH, bonds formed with SB-OAc adhesive maintained 51% (10.2 MPa) of the shear strength displayed by bonds formed after one week at 53% RH (Fig. 4). By comparison, nonderivatized SB adhesive and TitebondTM formed bonds that maintained 9% (1.5 MPa) and 70% (16.9 MPa), respectively, of the shear strength achieved after one week at 53% RH. Thus, substitution of the polysaccharide hydroxyl groups with more hydrophobic acetate esters effectively improves moisture resistance. These results support earlier evidence that the strength of the bond formed between wood substrates and SB adhesive depends on water exclusion.

3.5. Comparison of SB adhesive with MB adhesive produced from another microbial polysaccharide

In the current study, mean shear strengths for SB adhesive set at 53% RH on maple substrates were similar to shear strengths previously reported [11] for MB adhesive under the same conditions. However, SB adhesive did show improved performance over MB adhesive at high RH. As reported earlier, after a one-week set at 53% RH and exposure to 94% for 1.6 wk, MB adhesive retained only 1% of its initial strength (0.2 MPa, Fig. 4). As described above in Section 3.3, after exposure to 94% RH for 2.0 wk, SB adhesive retained 17% of its initial strength (2.8 MPa, Fig. 4). However, the shear strength of SB adhesive did reach essentially the same level as MB adhesive upon extended high RH exposure (three weeks total).

The partially acetylated SB adhesive, SB-OAc, exhibited significantly higher shear strength ($p = 0.0002$) than the corresponding partially derivatized MB adhesive, MB-OAc, which had a similar degree of acetylation (57%), after three weeks continuous exposure at 53% RH (Fig. 5). SB-OAc also showed a significantly higher ($p = 0.004$) shear strength than MB-OAc after one-week

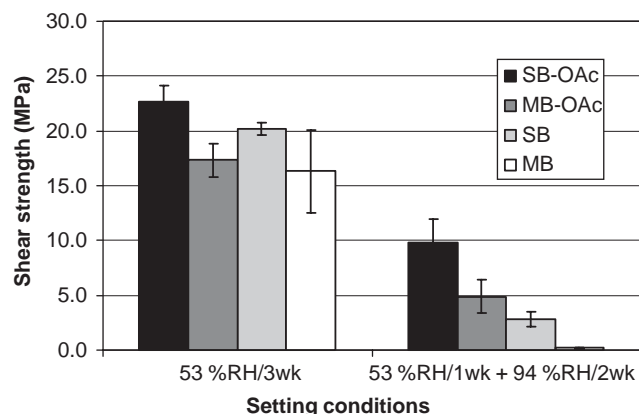


Fig. 5. Comparison of moisture resistance of SB and MB adhesives and their partially acetylated derivatives, SB-OAc and MB-OAc. Shear strengths of bonded maple substrates bonded at 53% RH for three weeks or 53% RH for 1 week followed by 94% RH for two weeks. Error bars represent \pm one standard deviation. MB data from Ref. [11] has been added for comparison (setting conditions were 53% RH for 2.6 weeks or 53% RH for one week followed by 94% RH for 1.6 weeks.)

set at 53% RH followed by exposure to 94% RH for two weeks.

Thus, SB and MB adhesives showed similar shear strengths at 53% RH and although both eventually lose virtually all their strength at 94% RH, the rate of loss, or the sensitivity to moisture, was lower for SB adhesive. The acetylated derivatives both showed improved moisture resistance in comparison to the nonderivatized materials, however, SB-OAc gave significantly higher shear strengths at both 53% and 94% RH than MB-OAc. These results show that the extent to which acetylation improves moisture resistance of bonds formed between wood substrates by polysaccharide adhesives depends to a large extent on the structure of the nonderivatized polymer.

4. Conclusions

Microbially derived biopolymers, such as SB adhesive, form strong bonds with sugar maple at low and moderate RH, achieving shear strengths comparable to commercial PVA-based adhesives. Higher shear strengths and faster set times are obtained with decreasing relative humidity and wood moisture content. A reversible setting mechanism is indicated by the dependence of shear strength on RH and wood moisture content. The set time at moderate RH indicates this adhesive is suitable for construction of indoor furniture and cabinetry. Improvement in overall shear strength,

particularly at high RH, is achieved by partial substitution of the polysaccharide hydroxyl groups with more hydrophobic acetate groups which supports a similar conclusion in our previous work. However, the degree of improvement in moisture resistance by acetylation depends on the composition of the nonderivatized polysaccharide. Although partial acetylation improves performance, the additional production operation adds to the product cost. Ultimately, the most efficient process for producing improved derivatives may result from engineering- known biosynthetic polysaccharide derivatization processes directly into adhesive-producing bacterial strains.

Acknowledgments

This research was funded by Grant BES-0116013 from the National Science Foundation, a grant from the Montana Board of Research and Commercialization Technology, Montana State Department of Commerce, and Grant 2004-33610-14384 from the US Department of Agriculture, Small Business Innovation Research.

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