Adhesive bonding of acetylated wood

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Eighteen thermoplastic and thermosetting adhesives, including emulsion polymer-isocyanates, polyurethane, moisture-curing hot-melt, polyvinyl acetates, neoprene and waterborne contacts, casein, epoxy, melamine, ureas, resorcinol, phenol-resorcinols, and phenolics, were tested for their adhesion to yellow-poplar wood acetylated to 0, 8, 14 and 20 weight percent gains. Effectiveness of adhesion was determined by measuring shear strength and wood failure in a dry condition and after saturation with water. Adhesion was reduced to varying degrees in proportion to the compatibility of the adhesive with the amount of non-polar, hydrophobic acetate groups in the acetylated wood. Seven of the adhesives developed bonds of high integrity at all levels of acetylation when tested in the dry condition. Two room-temperature-setting adhesives, one a resorcinol-formaldehyde and the other a phenol-resoroinol-formaldehyde, together with a hot-setting acid-catalysed phenol-formaldehyde, developed bonds of high strength and resulted in wood failure at all levels of acetylation when tested in the water-saturated condition.

Key words: adhesive bonding; acetylated wood; emulsion polymer-isocyanates; polyurethane; moisture-curing hot-melt; polyvinyl acetates; neoprene contact; waterborne contact; casein; epoxy; melamine; urea; resorcinol; phenol-resorcinol; phenol

The rate of biodeterioration and moisture-related dimensional changes can be drastically reduced by modifying the chemical structure of the woods cell wall. Chemical modification may inhibit specific enzymatic reactions that cause biodeterioration. Bonding chemicals may bulk the wood and make it hydrophobic so that moisture necessary for biodeterioration and dimensional change is excluded. One of the most studied chemical modifications for wood is acetylation, which has been researched from time to time worldwide since the mid-1940s. Acetylation is the esterification of the hydroxyl groups of wood by reaction with acetic anhydride to form esters, mainly on hemicelluloses and lignin. Acetylation is a single-site reaction where one acetyl group reacts with one hydroxyl group with no polymerization. For every acetyl group reacted, one hydroxyl group is blocked from hydrogen bonding with a water molecule, and the result is lower affinity of acetylated wood for water. Acetylated wood is also bulked, making it less permeable to water and less subject to dimensional change than untreated wood. Furthermore, acetylated wood is more resistant than untreated wood to common decay fungi because they must have high levels of moisture to survive[1].

In 1950, Rudkin[2] attempted to demonstrate that the reduced availability of hydroxyl groups of wood substance could reduce the adhesion of urea-formaldehyde resin to wood. To show this, he blocked hydroxyl groups with acetyl groups through esterification. This treatment decreased bond strengths. Then he hydrolysed the acetylated wood with 5% aqueous sodium hydroxide to 'restore' hydroxyl groups to the wood. This treatment increased bond strengths.

Narayanamurti and Handa[3] reported losses in strength by urea-formaldehyde, casein and protein adhesives on several Indian species. They also reported acetylation did not affect the bond strength of resorcinol-formaldehyde and animal adhesives. In recent work on bonding acetylated aspen flakes into flakeboard, Rowell and others[4] found that phenol-formaldehyde resin did not effectively wet and

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penetrate the hydrophobic surfaces of the flakes. Poor adhesion to acetylated flakes manifested itself in only 25% wood failure and low internal bond strength, modulus of rupture and modulus of elasticity of the flakeboard.

If acetylated wood could be effectively bonded, several potential applications for acetylated wood could radically change the way wood is utilized. One area of immediate interest is bonding of acetylated wood veneers, flakes, particles and fibres into composite products. Acetylation of small or thin pieces of wood is the most practical application, because penetration of chemicals into wood and removal of the excess after reaction is a problem in larger pieces of solid wood. Furthermore, a simplified dip procedure nas been developed for acetylation of softwood and hardwood flakes with acetic anhydride without using either cosolvent or catalyst[5]. Reaction time is shortened and chemical recovery is simplified.

Very little is currently known about the compatibility of different adhesive types with acetylated wood except for the limited information just cited. In general, it can be expected that conventional waterborne wood adhesives, which are highly polar and have strong attractions for the hydroxyl groups of wood, will be less attracted to the less polar, hydrophobic acetylated wood with its depleted hydroxyl groups. In contrast, non-polar adhesives may be more compatible with acetylated wood than normal wood.

The first step to achieving good adhesion to acetylated wood is to establish a data base on the compatibility of acetylated wood with a broad array of adhesive types, regardless of whether the adhesive application is appropriate for conventional wood-based products and applications. This basic information will provide a rationale for further experimentation with promising adhesives on acetylated wood and in combination with dissimilar materials.

Materials and methods

Adhesives

Eighteen adhesives (Tables 1 and 2) representative of thermoplastic and thermosetting adhesive types were evaluated for their adhesion capabilities to acetylated and untreated wood.

Acetylated wood

Straight-grained, defect-free, yellow-poplar sapwood lumber was sawn into strips 6 mm thick, 31 mm wide and 46 cm long for making test joint assemblies. After cutting, the strips were dried for 24 h at 105°C. The weight of each oven-dried strip was measured immediately after removal from the oven.

The strips were acetylated without use of cosolvent or catalyst[5] in the following manner. Strips separated by stickers were placed in a stainless-steel vacuum-pressure reactor. The reactor was filled with enough acetic anhydride not only to cover the strips at the initial filling, but also to cover them after absorption of chemical. A vacuum of 635 mm Hg was drawn and maintained for 30 min, then released. The strips were soaked at atmospheric pressure for 30 min. Excess chemical was drained: then the reactor was heated for 3 h at 120°C. After reaction, a vacuum (635 mm Hg) was drawn for 1 h while the reactor was still hot. Strips were dried in an oven for 24 h at 105°C. Weight gain caused by acetylation was determined after oven-drying by calculation as a percentage of the original oven-dried weight.

All wood strips, including the untreated controls, were conditioned to equilibrium moisture content (EMC) at 27°C and 65% relative humidity (RH). At these conditions, strips with acetyl weight percent gains (WPG) of 8. 14 and 20% had respectively lower EMCS of 5.5, 4.5 and 3.5%. Untreated controls averaged approximately 11% EMC. After the controls were bonded with hot-press adhesives, the strips were conditioned to 4% EMC at 34.4°C and 20% RH. Before planing, these strips were weighed for subsequent calculation of moisture content. The strips were planed before bonding.

Acetylated strips representative of each acetyl retention level and untreated controls were sampled for pH, and these values are shown in Table 3. The ASTM Method D 1583[6], designed for measuring pH of dry adhesive films. has been found satisfactory for measuring pH of groundwood particles.

Experimental methods

Experimental design

This experiment was designed to determine the ability of 18 adhesives to bond to wood that had been acetylated to increasing levels of 0, 8, 14 and 20 WPG. Effectiveness of the bonds was determined by measuring shear strength and wood failure in a dry and a wet condition after a vacuum-pressure soak (VPS). When used to differentiate bonding capabilities of phenolic resins, measuring wood failure after VPS has been proven to be more effective than cyclic boiling tests[7] and lengthy, cyclic VPS and drying tests[8]. The latter method has also been the industry standard for quality control testing of exterior-grade plywood since 1966[9].

The experiment was designed as two separate experiments - one for shear strength and wood failure in a dry condition and the other for shear strength and wood failure in a wet condition. Both experiments were completely randomized designs with sub-sampling. The treatments were arranged factorially for 18 adhesives and four levels of acetylation (0, 8, 14 and 20 WPG) to yield 72 treatment combinations. Each treatment combination was replicated four times with four observations of each property from each replicate to yield 16 observations for each treatment combination mean. A total of 4608 observations were made on shear strength and wood failure after testing in both dry and wet conditions.

Specimen preparation

A test joint assembly was prepared by laminating two conditioned and planed strips of acetylated wood, each 6 mm thick, 31 mm wide and 23 cm long.

For cold pressing, the adhesive was spread on both surfaces of the two-ply laminate at a rate approximating 340 g m^{-2}. For hot pressing, the adhesive was spread only on one surface at a rate of 220 to 245 g m-^{2}. A paint brush was used to spread the adhesive. Adhesive spread rate was accurately controlled by automatically tare-weighing the adhesive as it was spread on the laminates. Closed assembly times varied between 15 and 25 min, depending on individual curing characteristics. Hot-setting adhesives were cured in an electrically heated laboratory hot-press at 175°C. Pressure was maintained at 860 kPa for the manufacturer's recommended curing time.

Four block-shear specimens were cut from each joint assembly. The shear area measured 25.4 by 25.4 mm. After cutting, specimens were randomly assigned to either the dry or wet shear tests.

Specimen testing

Sixteen specimens representative of each treatment combination were subjected to a single VPS, then loaded to failure while in the water-saturated condition. The saturation procedure consisted of the following events:

Table 1. Mean values of dry shear strengths and wood failures and their comparisons by level of acetylation for 18 adhesives

Adhesive	Comparison of shear strength (MPa) by level of acetylation[a]				Comparison of wood failure (%) by level of acetylation[a]			
Polyurethane- and isocyanate-based adhesives								
Emulsion polymer-isocyanate (C) (cold set)	0 (13.00)	14 (12.39)	20 (12.24)	8[b] (15.21)	8 (100)	14 (99)	0 (96)	20 (89)
Emulsion polymer-isocyanate (A) (cold set)	0 (13.45)	8 (12.08)	14 (10.79)	20 (9.10)	0 (93)	8 (77)	14 (53)	20 (36)
Polyurethane (cold set)	20 (12.52)	0 (12.40)	14 (12.34)	8 (12.14)	0 (78)	14 (64)	20 (62)	8 (42)[c]
Polyurethane hot-melt (cold set)	20 (6.85)	14 (6.73)	0 (6.61)	8 (6.11)	0 (0)	8 (0)	14 (0)	20 (0)
Polyvinyl acetate emulsion adhesives								
Polyvinyl acetate (cold set)	0 (12.95)	8 (12.72)	14 (11.40)	20 (8.00)	0 (100)	8 (83)	14 (24)	20 (22)
Polyvinyl acetate cross-link (cold set)	0 (12.49)	14 (11.96)	20 (11.74)	8 (11.26)	0 (100)	8 (100)	14 (100)	20 (100)
Rubber-based contact-bond adhesives								
Neoprene contact-bond (cold set)	20 (10.78)	14 (10.77)	8 (10.24)	0 (9.69)	14 (13)	20 (8)	8 (1)	0 (0)
Waterborne contact-bond (cold set)	0 (3.84)	8 (3.45)	14 (2.96)	20 (2.61)	0 (0)	8 (0)	14 (0)	20 (0)
Casein adhesive (cold set)	0 (12.09)	8 (11.15)	14 (9.06)	20 (8.06)	0 (96)	8 (86)	14 (26)	20 (19)
Epoxy-polyamide adhesive (cold set)	0 (12.50)	8 (11.58)	20 (10.57)	14 (7.85)	0 (87)	8 (62)	20 (40)	14 (4)
Amino resin adhesives								
Melamine-formaldehyde (hot set)	0 (11.72)	8 (11.34)	14 (10.16)	20 (8.75)	0 (100)	8 (87)	14 (45)	20 (12)[c]
Urea-formaldehyde (hot set)	0 (11.06)	14 (10.10)	20 (9.71)	8 (9.45)	0 (78)	14 (78)	8 (73)	20 (41)
Urea-formaldehyde (cold set)	0 (12.20)	8 (11.40)	14 (7.68)	20 (4.59)	0 (90)	8 (82)	14 (4)	20 (1)

Table 1. — continued

Table 1. – Continued

Adhesive	Comparison of shear strength (MR) by level of acetylation[a]				Comparison of wood failure (%) by level of acetylation"			
Resorcinol and phenol-resorcinol adhesives								
Resorcinol-formaldehyde (cold set)	14 (11.82)	0 (11.74)	20 (11.37)	8 (10.98)	0 (99)	8 (98)	14 (93)	20 (82)[c]
Phenol-resorcinol-formaldehyde (cold set)	0 (11.54)	14 (10.91)	20 (10.83)	8 (10.81)	0 (93)	8 (93)	20 (89)	14 (75)
Phenol-resorcinol-formaldehyde (hot set)	14 (11.81)	0 (11.74)	8 (10.82)	20 (10.76)	0 (95)	14 (78)	8 (61)	20 (32)
Phenolic adhesives								
Phenol-formaldehyde (hot set)	8 (11.49)	0 (11.00)	20 (10.66)	14 (7.67)	0 (100)	8 (84)	20 (69)	14 (46)[c]
Acid-catalysed phenol-formaldehyde (hot set)	0 (12.36)	8 (10.69)	20 (10.00)	14 (9.99)	0 (100)	14 (95)	20 (91)	8 (87)[c]

[a] Comparisons of shear strength and wood failure: mean values underlined by the same line are not significantly different at the 0.05 level of probability.

[b] Levels of acetyl weight gain: 0 is untreated control, 8 WPG. 14 WPG and 20 WPG.

[c] Comparisons are based on medians of the percentage of wood failure which are slightly different from the comparisons of means (see statistical analysis section).

Table 2. Mean values of wet shear strengths and wood failures and their comparisons by level of acetylation for 18 adhesives

Adhesive	Comparison of shear strength (MPa) by level of acetylation[a]				Comparison of wood failure (%) by level of acetylation[a]			
Polyurethane- and isocyanate-based adhesives								
Emulsion polymer-isocyanate (C) (cold set)	14 (8.98)	8 (7.40)	20 (6.56)	0[b] (6.17)	0 (91)	8 (57)	14 (53)	20 (13)
Emulsion polymer-isocyanate (A) (cold set)	0 (6.02)	8 (5.09)	14 (3.01)	20 (1.88)	0 (32)	8 (1)	14 (1)	20 (0)
Polyurethane (cold set)	20 (7.69)	14 (6.31)	8 (6.15)	0 (5.71)	0 (14)	14 (7)	8 (5)	20 (3)
Polyurethane hot-melt (cold set)	14 (3.67)	20 (3.67)	8 (3.32)	0 (3.15)	0 (0)	8 (0)	14 (0)	20 (0)
Polyvinyl acetate emulsion adhesives								
Polyvinyl acetate (cold set)	20 (0.33)	14 (0.14)	8 (0.03)	0 (0.03)	0 (0)	8 (0)	14 (0)	20 (0)
Polyvinyl acetate cross-link (cold set)	0 (6.05)	8 (5.03)	14 (4.77)	20 (4.65)	0 (19)	8 (2)	14 (0)	20 (0)
Rubber-based contact-bond adhesives								
Neoprene contact-bond (cold set)	14 (3.89)	0 (3.78)	20 (3.77)	8 (3.54)	0 (0)	8 (0)	14 (0)	20 (0)
Waterborne contact-bond (cold set)	20 (0.54)	14 (0.50)	0 (0.48)	8 (0.44)	0 (0)	8 (0)	14 (0)	20 (0)

Table 2. –continued

Table 2. – Continued

Adhesive	Comparison of shear strength (MPa) by level of acetylation[a]				Comparison of wood failure (%) by level of acetylation[a]			
Casein adhesive	0	14	20	8	0	8	14	20
(cold set)	(2.10)	(0.83)	(0.75)	(0.62)	(0)	(0)	(0)	(0)
Epoxy-polyamide adhesive	0	20	8	14	0	8	14	20
(cold set)	(2.76)	(1.94)	(1.73)	(1.08)	(0)	(0)	(0)	(0)
Amino resin adhesives								
Melamine-formaldehyde	14	20	8	0	0	8	14	20
(hot set)	(7.44)	(7.30)	(6.86)	(6.02)	(99)	(95)	(43)	(10)
Urea-formaldehyde	14	8	20	0	0	8	14	20
(hot set)	(6.24)	(5.77)	(5.57)	(5.27)	(93)	(41)	(24)	(0)[c]
Urea-formaldehyde	8	0	14	20	8	0	14	20
(cold set)	(6.67)	(5.65)	(3.63)	(2.47)	(67)	(61)	(0)	(0)
Resorcinol and phenol-resorcinol adhesives								
Resorcinol-formaldehyde	14	20	8	0	8	0	14	20
(cold set)	(9.66)	(9.63)	(6.87)	(6.80)	(100)	(97)	(95)	(90)[c]
Phenol-resorcinol-	14	20	8	0	8	0	20	14
formaldehyde (cold set)	(9.54)	(9.28)	(7.08)	(6.38)	(100)	(95)	(83)	(77)
Phenol-resorcinol-	20	14	8	0	0	14	8	20
formaldehyde (hot set)	(7.03)	(7.00)	(6.67)	(5.43)	(98)	(70)	(50)	(13)
Phenolic adhesives								
Phenol-formaldehyde	0	20	8	14	0	8	14	20
(hot set)	(5.66)	(5.50)	(4.89)	(3.90)	(97)	(0)	(0)	(0)
Acid-catalysed phenol-	20	14	8	0	0	8	14	20
formaldehyde (hot set)	(7.60)	(6.58)	(6.35)	(6.25)	(100)	(100)	(100)	(93)

[a] Comparisons of shear strength and wood failure; mean values underlined by the same line are not significantly different at the 0.05 level of probability.
[b] Levels of acetyl weight gain: 0 is untreated control, 8 WPG, 14 WPG and 20 WPG.
[c] Comparisons are based on medians of the percentage of wood failure which are slightly different from the comparisons of means (see statistical analysis section).

- Submerge specimens in tap water at room temperature in a pressure vessel.
- Maintain a vacuum of 635 mm Hg for 30 min.
- Maintain a pressure of 450 ± 30 kPa for 30 min.
- Submerge in water until tested.

Dry and wet specimens were tested in a compression-loading shearing tool as described in ASTM Method D 905[10]. The load was applied at a constant 2.54 mm min^{-1} until failure. The maximum load at failure was measured, then shear strength was calculated for each specimen based on the shear area. The percentage of wood failure was estimated on the sheared area to the nearest 5%. The broken wet specimens were dried in an oven before estimating wood failure.

Statistical analysis

Analyses of variance (ANOVAS) were conducted for shear strength and wood failure in both dry and wet conditions. Mean shear strength values passed the test of normality at the 0.05 probability level; therefore, a parametric ANOVA was conducted using test joint assembly variation to test for treatment effects. Mean percentages of wood failure were not normally distributed; therefore, a non-parametric ANOVA based on median rather than mean values was used to test assembly variation against treatment effects. Parametric ANOVAS were also conducted using mean percentages of wood failure, recognizing the data were not normally distributed. Mean rather than median treatment values for wood failure are reported in Tables 1 and 2. When treatment mean values of wood failure were statistically compared without a notation, the comparisons based on parametric and non-parametric ANOVAS gave the same results. If the different ANOVAS produced different comparisons, this was then noted with an asterisk and the comparison shown was based on median values or non-parametric ANOVA.

Results and discussion

The ANOVAS for shear strength and wood failure in both dry and wet conditions indicated that adhesive type, level of acetylation and their interaction were very highly significant at the 0.0001 level of probability. The level of acetylation for wet shear strength was significant only at the 0.0279 level of probability. Because these interactions were so highly significant, it was necessary to statistically compare levels of acetylation for each adhesive for each of the four properties measured - shear strength and wood failure in dry and wet conditions. Mean values for each property and statistical comparisons of treatment mean values are shown for each adhesive in Tables 1 and 2. Adhesives are individually discussed within adhesive-type groups.

Polyurethane- and isocyanate-based adhesives

Emulsion polymer-isocyanate

The emulsion polymer-isocyanate (EPI(C)) adhesive was in the developmental stage, but its dry shear strength and wood failure were among the highest of all adhesives at all levels of acetylation (Table 1). Mean dry strength values were not significantly affected by higher levels of acetylation, and the 96% dry wood failure of control specimens was not significantly different from mean values at the other treatments. Wet shear strength values (Table 2) significantly increased at higher levels of acetylation when compared to the untreated controls. Mean values of wet wood failure decreased significantly from the control as acetylation levels increased.

The EPI(C) adhesive was a waterborne system, but it contained non-polar polymers that may have contributed to the compatibility of adhesive and non-polar acetylated wood. The adhesive spread well over the surfaces and did not overpenetrate, which may be a reflection of its high molecular weight and solids content.

Emulsion polymer-isocyanate

The emulsion polymer-isocyanate (EPI(A)) adhesive did not perform as well as the EPI(C), in either the dry or wet shear strength and wood failure tests. Each property value showed a significant decline as the level of acetylation increased (Tables 1 and 2). From microscopic inspection of failed adhesive joints, it was evident that the adhesive overpenetrated the acetylated wood surfaces. Rapid penetration of the surface was noticeable even while spreading adhesive. The EPI(A) adhesive was also a waterborne system but, unlike the EPI(C) adhesive that contained non-polar polymers, the EPI(A) contained polar polymers. Its poorer performance relative to the EPI(C) adhesive might also be attributed to lower molecular weight and solids content and to differences in surfactants.

Polyurethane

Polyurethane was a high-viscosity adhesive that did not appear to penetrate the wood effectively despite the fact that almost 24 h were needed for the adhesive to set. Furthermore, the moisture content of the acetylated wood was 3.5 to 5.5%, depending on level of acetylation, after conditioning at 27°C and 65% RH. The low moisture content of the wood and dry ambient air may have inhibited reaction of polyurethane with moisture. Even so, dry and wet strengths of bonds to acetylated wood were strong, but not strong enough to produce high wood failure. Treatment levels did not have significant effects on strength and wood failure in either dry or wet conditions (Tables 1 and 2).

Perhaps by lowering molecular weight and increasing moisture on the substrate, more effective bonds could be developed on acetylated wood with the polyurethane adhesive.

Moisture-curing polyurethane

Moisture-curing polyurethane is a relatively new type of hot-melt adhesive that not only sets by cooling to room temperature, but also cures by reaction of moisture with its primary component, methylene bisphenyl isocyanate. The cured polyurethane is a 100% solid system; therefore, no solvents or other emissions are lost during cure.

Dry and wet shear strengths of the polyurethane hot-melt adhesive were not affected by levels of acetylation, as indicated by no significant differences between mean values (Tables 1 and 2). The bonds were not strong enough to produce wood failure on acetylated wood in either the dry or wet conditions, but wood failure also did not occur on the untreated wood. Hot-melt adhesives do not generally produce bonds strong enough to fail wood, except on low-density woods.

Performance of the polyurethane hot-melt was as good on acetylated wood as on untreated wood, thus it could be used for apphcations where a hot-melt adhesive would be appropriate.

Polyvinyl acetate adhesives

Polyvinyl acetate

Polyvinyl acetate (PVA) adhesives set by loss of water primarily by diffusion of water from the adhesive film into the wood. Acetylated wood is hydrophobic and much less polar than untreated wood, so that wetting and penetration of the PVA was probably inhibited. Also, the rate of water loss slowed, so that PVA particles did not completely coalesce into a continuous film. Dry shear strengths of PVA bonds to untreated wood were very high, at 12.95 MPa and wood failure was 100%. However, as the level of acetylation increased, dry strength and wood failure declined to 8 MPa and 22% at 20 WPG. Except at the 8 WPG, PVA did not develop sound dry-strength bonds to acetylated wood (Table 1). After saturation, PVA bonds to untreated and acetylated wood had essentially no strength (Table 2).

Acetylation caused significant losses in dry strength and wood failure and a complete loss of bond integrity in the wet condition; therefore, the conventional PVA adhesive should not be used to bond acetylated wood. However, performance of the cross-linked PVA adhesive was much better, as the following discussion indicates.

Polyvinyl acetate, cross-linked

Polyvinyl acetate, cross-linked (PVAX) adhesives set by loss of water the same way as conventional PVAS, but they also cross-link on addition of acidic metal salts. The cross-linked structure increases their resistance to moisture, particularly when bonds are cured at elevated temperatures. These bonds were cured at room temperature. Dry shear strengths of bonds to acetylated wood were quite high and comparable to the untreated controls. Dry wood failure was 100% irrespective of treatment levels. Wet shear strengths of bonds to acetylated wood were not significantly different from each other, but all were significantly lower than the untreated controls. Wood failure of the water-saturated bonds was quite low (Table 2).

The PVAX adhesive performed as well in dry strength tests on acetylated wood as on untreated wood, but strengths deteriorated on both woods after water saturation. It seems quite probable that the hydrophobic acetylated wood slowed water loss and setting of the adhesive. By curing at elevated temperatures, the rate of water loss and cross-linking would accelerate, which might improve adhesion and water resistance significantly.

Rubber-based contact-bond adhesives

Neoprene contact

Neoprene contact is a high-solids adhesive dispersed in organic solvent. Typically, the adhesive is spread on both bonding surfaces, allowed to air dry, then both surfaces are brought into contact where the bond is formed immediately by autohesion. After the bond is formed, the adhesive sets by solvent loss to the atmosphere and wood surface during the open, air-drying time.

Both neoprene and organic solvents of the neoprene contact adhesive are non-polar and hydrophobic. The neoprene contact developed very strong bonds to the hydrophobic acetylated wood where dry bond strengths at the 14 and 20 WPG levels were actually significantly stronger than the untreated controls (Table 1). Contact-bond adhesives are elastomers and normally do not produce wood failure. No meaningful wood failure occurred on the acetylated wood. After water saturation, the neoprene contact retained 35 to 40% of its dry shear strength (Table 2). Neoprene contact adhesive should be considered for appropriate applications in bonding acetylated wood products.

Waterborne contact

The hydrophobicity of acetylated wood had an inhibiting effect on the strength of the waterborne contact adhesive when compared to the untreated control (Table 1). Furthermore, dry bond strengths of the waterborne contact amounted to only 31% on average of the organic solvent neoprene contact. Wet shear strengths of the waterborne system were very low (Table 2). Waterborne contacts generally develop lower dry and wet strengths than solvent-based contacts on wood. However, the acetylated wood had reduced polarity and a limited capacity to absorb water from the waterborne contact, so that the wetting, penetration and setting of the adhesive were diminished.

Casein adhesives

Casein adhesives develop very strong bonds to wood, but they are not capable of withstanding long-term exposures to moist environments without significant deterioration. Casein adhesives cure by chemical cross-linking of proteins with di- and poly-valent metal ions or in a condensation reaction with formaldehyde. This adhesive is also dispersed in water: therefore, it must also set by loss of water while cross-linking is taking place. From the comparisons of dry strength values shown in Table 2, it seems that increased hydrophobicity of higher acetylation levels contributed significantly to strength losses and the sharply declining levels of wood failure. The wet strengths of casein bonds were quite low (Table 2).

Casein adhesives develop water resistance by slow chemical reaction of calcium hydroxide with soluble sodium caseinate to form the insoluble calcium caseinate. Acetylated wood contains free acetic acid that is a by-product of the acetylation process. The pH of a 0.01 N aqueous solution of acetic acid is approximately 3.4, which is slightly more acidic than the pH of acetylated yellow-poplar (Table 3). If free acetic acid of this concentration was present in sufficient quantity, it might inhibit calcium caseinate formation and thus promote water resistance.

Epoxy-polyamide adhesive

Epoxy bonds to wood are generally strong when tested in a dry condition, but they weaken drastically when subjected to water saturation and drying. If primers are used to increase adhesion, epoxy bonds can withstand exterior environments. Poor exterior performance is probably caused by inadequate wetting and limited penetration of high molecular-weight adhesives into the wood. Epoxy-polyamide (EP) adhesive was diluted with 10% butyl glycidyl ether in an effort to increase its penetration, which helped somewhat. After examining failed bonds under the microscope, it was evident that the adhesive penetration was poor. Not only was there poor adhesion to the wood, as evidenced by failures in adhesion to the wood, but some cohesive failures were evident. Although the adhesive did bond well to the untreated controls, it was still negatively affected by the level of acetylation. as indicated by lowered dry shear strengths and wood failures (Table 1). Wet shear strengths were very low and wood failure was non-existent (Table 2). The lowered polarity of the acetylated wood probably contributed to the poorer wetting and penetration, hence the bond strengths, as the level of acetylation increased.

Amino resin adhesives

Melamine-formaldehyde

Melamine-formaldehyde (MF) is a hot-press adhesive that is well known for its strong and highly durable

Table 3. Values of pH for the untreated and the acetylated yellow-poplar wood strips

Acetylation level (WPG)	pH[a]
Untreated	4.23
8	3.64
14	3.87
20	3.90

[a]Based on six specimens

bonds to wood. This is also indicated by the high shear strengths and wood failures in both dry and wet tests of untreated controls (Tables 1 and 2). It is evident that acetylation interfered with adhesion because wood failure was significantly lower with each increasing level of acetylation. Dry shear strengths at the untreated and 8 WPG levels were significantly higher than at 20 WPG (Table 1). In the tests of wet bonds, significant declines in the percentage of wood failure occurred with higher levels of acetylation. However, wet shear strengths were high at all levels, and strengths at the 20 and 14 WPG levels were significantly higher than controls. As discussed in the resorcinolic and phenolic adhesive section, this consistent trend to higher wet strengths was associated with the higher density and lower moisture contents of the wood with the higher levels of acetylation.

While spreading adhesive on acetylated wood, the adhesive seemed to gel slightly, probably caused by the presence of acetic acid in the acetylated wood (Table 3). After hot pressing, the bonds had a milky appearance, indicating the film had not formed completely because of premature gelling and water had not dissipated properly from the film and interface during the curing process. Whether this speculation is accurate is not known, but it is apparent that acetylation caused marked deterioration of MF bonds.

Urea-formaldehyde (hot set)

Urea-formaldehyde (UF) hot bonds were almost as strong in dry and wet tests as the MF adhesive (Tables 1 and 2). Dry shear strengths at all levels of acetylation were not significantly weaker than the controls. Dry wood failure was not significantly lower than controls, except at the 20 WPG. Again, wet shear strengths tended to increase with increasing acetylation, as with the MF adhesive, and subsequently discussed resorcinolic and phenolic adhesives. Wet wood failure steadily declined with increasing acetylation.

With the exception of the acid-catalysed phenolic adhesive that will be discussed later, all of the hot-pressed adhesives tended to overpenetrate the acetylated wood but not the untreated wood. Overpenetration is attributed to the limited capacity of the acetylated wood to attract and hold water that comes from the aqueous polar adhesives and the condensed water vapour that builds at the bondline during hot pressing.

Urea-formaldehyde (cold set)

The urea-formaldehyde (UF) cold adhesive developed sound dry-strength bonds to untreated wood, but as levels of acetylation increased, shear strength and wood failure declined significantly to very low levels, particularly at the 14 and 20 WPG levels. When bonds were tested in the wet condition, wood failure was not acceptable even on the untreated wood. The UF-cold adhesive is not as durable an adhesive as the UF-hot adhesive, and the UF-cold adhesive also did not perform as well on the acetylated wood.

Resorcinol and phenol-resorcinol adhesives

Resorcinol-formaldehyde

The cold-setting resorcinol-formaldehyde (RF) adhesive developed bonds that were among the highest in integrity on acetylated wood whether tested in dry or water-saturated conditions (Tables 1 and 2). Dry shear strengths were not significantly different by level of acetylation, although dry wood failure was significantly lower than controls at 14 and 20 WPG. Even at 20 WPG, wood failure was still above 80%. Wet shear strengths were actually significantly higher at 14 and 20 WPG than untreated controls (explained later), whereas wet wood failure of the controls was not significantly different from that at any acetylation level.

The RF adhesives develop the strongest and most durable of bonds to wood. They are highly reactive compared to phenolic adhesives because they have two hydroxyl groups, rather than one, on the benzene ring. These hydroxyls, plus methylol groups of the resin, are highly polar and have strong molecular attraction for the polar hydroxyl groups of cellulose and lignin in wood. Readily available hydroxyl sites are occupied by acetate groups in acetylated wood - even more so as higher levels of acetylation are reached. Nonetheless, the abundance of hydroxyls in the resorcinolic resin still allows strong molecular attraction for the remaining limited supply of hydroxyls on acetylated wood. Even though lower wood failure in both dry and wet conditions developed with increasing levels of acetylation for reasons just explained, bond integrity was still exceptionally good.

Gel times for resorcinolic resins are near their slowest at pH 3.5 to 4.0[11], which is the same pH range of acetylated wood and low concentrations of acetic acid (Table 3). If pH did slow the cure of the resorcinolic resins, its effect could not be detected. Neither this nor the above theory were proven to actually contribute to reduced bond integrity, but both are plausible explanations.

Phenol-resorcinol-formaldehyde (cold set)

The cold-setting phenol-resorcinol-formaldehyde (PRF) adhesive performed about as well in dry and wet tests as the RF adhesive, except wood failure percentages at the 14 WPG level were slightly below 80% at 75 and 77%, respectively, in both tests. Dry shear strengths and wood failures were not significantly different by level of treatment (Table 1). Wet shear tests did show strengths significantly higher than controls at 14 and 20 WPG. This apparent anomaly is explained at the end of the discussion section. Wet wood failure was quite high, except for the drop at the 14 WPG level. Note that even though strong bonds with high wood failure occurred, wood failure tended to become increasingly shallow with increasing levels of acetylation. This indicates that wetting and penetration of the alcohol-waterborne adhesive was inhibited by the hydrophobicity of the acetylated wood. This observation also applies to the previously discussed RF adhesive, although deeper wood failure was more common with the RF adhesive. The RF adhesive has a greater abundance of hydroxyl groups than the PRF adhesive and. because of its greater molecular attraction to a limited number of hydroxyls on acetylated wood, produced more and deeper wood failure.

Phenol-resorcinol-formaldehyde (hot set)

This PRF adhesive was hot pressed and, from observations of failed joints, it was evident that the adhesive overpenetrated. Strong bonds probably would have developed if the adhesive had been cold pressed. The dry shear strengths were not significantly different by level of acetylation, but dry wood failures at all levels of acetylation were significantly lower than untreated controls (Table 1). Wet shear strengths at all levels of acetylation were significantly higher than controls, as was previously noted for the RF adhesive (Table 1). However, wood failure percentages steadily declined with increasing acetylation. Performance of this hot-pressed PRF adhesive was clearly not as good as the cold-pressed PRF and RF adhesives.

Phenolic adhesives

Phenol-formaldehyde

The phenol-formaldehyde (PF) adhesive performed as expected on untreated wood with high levels of shear strength and wood failure in both dry and wet tests. Its performance on acetylated wood was not up to this level. Dry shear strengths at 8 and 20 WPG were statistically comparable to the untreated wood, but dry wood failures on acetylated wood showed significant declines from the 100% level of the untreated. Wet shear strengths on acetylated wood were significantly lower than controls, but wood failure percentages were zero at all three acetylation levels. The non-existent wood failure on wet-tested bonds is the best indicator of poor performance by the PF adhesive on acetylated wood.

Poor performance was caused by overpenetration of the adhesive during hot pressing. Overpenetration could have been exacerbated by residual acetic acid in the acetylated wood that could have lowered the reactivity of the alkaline phenolic, thereby increasing its mobility. However, an excess of moisture, at least for acetylated wood, seemed to be the primary cause for excessive adhesive mobility. The moisture content of acetylated wood ranged between 3.5 and 5.5%, and the moisture content of untreated wood was approximately 4%. All acetylated wood was conditioned at 27°C and 65% RH: therefore, pieces of wood at the 20 WPG level had the lower moisture contents, and the 8 WPG level had the highest. The mobility of the waterborne PF adhesive is critically sensitive to moisture content changes of not greater than 2%. If water vapour condenses in the adhesive film or if water in the adhesive does not diffuse from the bondline. then the adhesive will become highly mobile and overpenetrate the wood. If too much water is present for the wood to absorb, the laminates will blow apart from steam pressure when platten pressure is released. This occurred several times when pressing wood laminates that were acetylated at the 14 and 20 WPG levels.

Acid-catalysed phenol-formaldehyde

Acid-catalysed phenolic-formaldehyde (APF) resin is used in the foundry industry to bond sand into cores for making metal castings. The APF adhesive developed strong and highly durable bonds (Tables 1 and 2), not only to untreated wood but to acetylated wood after testing in dry and water-saturated conditions. Dry shear strengths and wood failures at some acetylated levels did show significant declines from the untreated wood, but they were minor. The lowest dry wood failure was only 87%, which was significantly lower than the 100% of the control. The wet wood failures were unusually high and not significantly different from each other, thus indicating little interference from acetylation. As noted for the RF, PRF and MF thermosetting adhesives, including the APF adhesive, wet shear strengths increased with higher levels of acetyl content because the adhesive was strong enough in a wet condition to fully reflect the higher breaking strength of the acetylated wood, as explained in the next section.

Even though the APF adhesive was a very low molecular-weight resin relative to the alkaline PF adhesive, it did not overpenetrate the wood during hot pressing as did the alkaline phenolic adhesive. Increased reactivity provided by the acid catalyst probably caused the resin to gel faster at a lower temperature, thereby limiting its penetration. The resin also had limited solubility in water. This becomes an advantage if excess water vapour should condense in the bondline to further reduce the viscosity of the resin mixture. as may occur with the highly alkaline PF adhesives.

Wet strengths of thermosetting adhesives

A trend of increasing wet shear strength with increasing levels of acetylation was observed among all of the most durable thermosetting resin adhesives including the RF, two PRFS, APF, MF and even the hot-press UF adhesive. Acetylation increases the density of the wood and hardens it, so that the acetylated wood is capable of resisting higher shearing loads with increasing levels of treatment. Acetylation also makes the wood more hydrophobic, so that as higher levels of acetylation are reached, more water is repelled. The lower the moisture content of the wood, the harder it becomes. Thermosetting adhesives that develop highly durable bonds to wood penetrate deeply such that bonds are capable of reaching the full strength capability of the wood adherend. Because acetylated wood is dense and contains little water within cell walls, wet shear strengths increase as higher levels of acetylation are reached.

Conclusions

The adhesion of 18 thermoplastic and thermosetting adhesives was reduced by the level of acetylation - some adhesives to a minor degree and others to a severe degree. Many adhesives were capable of strong and durable bonds at the 8 WPG level of acetylation. but not at 14 and 20 WPG levels. Most adhesives contained polar polymers, and all but four were aqueous systems, so that their adhesion was diminished in proportion to the presence of the non-polar and hydrophobic acetate groups in acetylated wood. Thermosetting adhesives produced the strongest bonds in both dry and wet conditions, but thermoplastic adhesives were capable of high shear strengths in the dry condition. With the exception of the acid-catalysed phenol-formaldehyde adhesive, thermosetting adhesives that were hot pressed became highly mobile and tended to overpenetrate the wood because of the limited capacity of the acetylated wood to absorb water from the curing bond-line. The abundance of hydroxyl groups in the highly reactive resorcinol adhesive permitted excellent adhesion at room temperature, despite the limited availability of hydroxyl groups in acetylated wood.

An emulsion polymer-isocyanate adhesive, a cross-linking polyvinyl acetate adhesive, a resorcinol-formaldehyde adhesive, a phenol-resorcinol-formaldehyde adhesive, and an acid-catalysed phenolic-formaldehyde adhesive developed bonds of high shear strength and wood failure at all levels of acetylation in the dry condition. A neoprene contact-bond adhesive and a moisture-curing polyurethane hot-melt adhesive performed as well on acetylated wood as untreated wood in tests of dry strength. Only the cold-setting resorcinol-formaldehyde adhesive and the phenol-resorcinol-formaldehyde adhesive, along with the hot-setting acid-catalysed phenolic adhesive, developed bonds of high strength and wood failure at all levels of acetylation when tested in the water-saturated condition.

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