

# THE ABILITY OF WOOD TO BUFFER HIGHLY ACIDIC AND ALKALINE ADHESIVES

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**Abstract.** The ability of wood to buffer and mitigate the effects of strongly acidic or alkaline environments produced near the glue line by extreme pH structural adhesives was evaluated. The pH values of wood, cured adhesives, and mixtures of the two in water slurries were determined for different wood types. The pHs of slurries of seven highly alkaline phenol–formaldehyde adhesives were lowered when the adhesive was cured in the presence of wood dust with effects increasing with the proportion of wood in the mixture. The “acidities” or amounts of alkali needed to adjust the slurries to pH 12.5 were relatively high for all species because of weak acid groups in wood that dissociate at pH greater than 8. This explains the ability of wood to buffer highly alkaline adhesives. The pHs of slurries of two acidic melamine–urea–formaldehyde adhesives increased in the presence of wood, but the effect was less significant compared with the alkaline adhesives. Similarly, the “alkalinities” or amounts of acid required to adjust the slurries to pH 3 were relatively low. Aspen veneer samples had a greater effect on adhesive pH than spruce and Douglas-fir. These effects will help mitigate potentially adverse effects of strongly alkaline or acidic adhesives on wood adhesive bond strength.

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## INTRODUCTION

Most thermosetting wood adhesives are catalyzed by acidic or alkaline additives to ensure rapid curing under hot pressing. They also prevent the wood from excessively buffering the adhesive, thereby changing the adhesive pH and retarding its cure rate. Phenol–formaldehyde (PF) adhesives are used for many engineered wood products because of their good performance in exterior applications. Many PF formulations used for softwood plywood and laminated veneer lumber have high dry film pH (pH 11–13 when measured in water slurries). Melamine–urea–formaldehyde (MUF) adhesives, used where lower cost and colorless glue lines are important, are often formulated to a low pH.

There is concern that under high moisture exposure conditions, the extremely acidic or alkaline adhesives may lead to degradation of wood components and reduced strength at the adhesive–wood interface of bonded products. Wood hemicelluloses are susceptible to both acid and alkali degradation. Generally, cellulose is more resistant to alkali and lignin is more resistant to acids (Sjostrom 1993).

Adhesive standards often specify a maximum or minimum adhesive pH as characterized by measurement of dry, powdered adhesive film in a water slurry (eg D1583 (ASTM 2001)). Draft standard ISO/DIS 20152.1 (ISO 2009) restricts dry film pH to above 3.0 and below pH 11. D2559 (ASTM 2004), on the other hand, sets lower limits of dry film pH of 2.5 for structural adhesives and places no upper limit on pH for alkaline adhesives. Canadian adhesive standard O112.9-04 (CSA 2004) for structural exterior products specified a dry adhesive film lower pH limit of 3.0 and an upper pH limit of 11.0. Recent revisions to the standard lowered the lower pH limit to 2.5 and removed the upper limit; however, the standards committee is considering studies on the effects of extreme pH

adhesives on bond quality to determine whether these criteria are appropriate.

The initial wood pH and its ability to partially neutralize acidic and alkaline environments (buffering capacities) may contribute to a mitigation of potential effects of extreme pH on wood strength by decreasing alkalinity or acidity in the bond line, but may also affect adhesive curing. Mizumachi and Morita (1975) showed that the curing reaction of phenolic resin could be delayed by some wood species, resulting in higher activation energy during the curing process of PF resin with wood. Xing *et al.* (2004) found that the pH of raw materials could affect the pH of urea–formaldehyde adhesives. They established linear relationships among resin gel time, pH value, and acid buffering capacity.

The pH of cured film tested according to D1583 (ASTM 2001) is different from the pH of the adhesive in the glue line, because alkali or acid penetrates into wood (Huang *et al.* 2010) and the wood may affect its pH through buffering action. The curing process may also liberate acids or alkali and change the dry film pH. The acidity and alkalinity of solid materials such as wood and dry adhesives can be characterized in different ways. pH is the measure of direct acidic or alkaline nature (dissociated H<sup>+</sup> concentration); however, it does not consider the weak undissociated acids or bases that may become available under different pH conditions and contribute to the ability of the material to mitigate or buffer acidic or alkaline conditions. Blomquist (1949) suggested that dry film pH was not the best indicator of pH effects of alkaline adhesives on bond quality and that measurement of total alkalinity by titration was a better measure. The pH, acidity, and alkalinity of wood have been estimated in different ways. In most studies, wood is extracted with hot or ambient temperature water and pH is measured on the extract. Alkalinity and acidity (buffering

capacities) are estimated by titrating the extract with acid or alkali to a specific pH or until there is a change in pH by one unit (Johns and Niazi 1980; Hachmi and Moslemi 1990; He and Riedl 2004; Xing et al 2004; Passialis et al 2008; Pedieu et al 2008). While this gives a good representation of the wood pH, for estimating acidity, it only considers free acids and weak acidic groups that are dissociated at the natural wood pH. Carboxylic acid components of pectins and hemicelluloses are partially dissociated at typical wood pH of 4-5, but phenolic acidic groups in lignin are only dissociated at pH values above about 8 and require pH 11-12 for essentially complete dissociation (Cooper 1991; Ragnar et al 2000; Balaban and Ucar 2001). These "fixed" acids will contribute significantly to the ability of wood to moderate the effects of alkaline adhesives.

For these reasons, in this study, pH values and the acidity or alkalinity of wood, dry adhesives, and mixtures of the two were determined on the solid/water slurry rather than on the decanted water. Furthermore, acidity was determined to pH 12.5 as well as to the more standard pH 8, because the former value is typical of the pH environment produced by alkaline adhesives. The addition of wood to produce wood adhesive mixtures is meant to provide a realistic representation of glue line conditions in wood composites where adhesive has penetrated into the wood structure.

#### MATERIALS AND METHODS

pH estimates are relative measures based on the pH of a slurry of material in water at a ratio of 1:15 solid to water. "Acidity" is defined here as the amount (meq) of alkali needed to titrate 1 g dry wood, acidic adhesive, or a mixture to pH 8 or 12.5. "Alkalinity" of wood, alkaline adhesives, and mixtures is the amount (meq) of acid needed to titrate 1 g dry wood or adhesive to pH 3.

#### Wood Samples and Adhesives

Five wood types were chosen, including Douglas-fir heartwood, red pine sapwood, spruce heart-

wood, aspen sapwood (from lumber cut from a 35-yr-old tree harvested several years previously), and dry aspen veneer. Samples were ground and the fraction that passed a 35-mesh screen (about 0.29 mm) and was retained on a 60-mesh screen (about 0.15 mm) was used in the study. Seven PF adhesives and one MUF adhesive with two levels of acidic hardener, obtained from different adhesives companies (Tables 1 and 2), were used in the study.

#### Measurement of Wood pH Acidity and Alkalinity

The pH measurements and acid and alkali titrations were made on the wood-water mixture, not on decanted water, because dissociation of the acidic functional groups in wood is pH-dependent. The pH measurements were made on 2 g (oven-dry basis) of flour of each wood type mixed with 30 mL of cooled newly boiled distilled water (pH 7.3). Samples were periodically agitated at room temperature for 72 h and the pH recorded. This is a relative pH value for comparison of the different wood species. Five replicates of each type of wood were tested. Wood pH was measured by a pH meter (IQ150 pH meter; IQ Scientific Instruments Inc). Acidity and alkalinity were measured by titration of samples prepared the same way. The pH meter was calibrated with standardized buffer solutions and the initial pH of the mixture was recorded. It was then titrated to pH 3 with nominal 0.05 N HCl (for alkalinity determination) or to pH 8 with 0.05 N NaOH or pH 12.5 with 0.25 N NaOH (for acidity determination). Acidity and alkalinity were expressed as meq/g of dried wood after correction for the volume of titrant required to adjust the distilled water to the target pH. To evaluate the longer-term dissociation and diffusion of reactive components in the wood substance, samples were sealed and stored for 24 h after each titration and more alkali or acid was added to reach the target pH. When the pH did not change by more than 0.10 pH units over 24 h, it was assumed that equilibrium was reached.

Table 1. pH of wood and wood + adhesive slurries and alkalinity (meq/g dry adhesive) of different phenol formaldehyde adhesives with and without different amounts of wood powder (0.5 N HCl to pH 3).<sup>a</sup>

| Wood to dry adhesive ratio | pH              |                 |                 | Alkalinity (meq/g dry adhesive) |                             |                            |
|----------------------------|-----------------|-----------------|-----------------|---------------------------------|-----------------------------|----------------------------|
|                            | Spruce          | Aspen           | Douglas-fir     | Spruce                          | Aspen                       | Douglas-fir                |
| Neat resin 1               |                 | 12.50 (0.17)    |                 |                                 | 3.28 (0.05)                 |                            |
| 1 to 2                     | 12.28<br>(0.02) | 12.13<br>(0.20) | 12.53<br>(0.10) | 3.39 (0.03)<br><b>3.32</b>      | 3.00 (0.155)<br><b>3.31</b> | 3.50 (0.02)<br><b>3.29</b> |
| 1 to 1                     | 11.99<br>(0.01) | 11.70<br>(0.12) | 11.71<br>(0.22) | 3.38 (0.01)<br><b>3.36</b>      | 3.04 (0.03)<br><b>3.35</b>  | 3.48 (0.03)<br><b>3.30</b> |
| 2 to 1                     | 11.20<br>(0.13) | 10.44<br>(0.10) | 11.05<br>(0.06) | 3.38 (0.06)<br><b>3.44</b>      | 2.99 (0.01)<br><b>3.41</b>  | 3.43 (0.13)<br><b>3.32</b> |
| Neat resin 2               |                 | 12.37 (0.02)    |                 |                                 | 2.96 (0.12)                 |                            |
| 1 to 2                     | 12.10<br>(0.30) | 11.20<br>(0.59) | 12.08<br>(0.27) | 2.55 (0.02)<br><b>3.00</b>      | 2.55 (0.04)<br><b>2.99</b>  | 2.83 (0.01)<br><b>2.97</b> |
| 1 to 1                     | 11.68<br>(0.18) | 10.84<br>(0.03) | 11.38<br>(0.17) | 2.58 (0.01)<br><b>3.04</b>      | 2.61 (0.01)<br><b>3.03</b>  | 2.81 (0.06)<br><b>2.98</b> |
| 2 to 1                     | 10.99<br>(0.16) | 9.65<br>(0.15)  | 10.37<br>(0.06) | 2.60 (0.00)<br><b>3.12</b>      | 2.59 (0.04)<br><b>3.09</b>  | 2.86 (0.15)<br><b>3.00</b> |
| Neat resin 3               |                 | 12.61 (0.01)    |                 |                                 | 3.34 (0.04)                 |                            |
| 1 to 2                     | 11.90<br>(0.38) | 12.12<br>(0.04) | NA              | 3.50 (0.08)<br><b>3.38</b>      | 3.35 (0.15)<br><b>3.37</b>  | NA                         |
| 1 to 1                     | 11.76<br>(0.08) | 11.36<br>(0.03) | NA              | 3.44 (0.10)<br><b>3.42</b>      | 3.27 (0.03)<br><b>3.41</b>  | NA                         |
| 2 to 1                     | 11.04<br>(0.10) | 10.15<br>(0.21) | NA              | 3.33 (0.07)<br><b>3.50</b>      | 3.27 (0.03)<br><b>3.47</b>  | NA                         |
| Neat resin 4               |                 | 12.50 (0.025)   |                 |                                 | 3.07 (0.161)                |                            |
| 1 to 2                     | 12.03<br>(0.07) | 11.71<br>(0.23) | 12.34<br>(0.35) | 2.60 (0.07)<br><b>3.11</b>      | 2.52 (0.06)<br><b>3.10</b>  | 2.48 (0.18)<br><b>3.08</b> |
| 1 to 1                     | 11.57<br>(0.03) | 10.69<br>(0.29) | 11.55<br>(0.18) | 2.58 (0.02)<br><b>3.15</b>      | 2.78 (0.30)<br><b>3.14</b>  | 2.49 (0.02)<br><b>3.09</b> |
| 2 to 1                     | 10.86<br>(0.03) | 9.85<br>(0.22)  | 10.90<br>(0.20) | 2.70 (0.01)<br><b>3.23</b>      | 2.63 (0.13)<br><b>3.20</b>  | 2.52 (0.28)<br><b>3.11</b> |
| Neat resin 5               |                 | 12.42 (0.01)    |                 |                                 | 2.61 (0.01)                 |                            |
| 1 to 2                     | 12.23<br>(0.01) | 11.66<br>(0.60) | 12.00<br>(0.03) | 2.23 (0.04)<br><b>2.65</b>      | 2.16 (0.05)<br><b>2.64</b>  | 2.48 (0.01)<br><b>2.62</b> |
| 1 to 1                     | 10.98<br>(0.20) | 11.04<br>(0.13) | 11.35<br>(0.26) | 2.38 (0.08)<br><b>2.69</b>      | 2.36 (0.05)<br><b>2.68</b>  | 2.48 (0.04)<br><b>2.63</b> |
| 2 to 1                     | 10.87<br>(0.16) | 9.62<br>(0.09)  | 10.47<br>(0.23) | 2.38 (0.02)<br><b>2.77</b>      | 2.55 (0.04)<br><b>2.74</b>  | 2.34 (0.24)<br><b>2.65</b> |
| Neat resin 6               |                 | 12.53 (0.04)    |                 |                                 | 3.33 (0.058)                |                            |
| 1 to 2                     | 11.59<br>(0.27) | 11.81<br>(0.12) | 12.24<br>(0.04) | 2.71 (0.03)<br><b>3.37</b>      | 3.30 (0.01)<br><b>3.36</b>  | 3.37 (0.14)<br><b>3.34</b> |
| 1 to 1                     | 11.35<br>(0.05) | 10.92<br>(0.10) | 11.55<br>(0.07) | 2.80 (0.04)<br><b>3.41</b>      | 3.21 (0.02)<br><b>3.40</b>  | 2.97 (0.41)<br><b>3.35</b> |
| 2 to 1                     | 10.85<br>(0.04) | 9.87<br>(0.07)  | 10.75<br>(0.10) | 2.87 (0.04)<br><b>3.49</b>      | 3.24 (0.05)<br><b>3.46</b>  | 3.13 (0.24)<br><b>3.37</b> |
| Neat resin 7               |                 | 12.60 (0.05)    |                 |                                 | 3.48 (0.007)                |                            |
| 1 to 2                     | 12.08<br>(0.01) | 11.62<br>(0.29) | 12.00<br>(0.02) | 3.41 (0.10)<br><b>3.52</b>      | 3.49 (0.12)<br><b>3.51</b>  | 3.40 (0.05)<br><b>3.49</b> |
| 1 to 1                     | 11.59<br>(0.22) | 10.90<br>(0.11) | 11.22<br>(0.04) | 3.44 (0.07)<br><b>3.56</b>      | 3.44 (0.08)<br><b>3.55</b>  | 3.41 (0.03)<br><b>3.50</b> |
| 2 to 1                     | 10.84<br>(0.16) | 9.64<br>(0.10)  | 10.54<br>(0.25) | 3.39 (0.16)<br><b>3.64</b>      | 3.49 (0.08)<br><b>3.61</b>  | 3.30 (0.35)<br><b>3.52</b> |

<sup>a</sup> Numbers in parentheses are standard deviations. Numbers in bold italics represent the predicted combined alkalinities of the adhesive and wood with no neutralization effect by the wood.

NA, not analyzed.

Table 2. pH and acidity (meq/g dry adhesive) of MUF adhesive with different amount of acidic hardener with and without different amounts of wood powder in water slurry (1.0 N NaOH titrand to pH 8; means [SD]).<sup>a</sup>

| Wood to dry adhesive ratio | pH          |             |             | Acidity (meq/g dry adhesive) |              |              |
|----------------------------|-------------|-------------|-------------|------------------------------|--------------|--------------|
|                            | Spruce      | Aspen       | Douglas-fir | Spruce                       | Aspen        | Douglas-fir  |
| Resin 8 <sup>b</sup> only  |             | 2.97 (0.02) |             |                              | 0.61 (0.01)  |              |
| 1 to 2                     | 3.23 (0.03) | 3.39 (0.20) | 3.09 (0.10) | 0.69 (0.01)                  | 0.45 (0.07)  | 0.65 (0.15)  |
| 1 to 1                     | 3.43 (0.02) | 3.44 (0.05) | 3.40 (0.24) | 0.65 (0.01)                  | 0.35 (0.01)  | 0.37 (0.06)  |
| 2 to 1                     | 3.48 (0.09) | 3.54 (0.03) | 3.31 (0.10) | 0.66 (0.01)                  | 0.38 (0.02)  | 0.62 (0.07)  |
| Resin 9 <sup>c</sup> only  |             | 2.93 (0.03) |             |                              | 0.60 (0.00)  |              |
| 1 to 2                     | 3.15 (0.04) | 3.12 (0.12) | 3.00 (0.01) | 0.72 (0.02)                  | 0.72 (0.01)  | 0.73 (0.001) |
| 1 to 1                     | 3.38 (0.09) | 3.25 (0.05) | 3.09 (0.01) | 0.65 (0.02)                  | 0.72 (0.004) | 0.73 (0.01)  |
| 2 to 1                     | 3.53 (0.02) | 3.35 (0.03) | 3.14 (0.03) | 0.33 (0.01)                  | 0.73 (0.004) | 0.76 (0.01)  |

<sup>a</sup> Numbers in parentheses are standard deviations. Numbers in bold italics represent the predicted combined acidities of the adhesive and wood with no neutralization effect by the wood.

<sup>b</sup> Ratio of MUF resin to hardener = 100:25.

<sup>c</sup> Ratio of MUF resin to hardener = 100:30.

MUF, melamine-urea-formaldehyde.

### Measurement of pH and Alkalinity/Acidity of Adhesives with and without Wood

The relative pHs, acidities, and alkalinities (meq/g cured adhesive) of the adhesives were measured by using 2.0 g of powdered cured resin (4 h at 60°C followed by 4 h at 103°C) in 30 mL water with five replicates for each resin. To evaluate the effects of wood on the pHs, acidities, and alkalinities of adhesives, ground wood meal (40 mesh and smaller) of spruce, aspen veneer, and Douglas-fir wood were mixed with different resins in weight ratios of 2:1, 1:1, and 1:2, respectively, and cured at the same condition as resins only (three replicates). These cured resin or wood/resin samples were ground to less than 40 mesh with a mortar and pestle. For the measurement of pH, acidity, and alkalinity, sufficient mass of wood-resin mixture was taken to provide 2.0 g of dried resin as for the pure resin samples. The dried mixture was stirred with 30 mL of water and allowed to equilibrate for 72 h. The pH of the mixture was determined, then it was titrated with standard HCl (0.5N) to pH 3.0 for PF resins and the alkalinity of the resin estimated

from the acid consumed (meq/g of dried resin). Like with the wood samples, the mixtures were held overnight after each acid addition and if the pH increased, more acid was added until the target pH was reached and stabilized. The additive alkalinities for each mixture of cured adhesive and wood were estimated for comparison with the measured values by the rule of mixtures, ie assuming that the resin and wood contributed alkalinity in proportion to their proportion in the mixture (Eq 1). Similarly, the MUF resins and wood-adhesive mixtures were titrated to pH 8.0 with 1.0 N NaOH solution and the acidity of resin was estimated from the volume of alkali used and compared with the estimated additive acidities of the wood and adhesive (Eq 1):

$$A_M = A_A + xA_W \quad (1)$$

where  $A_M$  is the expected acidity or alkalinity of the mixture containing 1 g of adhesive and the various amounts of wood dust,  $A_A$  is the acidity or alkalinity of 1 g of cured adhesive, and  $A_W$  is the acidity or alkalinity of 1 g of wood (all in meq);  $x$  is the amount of wood added per g cured

adhesive (0.5, 1.0, or 2.0 for 1:2, 1:1, and 2:1 wood-to-resin mixtures, respectively).

## RESULTS AND DISCUSSION

### pH, Acidity, and Alkalinity of Wood

The acidities (alkaline buffering capacities) of the different wood species to pH 8 were relatively low (Table 3). These values reflect the relative amounts of the stronger carboxylic acids in the different wood types. The more acidic species, Douglas-fir and red pine, had greater acidities to pH 8 but lower alkalinities (to pH 3) compared with more neutral species such as spruce and aspen. However, when titrated to pH 12.5 (Table 3), all woods had much higher acidities as the very weak lignin phenolic acid groups and previously undissociated acetyl groups in the hemicelluloses dissociated and neutralized the NaOH. Alkali could also be consumed through the solution or hydrolysis of hemicelluloses and oxidation of wood sugars to produce more organic acids (Nikitin 1966). This suggests that wood may have significant potential to mitigate the effects of highly alkaline adhesives. The species trend was different than for the lower pH conditions with the aspen samples having a much higher acidity than the initially more acidic (low pH) Douglas-fir. This suggests that aspen may be able to mitigate high pH conditions better than Douglas-fir.

Alkalinity of all species was relatively low, suggesting that effects of wood to buffer the low pH of acidic adhesives may be minor. This was confirmed in a study that monitored the pH in the glue line area of wood bonded with acidic and alkaline adhesives (Huang et al 2010). The aspen veneer had higher pH and lower acidity to pH 8

than the aspen sapwood lumber. This may result from the high temperature drying of the veneer that may have evaporated or chemically changed some of the low molecular mass acids from the veneer, resulting in lower acidity. However, both aspen veneer and lumber had similar alkalinities.

In all cases, when the samples were adjusted to pH 8 (acidity) or pH 3 (alkalinity) and allowed to stand for 24 h after titration, the pH decreased or increased, respectively, and additional alkali or acid had to be added to titrate the mixture to the target pH. This change in pH was especially evident in measuring the acidities. The effect is attributed to weak acids continuing to slowly dissociate, the diffusion of reactants into and out of the wood, and possible hydrolysis of hemicelluloses and oxidation of sugars as noted previously. As a result, it was difficult to achieve equilibrium and to determine the true acidities of samples to pH 8.0 or to characterize the different woods with respect to their abilities to neutralize alkaline resins. In the case of adjusting to pH 12.5 with more concentrated NaOH, the pH of the mixtures tended to stabilize at the target pH after four titrations.

### pH and Alkalinity/Acidity of Adhesives with and without Wood

When wood powder was mixed with alkaline resins and cured, the resulting mixtures had a lower pH than the pure resins (Table 1). As the proportion of wood to dry adhesive was increased from 1:2 to 1:1 and to 2:1, the initial pH decreased as the acidic wood buffered or partially neutralized the adhesive. For all of the alkaline adhesives evaluated, a mixture of 2:1 wood to dry adhesive resulted in a pH drop from

Table 3. Comparison of pHs of wood/water slurries and buffering capacities of different wood samples (0.05 N HCl to pH 3, 0.05 N NaOH to pH 8 and 0.25 N NaOH to pH 12.5; means [SD]).

| Wood sample  | pH  | Acidity to pH 8 (meq/g) | Acidity to pH 12.5 (meq/g) | Alkalinity to pH 3 (meq/g) |
|--------------|-----|-------------------------|----------------------------|----------------------------|
| Douglas-fir  | 3.6 | 0.139 (0.004)           | 1.20 (0.047)               | 0.020 (0.001)              |
| Red pine     | 4.0 | 0.124 (0.033)           | 0.99 (0.019)               | 0.062 (0.002)              |
| Aspen lumber | 4.2 | 0.111 (0.001)           | 1.34 (0.026)               | 0.068 (0.001)              |
| Spruce       | 4.6 | 0.104 (0.012)           | 0.84 (0.043)               | 0.082 (0.003)              |
| Aspen veneer | 4.8 | 0.053 (0.003)           | 1.26 (0.029)               | 0.066 (0.001)              |

above 12 for the adhesive alone to less than 11, a level considered to have little if any effect on wood. Lower proportions of wood had less effect but nevertheless significantly reduced the pH of the adhesive–wood mixtures. The aspen veneer samples consistently lowered the adhesive pH the most, reaching pH less than 10 for many 2:1 ratios for several of the adhesives, consistent with its highest acidity to pH 12.5 of the three species. Douglas-fir, with its higher acidity and lower wood pH compared with spruce, usually produced a greater drop in pH of the adhesive–wood mixture.

The PF adhesives had dry film pH values ranging from 12.37 to 12.61. Their alkalinities to pH 3 ranged from 2.61 to 3.48 meq/g of resin (Table 1), which were much higher than the alkalinities of the wood (Table 3). Although it was expected that adhesives with lower initial pH and lower alkalinity would be moderated to a greater extent by the wood, there was no consistent effect of either on the pH change when combined with wood dust. In most cases, the presence of wood caused a decrease in the alkalinity of the adhesive wood mixture to levels considerably below the expected alkalinities (additive effect) of the adhesive–wood mixtures (bold italics numbers in Table 1 calculated using Eq 1). This can be attributed to the buffering effect of the acidic groups in wood to partially neutralize the alkaline adhesives. However, in some cases (notably Adhesives 1 and 3 with lower spruce or Douglas-fir wood contents), the alkalinity of the adhesive mixture was higher than that of the adhesive alone (when expressed on the basis of weight of resin only) indicating that the wood alkalinity contribution was sometimes greater than the wood's ability to buffer the alkaline adhesives. Again, there was no consistent relationship between the initial pH and alkalinity and the ability of the wood dust to reduce the alkalinity of the mixture.

When the acidic MUF adhesives were mixed with wood powder and cured, the pH increased to above 3.0 in all cases (Table 2). However, the pH increase was limited by the low alkalinity or

acid buffering capacity of the wood. The pH increased more with higher proportions of wood in the mixtures. Low pH and low alkalinity Douglas-fir generally had the least effect to buffer the pH of the acidic adhesives. These cured adhesives had relatively low acidities and when they were mixed with the wood, the acidity usually increased slightly because of the presence of the acidic wood. The exception to this was Adhesive 8 with a lower amount of acidic hardener, where the aspen wood and in one case the Douglas-fir wood appreciably decreased the acidity of the mixture.

These results show that wood has considerable capacity to buffer the effects of alkaline wood adhesives, thereby reducing the potential for adverse effects of strongly alkaline wood adhesive joints in structural composites used in wet service conditions. This effect was also seen in an evaluation of the pH environment around wood adhesive bond lines (Huang et al 2010); the cited study also showed that wet service conditions promoted diffusion of alkali away from the bond line, thereby minimizing the potential for alkaline degradation of wood in the glue line. Based on these results, standards for structural adhesives used in products in wet service conditions likely do not have to specify upper limits on the dry adhesive film pH. However, wood is less able to buffer the effects of highly acidic conditions in the wood bond line and adhesive standards may have to set lower limits on the dry film pH of adhesives used in these conditions.

## CONCLUSIONS

The presence of wood significantly moderated the pH of the adhesive–wood mixtures, especially for alkaline adhesives. The acidities to pH 12.5 for all five species of wood were much higher than to pH 8, which results from the weak acid groups of wood components that are dissociated at pH greater than 8; this contributes to wood's significant ability to neutralize alkaline adhesives. The five types of wood powders (red pine, Douglas-fir, spruce, aspen lumber, and

aspen veneer) had different pH, acid, and alkaline buffering capacities that affect the ability of the wood to mitigate any adverse effects of acidic and alkaline adhesives on the bond line. The aspen veneer had a greater effect than spruce and Douglas-fir to reduce the pH, alkalinity, and acidity of wood–adhesive mixtures. There were some differences in alkalinity and acidity among adhesives, but this had no consistent effect on the ability of wood to moderate the extreme pHs. These effects will help reduce the potential for wood degradation in adhesive joints of wood bonded with strongly alkaline adhesives. The wood also buffers highly acidic adhesives, but to a lesser extent.

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#### REFERENCES

- ASTM (2001) D 1583–01, Standard test method for hydrogen ion concentration of dry adhesive films. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM (2004) D 2559–04. Standard specification for adhesives for structural laminated wood products for use under exterior (wet use) exposure conditions. American Society for Testing and Materials, West Conshohocken, PA.
- Balaban M, Ucar G (2001) The correlation of wood acidity to its solubility by hot water and alkali. *Holz Roh Werkst* 59:67–70.
- Blomquist RF (1949) Effect of alkalinity of phenol- and resorcinol-resin glues on durability of joints in plywood. USDA FPL Report R1748. (Reaffirmed 1962), USDA Forest Service.
- Cooper PA (1991) Cation exchange adsorption of copper on wood. *Wood Protect* 1(1):9–14.
- CSA (2004) O112.9-04 Evaluation of adhesives for structural wood products (exterior exposure). Canadian Standards Association, Mississauga, Ontario, Canada.
- Hachmi MH, Moslemi AA (1990) Effect of wood pH and buffering capacity on wood–cement compatibility. *Holzforschung* 44(6):425–430.
- He G, Riedl B (2004) Curing kinetics of phenol formaldehyde resin and wood–resin interactions in the presence of wood substrates. *Wood Sci Technol* 38(1):69–81.
- Huang Z, Cooper P, Wang X, Wang X-M, Zhang Y, Casilla R (2010) Effects of conditioning exposure on the pH distribution near adhesive–wood bond lines. *Wood Fiber Sci* 42(2):219–228.
- ISO (2009) DIS 20152.1, ISO/TC 165 Timber structures—Bond performance of adhesives—Part 1: Basic requirements. International Organization for Standardization, Geneva, Switzerland.
- Johns WE, Niazi KA (1980) Effect of pH and buffering capacity of wood on the gelation time of urea formaldehyde resin. *Wood Fiber Sci* 12(4):255–263.
- Mizumachi H, Morita H (1975) Activation energy of the curing reaction of phenolic resin in the presence of woods. *Wood Sci* 7:256–260.
- Nikitin NI (1966) The chemistry of cellulose and wood. Israel Program for Scientific Translations Ltd., Jerusalem, Israel. 691 pp.
- Passialis C, Voulgaridis E, Adamopolous S, Matsouka M (2008) Extractives, acidity, buffering capacity, ash and inorganic elements of black locust wood and bark of different clones and origin. *Holz Roh Werkst* 66:395–400.
- Pedieu R, Riedl B, Pichette A (2008) Measurement of wood and bark particles acidity and their impact on the curing of urea formaldehyde resin during the hot pressing of mixed panels. *Holz Roh Werkst* 66(2):113–117.
- Ragnar M, Lindgren CT, Nilvebrant N-O (2000) pK<sub>a</sub>-values of guaiacyl and syringyl phenols related to lignin. *J Wood Chem Technol* 20(3):277–305.
- Sjostrom E (1993) *Wood chemistry: Fundamentals and applications*. 2nd ed. Academic Press Limited, London, UK. 293 pp.
- Xing C, Zhang SY, Deng J (2004) Effect of wood acidity and catalyst on UF resin gel time. *Holzforschung* 58:408–412.