Influence of chemical treatments on moisture-induced dimensional change and elastic modulus of earlywood and latewood

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Abstract
To better understand the performance of bonded, coated, and modified wood, knowledge of how these processes alter the dimensional change and mechanical properties of wood at a given moisture content (MC) are important. These localized influences on earlywood (EW) and latewood (LW) properties are not well understood. In the present study, the influence of chemical treatments by hydroxymethylated resorcinol (HMR) and acetylation on moisture-induced dimensional change and longitudinal modulus of elasticity (MOE) of isolated EW and LW specimens of Loblolly pine (Pinus taeda L.) was evaluated. The dimensional change was not altered by the HMR treatment, whereas acetylation lowered it by ~50% in EW and LW in both radial and tangential directions. The MOE was not influenced by the two chemical treatments tested. Based on results of swelling, shrinkage, and MOE it can be concluded that chemical treatment does not modify EW selectively compared with LW neither in radial nor in tangential orientation.

Keywords: acetylation; earlywood; dimension change; hydroxymethylated resorcinol; latewood; loblolly pine; micromechanics; modulus of elasticity; shrinking; swelling.

Introduction
For many adhesives, the durability of wood-adhesive bonded assemblies drops considerably in moisture-changing environments (Gillespie 1976; Caster 1980). Wood is a hygroscopic material, and fluctuations in both relative humidity (RH) and temperature alter the wood moisture content (MC), resulting in dimensional changes. Frihart (2003) suggested that changes in RH result in a strain differential between the adhesive and wood interface and interphase regions, producing stresses along the bondline region that could modify its long-term mechanical and fracture properties. Chemical treatments that decrease dimensional changes in moisture-changing environments have the potential to increase the durability of bonded assemblies (Brandon et al. 2005).

Chemical modifications of wood are suited to decrease dimensional changes and improve mechanical properties, fire retardancy, and durability against biological decay (Hill 2006). Typically, the influence of chemical modification on a particular property has been measured in comparatively large specimens to obtain information in terms of bulk wood. Wood is extremely heterogeneous. Its chemical composition, extractives content, and cell geometry can be different depending on the size and origin of the specimen [sapwood, heartwood, juvenile wood, mature wood, earlywood (EW), latewood (LW), reaction wood, etc.]. These differences influence the localized properties and reactivity toward chemicals. Selective modification of wood could be a technique to homogenize wood properties. The present study has the effects of hydroxymethylated resorcinol (HMR) treatment (adhesive bonding) and acetylation (wood preservation) in focus in terms of moisture-induced dimensional changes and the longitudinal modulus of elasticity (MOE). Quantitative measurements were performed on separated EW and LW bands of loblolly pine (Pinus taeda L.).

Background
Dimensional stability of EW and LW
Wood shrinks or swells in response to changes in MC and this property has been extensively modeled and experimentally tested (Vintila 1939; Pentoney 1953; Erickson 1955; Browne 1957; Boutelje 1962; Kelsey 1963; Barrett et al. 1972; Boyd 1974; Quirk 1984; Skaar 1988; Pang 2002; Pfeil, unpublished results). Change in dimension is influenced by several factors, such as specific gravity, temperature, extractives, solvent type, moisture cycles, chemical treatment, anatomical orientation, wood type, and specimen size. Longitudinal shrinkage is an order of magnitude lower than radial or tangential shrinkage, presumably because of the orientation of the cellulose microfibrils in the cell walls (Kelsey 1963; Barrett et al. 1972; Skaar 1988; McAlister and Clark III 1992; Pang 2002). Previous work on tangential and radial shrinkage in isolated EW and LW is summarized in Table 1. The resulting shrinkage values are influenced by the size of specimen tested (results will be different for bulk wood, isolated EW or LW, and microtomed EW or LW sections) and the height in the tree where the sample is taken. The effects of chemical treatment on the tangential and radial shrinkage
Table 1 Percentage of dimensional change in isolated EW and LW.

<table>
<thead>
<tr>
<th>Study</th>
<th>Species</th>
<th>Δ Moisture content</th>
<th>EW</th>
<th>LW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T</td>
<td>R</td>
</tr>
<tr>
<td>Vinítila (1939)</td>
<td>Douglas-fir</td>
<td>Green to OD</td>
<td>5.7</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Scots pine</td>
<td>Green to OD</td>
<td>8.0</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>European larch</td>
<td>Green to OD</td>
<td>7.1</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>European silver fir</td>
<td>Green to OD</td>
<td>5.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Pentoney (1953)</td>
<td>Douglas-fir</td>
<td>FS to OD</td>
<td>4.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Erickson (1955)</td>
<td>Douglas-fir</td>
<td>Green to OD</td>
<td>4.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>W. red cedar</td>
<td>Green to OD</td>
<td>3.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Browne (1957)</td>
<td>Douglas-fir</td>
<td>OD to FS</td>
<td>6.7</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>Southern yellow pine</td>
<td>OD to FS</td>
<td>6.4</td>
<td>7.7</td>
</tr>
<tr>
<td>Quirk (1984)</td>
<td>Douglas-fir</td>
<td>Green to OD</td>
<td>6.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Pang and Herritsch (2005)</td>
<td>Radiata pine</td>
<td>Green to 12%</td>
<td>3.2</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green to OD</td>
<td>5.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Pfeil (unpublished)</td>
<td>Loblolly pine</td>
<td>Green to OD 1 m³</td>
<td>5.8</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green to OD 2.5 m³</td>
<td>6.3</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green to OD 7 m³</td>
<td>6.6</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green to OD 10 m³</td>
<td>6.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Height from ground.
ΔMC, change in moisture content; T, tangential; R, radial; OD, oven dry; FS, fiber saturation.

or swelling of isolated EW and LW specimens are not yet explored.

**Mechanical properties of EW and LW**

Prior work on mechanical properties of isolated EW and LW specimens is summarized in Table 2. In general, the EW longitudinal MOE is lower than LW MOE. Kretschmann et al. (2002, 2006) and Cramer et al. (2005) showed that in matchstick-sized specimens of loblolly pine isolated EW and LW, the shear modulus and longitudinal MOE differ as a function of anatomical position within the tree (i.e., growth ring, cardinal orientation, and height within the tree), and changes in MOE were further associated with changes in cellulose microfibril angle and specimen density. Previous work has not evaluated the effect of chemical treatment on the mechanical properties of isolated EW or LW specimens.

**Hydroxymethylated resorcinol (HMR)**

HMR is a priming agent applied onto wood surfaces that enhances the durability of wood adhesive bondlines for several adhesives and wood species (Vick et al. 1998; Christiansen 2005). HMR decreases swelling (Son and Gardner 2004) and water uptake (Son et al. 2005) for specimens immersed in liquid water. The mechanisms of the beneficial effects of HMR are still unresolved. Molecules with low molecular weight within the HMR solution are hypothesized to diffuse into the cell wall and chemically react with the cell wall components (Gardner et al. 2005). Dynamic mechanical thermal analysis, differential scanning calorimetry measurements, and theoretical analysis are interpreted in a way that HMR has an increased compatibility with lignin rather than carbohydrate components of the cell wall (Son et al. 2005). Isothermal stress-relaxation testing revealed that

Table 2 Longitudinal MOE (GPa) of isolated EW and LW.

<table>
<thead>
<tr>
<th>Study</th>
<th>Species</th>
<th>MC (%)</th>
<th>EW</th>
<th>LW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Range</td>
<td>Average</td>
</tr>
<tr>
<td>Mott et al. (2002)*</td>
<td>Loblolly pine</td>
<td>Not given</td>
<td>5–21</td>
<td>16</td>
</tr>
<tr>
<td>Cramer et al. (2005)*</td>
<td>Loblolly pine</td>
<td>8–10</td>
<td>1–5</td>
<td>4</td>
</tr>
<tr>
<td>Eder et al. (2009)*</td>
<td>Norway spruce</td>
<td>FS</td>
<td>–</td>
<td>3</td>
</tr>
</tbody>
</table>

*Individual EW and LW fibers tested in tension, MOE calculated based on cell cross-section.
*Matchstick samples containing either 100% EW or LW tested in three-point bending.
HMR stiffens wood (Sun and Frazier 2005), possibly implicating HMR as a crosslinker between lignin and hemicellulose; it becomes part of the interpenetrating polymer network of the cell wall.

**Acetylation**

Acetylation of wood has been extensively studied (Rowell 2005) and provides a unique chemical treatment for investigating wood-adhesive bonds. Acetylation leads to esterification of accessible hydroxyl groups but not to polymerization in the cell wall. As the degree of acetylation increases, the volume and mass of the treated wood also increase; the so-called weight percentage gain (WPG) is a measure of the extent of acetylation. Acetylated wood shows decreased shrinkage and swelling with changing RH conditions and a lower equilibrium moisture content (EMC), presumably as a result of the paucity of active hydroxyl sites to which water can bond (Ohmae et al. 2002; Obataya and Gril 2005; Rowell 2005). Moreover, the shrinkage and swelling anisotropy in the radial direction is diminished compared with that of the tangential direction (Ohmae et al. 2002).

After acetylation, the values of MOE, modulus of rupture, and toughness are similar to those of untreated wood; shear strength parallel to the grain is lower and the wet and dry compressive strengths, hardness, and wood density are elevated in comparison with untreated wood (Dreher et al. 1964; Norimoto et al. 1992). Increased mechanical properties are generally attributed to the lower MC in acetylated wood (Dreher et al. 1964).

**Materials and methods**

**Sample description**

The loblolly pine investigated is from the same tree described in previous studies (Cramer et al. 2005; Kretschmann et al. 2006). In the course of a multi-step process (Figure 1), pure EW and pure LW matchstick-sized monolithic samples were produced. The wedge of the tree (Figure 1i) used to make specimens had been slowly conditioned from green at 20°C and 50% RH. The Northwest quadrant, 30 mm thick, was cut from a bolt (i), then the 10th–13th growth rings were removed with a 0.5-mm kerf scroll saw (ii). From this, individual plates ~2–3 mm×20 mm×30 mm were split with a chisel (iii). Splitting the plates ensures that there is no appreciable slope of grain in the subsequent steps. The resulting plates (iv) were further aligned radially and tangentially and sanded and end-milled to a thickness of 1.2 mm. Matchstick-shaped specimens, 1.2 mm×1.2 mm×30 mm, were then cut from the LW and EW bands of the 12th growth ring with a miniature table saw (0.5-mm-thick blade). The abrupt growth ring transition between EW and LW in loblolly pine simplified the elimination of EW-LW transitional cells from each specimen. The 12th growth ring was ~7.5 mm radially, with a ~2-mm-thick LW band; the latest LW and earliest EW were selected. Each specimen was then planed on one radial and one tangential surface by means of a specially designed micro-planer with disposable razor blades. The resulting specimen dimensions were ~1.1×~1.1×~30 mm³. The quality of specimens were evaluated with a light microscope and culled so that the only specimens tested were those with their dimensions nearly perfectly aligned to the wood structure (Figure 1), without cracks, with few longitudinal resin canals, and with minimal variation in specimen surface quality.

**Experimental design**

Fifteen EW-LW pairs, divided evenly into three chemical treatment groups (control, HMR, and acetylation), underwent dimensional and mechanical testing before chemical treatment (pre-treatment testing) and after chemical treatment (post-treatment testing). The results of pre-treatment testing of each treatment group were combined to provide the data of base shrinkage, swelling, and MOE in the unmodified state. The comparative results are reliable because the specimens for the pre- and post-treatment testing were the same.

Conditioning environments: CE-1 (60°C under 85 kPa vacuum for 5 h, oven-dry); CE-2 (32°C, 30% RH, wood MC of ~6%); CE-3 (24°C, 65% RH, wood MC of ~12%); and CE-4 (27°C, 90% RH, wood MC of ~20%). After specimens were conditioned in CE-1, initial measurements of mass and dimensions were obtained in the CE-2 conditioning room, taking great care to minimize moisture uptake.

Dimensional measurements were made for specimens conditioned at CE-1 and for specimens moved sequentially from CE-1 to CE-3 (sorption), CE-3 to CE-4 (sorption), and CE-4 to CE-3 (desorption). The labeling scheme CE-1, CE-3s, CE-4, and CE-3d, respectively, is used hereafter in the text, tables, and figures. After being introduced into a new environment, the specimen mass was measured several times, and once mass stabilized (typically less than 24 h), it was inferred that equilibrium MC had been reached. After a minimum of 48 h conditioning, the mass and dimensions were measured. For CE-3s, CE-4, and CE-3d all measurements were completed in the CE-3 conditioning room and great care was taken to minimize the effect of moisture loss for specimens conditioned at CE-4. Following the dimensional measurements, MOE testing was completed for all specimens conditioned at CE-3d. The same

![Figure 1](image_url)
sequence of dimensional measurements at the various CEs followed by MOE measurement at CE-3d was used for both the pre- and post-treatment testing.

The RH stability of the CE-3 and CE-4 condition rooms was monitored. The average RH for CE-3s and CE-3d during pre-treated specimens conditioning was 67%, however, during conditioning of post-treatment specimens, the average RH was 64%. The CE-4 conditioning room RH was constant at 90% for the duration of the study.

**Dimension change measurement**

Caliper measurements were completed at the same location within the matchstick center region by squaring each specimen within the caliper grips. Three to five measurements were taken to the nearest 0.01 mm, and an average value was then calculated for the final dimension measurement, both radially and tangentially. Percent dimension change, $\varepsilon$, relative to the CE-1 (oven dried) condition was calculated by comparing the corresponding bend bar transverse dimension, $w$, between CE-1 and the CE of interest (CE-3s, CE-4, and CE-3d).

$$\varepsilon(\%) = \frac{w_{CE-1} - w_{CE-d}}{w_{CE-1}} \times 100$$ (1)

**Measurements of longitudinal MOE**

The MOE in the longitudinal direction ($E_L$) was calculated based on the static three-point bending and basic beam theory (Cook and Young 1985):

$$E = \frac{P}{d} \cdot \frac{L^3}{4w^2h^3}$$ (2)

where $d$ is the beam deflection (mm) as measured at $L/2$, $L$ is the span of the three-point bend supports (21 mm), $P$ is the applied load (N), $w$ is the sample width (mm), and $h$ is the sample height (mm).

Basic beam theory assumes that the tested material is homogeneous, linear elastic and has isotropic properties. Bulk wood violates all these assumptions. The present study minimized these assumptions violations by using small, isolated EW and LW specimens with minimal flaws. Viscoelasticity and creep artifacts were minimized by application of small loads (less than 0.80 N), small deflections ($d_{maximum} \sim 0.2$ mm), and short testing times ($\sim 2$ min). $E_L$ was measured by loading the specimens on the radial face, and then on the tangential face. The calculation of $E_{LT}$ and $E_{LB}$ is based on the corresponding bend-bar deflection in the tangential and radial directions, respectively.

MOE measurements were completed at the CE-3d condition for both pre- and post-treatment specimens. All specimens were equilibrated to CE-3 and their dimensions were measured immediately before MOE measurement. Specimens were placed in the three-point bending fixture, in which the upper loading pin translation was controlled by manually turning a micrometer with a precision of 0.001 mm. Load was measured in a miniature load cell with a precision of 0.001 N. To minimize the effect of crushing at the wood-pin contact points on modulus measurements, all specimens were preloaded to $\sim 0.8$ N and held for 1 min, then released. This process was repeated once; then the loading pin translation was adjusted such that all loading pins were barely in contact with the specimen but not yet applying a measurable load. At this point, the load cell and the micrometer were set to zero. A load-displacement data series was collected at approximate load levels of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 N, with a 10-s pause at each load level to allow the specimen to stabilize. After the final load of 0.6 N, the load was then removed. The process was repeated four times, giving a total of five load-displacement data series for each specimen. Each load-displacement series was fitted with a linear curve fit and the slope $P/d$ was used with Eq. (2) to calculate the MOE. The average of these five modulus values are presented as a typical $E_L$.

**Chemical treatment: HMR**

Specimens were treated with the n-HMR process as described in Christiansen et al. (2001) and Christiansen and Okkonen (2003). EW and LW specimens were initially dried at CE-1, and the mass and the dimensions were measured. Specimens were dipped in the n-HMR solution at room temperature for 1 min, dried at CE-3 for at least 20 h, dried at CE-1, and then the data were measured again. Average weight gain was 0.6 g for EW and 0.8 g for LW, corresponding to a WPG of $\sim 5.1\%$ and $\sim 2.7\%$, respectively (Table 3), which is greater than that of similar studies (Son and Gardner 2004; Son et al. 2005; Sun and Frazier 2005). The average increase in specimen dimensions (at CE-1 conditions) was 1% radial and 2% tangential for both EW and LW. After the completion of all testing, specimens were sectioned, and visual inspection revealed complete penetration of the dark HMR solution through the cross-section.

**Chemical treatment: acetylation**

EW and LW specimens were initially dried at CE-1, and the mass and the dimensions were measured. One EW-LW pair was placed for 1 h in a reaction flask containing acetic anhydride at 130–140°C. The temperature was adjusted until boiling was observed from the specimen surface. Specimens sank to the flask bottom within 5 min for LW and 30 min for EW. Afterward, specimens were dried at CE-3 for at least 20 h, dried at CE-1, and then the mass and dimensions were measured. The average weight gain was 1.8 g for EW and 5.8 g for LW, corresponding to a WPG of $\sim 16.7\%$ and $\sim 18.8\%$, respectively (Table 3), which is typical. The average increase in specimen dimensions (at CE-1 conditions) was 2% radial and 6% tangential for EW, and 7% radial and 8% tangential for LW. Note that the same 40 ml of acetic anhydride solution was used for all reactions, after which there was a slight color change, indicating some extraction of wood components.

**Table 3** Data of specimens conditioned at CE-1.

<table>
<thead>
<tr>
<th>Treatment group</th>
<th>Pre-treatment mass (g)</th>
<th>WPG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>EW 11.1 (0.4)</td>
<td>~0.9</td>
</tr>
<tr>
<td></td>
<td>LW 29.2 (2.5)</td>
<td>~0.3</td>
</tr>
<tr>
<td>HMR</td>
<td>EW 11.0 (0.3)</td>
<td>~5.1</td>
</tr>
<tr>
<td></td>
<td>LW 29.4 (0.6)</td>
<td>~2.7</td>
</tr>
<tr>
<td>Acetylation</td>
<td>EW 10.8 (0.3)</td>
<td>~16.7</td>
</tr>
<tr>
<td></td>
<td>LW 31.0 (1.2)</td>
<td>~18.8</td>
</tr>
</tbody>
</table>

*Numbers in parentheses represent one standard deviation (SD).*
Statistical analysis

The statistical significance of a measured changes was assessed by means of a split-plot design. Two types of variability were investigated: specimen-to-specimen (chemical treatment group effects, EW-LW effects and tangential-radial effects measured on separate specimens) and within-specimen (pre-treatment vs. post-treatment effects and conditioning environmental effects measured on the same specimen). To protect against possible heterogeneity of variance, the data were analyzed both parametrically and non-parametrically. Because most of the practical comparisons between pre-treatment and post-treatment specimens in dimensional change and MOE had obvious outcomes, thus the statistical significance seems unnecessary.

Results and discussion

Moisture content

The specimen EMC at each conditioning environment for both pre- and post-treatment testing is summarized in Figure 2. For the pre-treatment testing, all specimens of untreated EW and LW have similar MCs for a given conditioning environment, although LW has ~1% greater MC than EW at each conditioning environment. The higher MC for CE-3d compared with CE-3s is consistent with known sorption hysteresis effects on bulk wood MC (Stamm 1964). Note that the RH in CE-3s and CE-3d was the same, and thus, did not contribute to the difference in MC.

For the post-treatment testing, the MC profiles for the HMR specimens are nearly identical to the control specimens, whereas acetylated specimens have a much lower MC in each conditioning environment. Despite the WPG from the HMR treatment in this study, HMR did not alter the EMC of EW or LW specimens.

![Figure 2](image)

*Figure 2* The average MC of EW and LW for pre- and post-treatment cases as a function conditioning environment. Each point is an average of five specimens. Plots show that acetylation lowered MC, whereas HMR had minimal effect on MC. One standard deviation (not shown) for each data point was approximately 1 for EW and 0.5 for LW.

Dimension change

The average specimen dimensional change at each conditioning environment for both pre- and post-treatment testing is summarized in Figure 3. Also here, the pre-treatment testing was performed at untreated EW and LW. When combining all specimen groups, the average EW tangential dimensional change was more than twice the average radial change, in which the maximum swelling strain (i.e., CE-1 to CE-4) was $e_r = 7.6\%$ (1.4 SD – one standard deviation), and $e_\theta = 2.9\%$ (0.8 SD), respectively. For LW, there was minimal anisotropy in tangential-radial dimensional change; the average maximum swelling strain was $e_r = 7.8\%$ (0.8 SD), and $e_\theta = 7.4\%$ (0.8 SD), respectively. These results are in general agreement with those of previous studies (Table 1).

The control group dimensional changes were generally lower in post-treatment testing than in pre-treatment testing even though they did not undergo a chemical treatment. Additionally, sorption hysteresis, observed in the pre-treatment testing between CE-3s and CE-3d, was not observed in the post-treatment group. These differences between pre- and post-treatment testing can be interpreted that the history of pre-treatment testing altered the specimen swelling and shrinkage response during the post-treatment testing. For the HMR group, the dimensional change for both EW and LW shows a similar trend and magnitude to that of the control group. Combined with the large scatter in the data, this indicates a small influence of HMR treatment on swelling and shrinkage. For the acetylated group, the decreases in dimensional change between the pre- and post-treatment testing are larger than that of the control group; acetylation reduced swelling and shrinkage in both EW and LW.

The scatter in the measured dimensional change across all groups could be attributed to three main effects: the 0.01-mm measurement resolution of the calipers, possible errors in specimen placement relative to the caliper-measurement surfaces, and specimen compression by the caliper-measurement surfaces. The uncertainty resulting from the caliper resolution could be estimated conservatively as $\pm 0.005$ mm, which for a 1.1-mm bend bar cross-section represents a variation in strain of $\pm 0.45\%$

The apparent effect of pre-treatment history could be confounded by the influence of a given chemical treatment on swelling and shrinkage. This possibility was addressed by comparing the post-treatment dimensional changes of the control group with those of the HMR and acetylation treatment groups. The dimensional change values for all specimens in the pre-treatment testing were not significantly different at a 0.05 significance level, demonstrating that for each group the untreated specimens had a similar dimensional change response. Because of this, it is indeed reasonable to compare the post-treatment dimensional change of the control group with either the HMR or acetylation treatment groups to assess the extent to which a given chemical treatment altered swelling or shrinkage. This approach prevented large errors in the interpretation of the results. The significance of any differences was assessed by statistical analysis (Table 4).
The HMR treatment did not greatly alter the swelling or shrinkage of either EW or LW. Any apparent difference in dimensional change between the pre- and post-treatment testing (Figure 3) was generally similar to that observed in the control treatment group, indicating minimal influence of HMR treatment. Statistical analysis showed that the differences between the control group and the HMR group for either the radial or tangential dimensional change for both EW and LW were not statistically significant (Table 4). This result seems to be in contrast to the studies of Son and Gardner (2004) and Son et al. (2005) that showed decreased dimensional change and water uptake of HMR-treated specimens when immersed in liquid water or that veneer surfaces behave differently from these bulk type values. Interpretation: HMR might differentially affect interactions with water vapor and liquid water or that veneer surfaces behave differently from these bulk type values. Acetylation reduced swelling and shrinkage in both EW and LW (Figure 3). Statistical analysis showed that for LW, the differences in radial and tangential dimensional change between the acetylated and control groups were significant, whereas for EW only, radial dimensional change was significantly different from that of the control group.

Longitudinal MOE

The longitudinal MOE results for the three treatment groups are summarized in Figure 4. There were no measurable effects of the bending orientation (i.e., $E_{LT}$ vs. $E_{LR}$) on the longitudinal MOE for either EW or LW. The insensitivity of bending orientation shows that for small isolated EW and LW specimens rotated along the longitudinal axis, the cellular structure has minimal influence on the longitudinal MOE. The MOE measurements from the radial and tangential testing orientations were combined, and the untreated loblolly pine longitudinal MOE for EW and LW at CE-3d conditions were $E_{LT} = 3.6$ GPa (0.8 SD) and $E_{LR} = 14.7$ GPa (1.3 SD), respectively. These values are within the range reported by Cramer et al. (2005). Additionally, and as expected, these values bound the reported longitudinal MOE of 12.3 GPa for bulk loblolly pine specimens at 12% MC tested in static bending (Green et al. 1999).
Table 4 Statistical analysis of results concerning moisture-induced dimensional changes obtained by post-treatment.

<table>
<thead>
<tr>
<th>Conditioning environment</th>
<th>CE-3s</th>
<th>CE-4</th>
<th>CE-3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>EW</td>
<td>A H C</td>
<td>A H C</td>
<td>A H C</td>
</tr>
<tr>
<td>Radial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tangential</td>
<td>A C H</td>
<td>A H C</td>
<td>A H C</td>
</tr>
<tr>
<td>LW</td>
<td>A H C</td>
<td>A H C</td>
<td>A H C</td>
</tr>
<tr>
<td>Radial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tangential</td>
<td>A H C</td>
<td>A H C</td>
<td>A H C</td>
</tr>
</tbody>
</table>

Treatments connected by a line are not significantly different at the 0.05 significance level. For example: the EW radial dimensional change at CE-3s, A, H, and C are not significantly different from each other, whereas at CE-4, H and C are not significantly different from each other, but both are significantly different from A. At CE-3d, A and H, and H and C are not significantly different from each other, but A is significantly different from C.

A, acetylation; C, control; H, HMR.

The post-treatment results show that HMR and acetylation did not alter the longitudinal MOE for either EW or LW, nor $E_{E,W}$ and $E_{L,W}$ within each treatment group. The small increase in the control LW MOE between the pre- and post-treatment tests is probably a result of the lower specimen MC as illustrated in Figure 2 (pre- vs. post-treatments at CE-3d).

HMR treatment had no measurable influence on the EW or LW longitudinal MOE (Figure 4). Previous studies (Son et al. 2005; Sun and Frazier 2005) hypothesized that HMR crosslinks with lignin and hemicellulose, resulting in lower water uptake and increased mechanical properties. In the present study, specimen weight gain and visual inspections of sectioned specimens confirmed that the dark HMR solution had complete penetration through the specimen cross-section. Despite this, HMR treatment did not affect EMC for a given conditioning environment (Figure 2).

Acetylation had no measurable influence on EW or LW longitudinal MOE (Figure 4), contrary to previous findings with bulk wood. Dreher et al. (1964) investigated specimens of $50 \times 50 \times 760$ mm$^3$ ($T \times R \times L$) in static bending and found that the average MOE changed as a result of acetylation for the following wood species: Ponderosa pine had an increase of 2%, red oak had a decrease of $\sim 6\%$, and sugar maple had a decrease of 4%. Likewise, Norimoto et al. (1992) tested spruce specimens of $2 \times 12 \times 100$ mm$^3$ ($T \times R \times L$) in static bending and found that the average MOE decreased by 9% as a result of acetylation.

In the present study, WPG and lower MC for a given conditioning environment (Figure 2) confirm that the acetylation treatment chemically modified the specimens. It is possible that acetylation causes two competing mechanisms: one lowers and one elevates MOE. During acetylation, acetyl groups replace hydroxyl groups on lignin and hemicelluloses, resulting in an extended separation distance between the cell wall components (as manifest by the increase in specimen dimensions) and diminish hydrogen bonding between cell wall components. If a given percentage of the hydrogen bonding sites necessary for wood stiffness is replaced with acetyl groups, the wood is plasticized; this would be the MOE-decreasing mechanism. Increased MOE could result from the lower moisture uptake of acetylated wood at a given RH (Figure 2), effectively stiffening the wood. If these two mechanisms were operating, it would appear that the CE-3d conditions, at which the longitudinal MOE testing was com-

Figure 4 The average MOE of EW and LW for pre- and post-treatment cases and as a function of testing orientation (for bend-deflections in the tangential direction $E_{E,W}$, radial direction $E_{R,W}$, and combined $E_{T,W}$): (a) control, (b) HMR and (c) acetylated treatment groups. All measurements completed at CE-3d conditions. Plots show the minimal influence of chemical treatments and testing orientation on MOE. Circular (■) and triangular (▲) symbols represent LW and EW, respectively. Error bars are one standard deviation.
pleted, represents a balance point between them, where the effects of one cancel that of the other: the longitudinal MOE remains apparently unchanged.

Selectivity of chemical modification on dimensional changes and MOE

HMR treatment and acetylation did not selectivity modify the swelling, shrinkage or MOE in EW compared with LW. Even though the acetylation treatment decreased dimensional changes, EW and LW were altered to similar extents; swelling and shrinkage was confined by approximately 50%, irrespective of EW, LW, or radial and tangential directions.

Interactions between variables

Graphical summaries of the statistical results (results not presented) revealed several possible interactions between variables. For example, the results of treatment effects were often different for EW and LW, meaning an interaction was present that requires analysis. Some graphical summaries indicate greatly different levels of variability in subsets of the data. Often, interactions caused extensive breakup of the data into subgroups for analysis, but the small n of these subgroups precluded full exploration of these interactions.

Conclusions

Dimensional change and longitudinal MOE were measured for isolated EW and LW specimens of loblolly pine (Pinus taeda L.). The unique feature of this investigation was the comparison between the same EW and LW specimens in pre- and post-chemical treatment, giving the opportunity to quantify the change in specimen swelling, shrinkage and MOE as a direct result of the given chemical treatment. It can be concluded:

1. HMR did not greatly alter the dimensional change or the longitudinal MOE observed for a comparable change in MC.
2. Acetylation restricted the dimensional change (generated by change in MC in isolated EW and LW) by approximately 50%, but did not alter longitudinal MOE.
3. There was no influence of bending orientation (i.e., bending deflections in the tangential direction $E_{LT}$ or radial direction $E_{LR}$) on the longitudinal MOE. It is interpreted as an insensitivity of different cellular orientation for rotations along the longitudinal axis in small isolated EW and LW specimens.
4. HMR treatment and acetylation did not selectivity modify specimen properties according to specimen origin as EW versus LW or orientation (radial vs. tangential).

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References


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