Modern Methods of Dimensional Stability

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Wood Chemistry

Primary wall

Middle lamella

Inner layer ($S_3$)

Middle layer ($S_2$)

Outer layer ($S_1$)

Secondary wall
Chemistry Summary

• **Cellulose**
  - Linear polymer, 40-70% crystalline in wood

![Cellulose structure](image)

Chemistry Summary

• **Hemicellulose**
  - Linear but also branched, amorphous

![Hemicellulose structure](image)
Chemistry Summary

- Lignin

- Amorphous, irregular

Chemistry Summary

Water in Wood

Hemicellulose

More hydrophilic

More accessible hydroxyl groups

Cellulose

Less hydrophilic

Less accessible hydroxyl groups

Lignin

Hydrogen bond

Water

Lignin has ton of phenolic hydroxyl groups but not accessible like polysaccharides
Water in Wood

Volumetric change with adsorption/desorption of water

Dimensional Stability

- **Ability to maintain original dimensions**
  - Stop volumetric changes due to water
- **Anisotropic shrinkage**
  - Longitudinal negligible (usually)
  - Radial approximately half tangential

Figure 2.2—Generalized shrinkage across the grain as wood dries.
## Anisotropic Shrinkage

<table>
<thead>
<tr>
<th>Species</th>
<th>Radial (%)</th>
<th>Tangential (%)</th>
<th>Volumetric (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar Maple</td>
<td>4.8/3.5</td>
<td>9.9/7.3</td>
<td>14.7/10.8</td>
</tr>
<tr>
<td>White Ash</td>
<td>4.9</td>
<td>7.8</td>
<td>13.3</td>
</tr>
<tr>
<td>Red Oak</td>
<td>4.0</td>
<td>8.6</td>
<td>13.7</td>
</tr>
<tr>
<td>White Pine</td>
<td>2.1</td>
<td>6.1</td>
<td>8.2</td>
</tr>
</tbody>
</table>

FSP to oven dry/FSP to 8%  

\[ S_m = \frac{S_o(30 - m)}{30} \]

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## Defects Related to Volumetric Changes

- **Cabinet fractures**
- **Fasteners loosening**
- **Flooring gaps**
- **Joints opening**
Measuring Dimensional Stability

\[ S = \frac{V_2 - V_1}{V_1} \times 100 \]

\[ R = \frac{S_2 - S_1}{S_1} \times 100 \]

- \( S \) = volumetric swelling coefficient
- \( V_2 \) = volume after wetting, RH exposure
- \( V_1 \) = volume of ovendry sample
- \( R \) = reduction in swelling
- \( S_2 \) = volume of treated wood
- \( S_1 \) = volume of untreated wood

\( ASE \) = anti shrink efficiency

Dimensional Stabilization Methods

*Dimensional Stabilizers by Reduction in Rate of Vapor or Liquid Absorption*

- Design
- Water repellants

*True Dimensional Stabilizers*

- Thermal treatments
- Chemical treatments
Design

- Cross lamination
  - Thickness swell, but stable across panel
- No change to rate of adsorption or EMC

Water Repellents and Coatings

<table>
<thead>
<tr>
<th>Finish</th>
<th>No of coats</th>
<th>Moisture-excluding effectiveness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 day</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>33</td>
</tr>
<tr>
<td>Water repellent</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>78</td>
</tr>
<tr>
<td>Latex flat wall paint (vinyl acrylic resin)</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>22</td>
</tr>
<tr>
<td>Latex primer wall paint (butadiene-styrene resin)</td>
<td>1</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>88</td>
</tr>
<tr>
<td>Alkyd flat wall paint (soya alkyd)</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>Acrylic latex house primer paint</td>
<td>1</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>72</td>
</tr>
<tr>
<td>Acrylic latex flat house paint</td>
<td>1</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>Solid-color latex stain (acrylic resin)</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 16-3. Moisture-excluding effectiveness of various finishes on ponderosa pine

ASE <10%
Thermal Treatments

• Wood is subjected high temperature treatment 160-260°C (320-500°F)
• Results in removal of hemicelluloses

Thermal Treatments Impart Dimensional Stability

• Removal of hydroxyl (-OH) groups

Degradation products lost as VOCs
Thermal Treatment Overview

- **Treatment temperature**: 160–260°C (320–500°F)
- **Flame point**: 225–260°C (437–500°F)
  - Gases formed from wood decomposition will ignite
- **Burn point**: 260–290°C (500–554°F)
  - Wood will steadily burn with flame
- **Must remove oxygen to prevent burning**
  - **Shielding gases (N₂)**
- **Mass loss**: a general indicator of quality
  - 2–12% is typical for commercial treatments
  - 4–6% limit for EMC reduction

Thermal Treatments

- **Negative attributes**
  - Color change
  - Reduced surface energy (lower OH availability)
  - Poor gluability, paintability
  - Splits, cracks, loose knots, etcetera
- **Need high grade lumber**
  - Reduced mechanical properties

ASE 40%
Chemical Treatments

• Two types
  – Bulking
    • Nonbonded-leachable
    • Nonbonded-nonleachable
    • Bonded-nonleachable
    – Single site addition*
    – Polymerizing addition
  – Cross-linking
*most important commercially

Cross-linking

• Hydroxyls are replaced with covalent bonds linking cell wall components
• High ASE with minimal treatment level
• Reduced mechanical properties
  – Embrittlement
  – Acid catalysts result in hydrolysis
Cross-linking

- Many cross-linking agents have been used

\[
\text{Cellulose monomer} + \text{Formaldehyde} \rightarrow \text{Cross-linked polymer}
\]

Cross-linking treatment

- Wood hydroxyl
- Water molecule
- Crosslinking agent
Bulking Treatments

• Nonbonded-leachable
  – Wood is soaked in solution
    • Salts or sugars (manganese, sodium, barium, lithium chloride, potassium iodide, sucrose, glucose, fructose, etcetera)
    • Polyethylene glycol (PEG)
  – Bulking chemical replaces water in the cell wall
    • Wood is swollen to ‘green’ volume after treatment
  – Water soluble, samples must be sealed
  – Slow diffusion limited process at ambient temperature (days weeks months)
Bulking Treatments

- Nonbonded-nonleachable
  - Water-soluble low molecular weight resins
    - Phenol formaldehyde (PF) “Impreg”
    - Styrene, methyl methacrylate

ASE 70%
Bulking Treatments

• Bonded-nonleachable (single site addition)
  – Two methods have reached industrial scale
    • Acetylation
      – Accoya wood
    • Furfurylation
      – Kebony wood

Acetylated Wood
Acetylated Wood

• Increased durability
• FSP below 15%
• Increased hardness
• No negative effect on mechanical properties
• Very expensive

Furfurylated Wood

• Wood is vacuum impregnated with furfuryl alcohol and catalysts
• Pressure vessel is then heated to polymerize the furfuryl alcohol
• The actual chemical interaction between furfuryl polymer and wood is unknown – May bond with lignin and hemicellulose
Furfurylated Wood

**ASE 60%**

Beach Pavilion: New | After 3 years

**Summation of Methods**

- Coatings and water repellants do not alter the dimensional stability of wood, but reduce rate at which water is absorbed
  - Low effective ASE (none over time)
  - Low cost
  - Ease of application
Summation of Methods

- Chemical and thermal treatments impart dimensional stability to wood through bulking or alteration of available hydroxyl groups
- They are considered to be ‘green’ treatments unlike wood preservatives
- ASE varies by severity or treatment loading

<table>
<thead>
<tr>
<th>Treatment</th>
<th>ASE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal treatment</td>
<td>40</td>
</tr>
<tr>
<td>Impreg</td>
<td>70</td>
</tr>
<tr>
<td>Acetylation/Furfurylation</td>
<td>60-75</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>85</td>
</tr>
</tbody>
</table>

Conclusion

- Dimensional stability is of critical importance in utilization of wood
- Technologies to impart dimensional stability are not new developments, however the importance in marketplace is growing
- Acetylation, furfurylation, and thermal treatments allow for use of nondurable species in exterior applications
- Thermal treatments allow for exterior use of nondurable hardwoods (yellow poplar, ash, etcetera)
Cellulose

• What is it?
  – 1→4 β-D-glucopyranose
  – Linear polymer of glucose molecules
  – Degree of polymerization (molecules in polymer)
    8,000 to 11,000
  – Long chains of cellobiose (glucose + flipped glucose)

Cellulose

• Organization
  – Cellulose chains bond to adjacent chains
    (hydrogen bonds and van der Waals forces) to form ‘elementary fibrils’ and larger ‘microfibrils’
  – The spatially ordered structure leads to regions of crystallinity in the cellulose and higher order organizations of cellulose chains
Biosynthesis of Cellulose

Individual cellulose chain → Cellulose microfibril

Cellulose synthase complex → Rosette subunit → Rosette
(in plasma membrane, microfibril deposited onto the cell wall)

Cellulose

- Degree of Crystallinity
  - Cellulose microfibrils are crystalline (at least partially, ~40-70%)
  - Crystallinity = mechanical strength, resistance to biological attack
Hemicellulose(s)

- **Structure**
  - Similar to cellulose, well-defined enzyme controlled synthesis but not crystalline
  - Branched, more hydrophilic (more readily adsorb water than cellulose)
  - Differ between hardwoods and softwoods
    - Hardwoods highly acetylated

![Hemicellulose structure](image)

Hardwood xylan (glucuronoxylan)
15-30% of dry weight

Lignin

- **Structure**
  - Amorphous structure
  - 3 basic subunits that combine randomly (in 3D) through radical-radical coupling reactions

![Lignin polymer units](image)
Lignin

- Structure continued
Chemistry Summary

• Cellulose

- Linear polymer, 40-70% crystalline in wood

Chemistry Summary

• Hemicellulose

- Linear but also branched, amorphous
Chemistry Summary

• Lignin

— Amorphous, irregular

Chemistry Summary

Water in Wood

Hemicellulose

Cellulose

Lignin

More hydrophilic

Less hydrophilic
Chemistry Summary

Water in Wood

Hemicellulose

More hydrophilic

More accessible hydroxyl groups

Cellulose

Less hydrophilic

Less accessible hydroxyl groups

Lignin

Lignin has ton of phenolic hydroxyl groups but not accessible like polysaccharides

Chemistry Summary

Hemicellulose

Less thermally stable

Cellulose

Lignin

More thermally stable
Chemistry Summary

• What is the chemical ‘architecture’ of cell wall
  – We know the cell wall in wood is composed of a multiple layers
    • Wood tracheid (6-20 GPa)
  – The cellulose microfibrils impart strength and stiffness to the cell wall
    • Rebar (130-140 GPa)
  – Hemicellulose bonds with lignin (lignin carbohydrate complex) and also with cellulose
    • Poured concrete (3-8 GPa)
  – Lignin ‘encruts’ the polysaccharide components
    • Concrete masonry unit (2-7 GPa)
Chemistry Summary

- How does it look in wood?
  - Maybe like this: or this:

Chemistry Summary

- How does it look in wood?
  - Or maybe like this:

Or this:
Chemistry Summary

How does it look in wood?
– Or maybe like this:

Chemistry Summary

Wood cell wall

inner layer \( (S_1) \)
middle layer \( (S_2) \)
outer layer \( (S_3) \)
primary wall
Thermal Treatment Processes

• Many different commercial methods (all European)
  – Treatment temperature 160-260°C (320-500°F)
  – Temperature rise, thermal treatment stage, cooling and equilibration stage
• Thermowood (Finland)
  – Heat and vapor, green or dry lumber,
  – 180-250°C treatment temperature
• Plato wood (Netherlands)
  – Heat and vapor, green lumber
  – 160-190°C treatment temperature
• Retification (France)
  – Heat and nitrogen, dry lumber
  – 200-240°C treatment temperature
• Le Bois Perdure (France)
  – Heat and wood vapors, green lumber
  – 200-250°C treatment temperature
• Oil Heat Treatment (Germany)
  – Heat and crude vegetable oil, green lumber
    • Mass increases, oil adsorbed
  – 180-220°C treatment temperature
Thermal Treatment Process

• Chemical changes are occurring during two stages of thermal treatment

• Drying stage <150°C (<302°F)

  followed by

• Thermal treatment stage <260°C (<500°F)

Very generalized, treatments vary greatly

Thermal Treatment Process

• Thermal treatment stage time varies

• Influenced by specific gravity, MC, initial temperature, target temperature, board dimensions, heat transfer medium (shielding gas, steam)
  – Hours to many hours
Drying Stage <150°C (<302°F)

- Moisture loss from wood
  - Free water followed by bound water
- Loss of volatile extractives
  - Monoterpenoids (α-pinene, β-pinene)
  - Acids (acetic, formic, propionic)
- Net effect is minor
  - Extractives are nonstructural

Thermal Treatment Stage <260°C (<500°F)

- Water pKa decreases with temperature

  ![Graph showing pKa decrease with temperature]

  - It’s becoming a stronger acid
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

• Acetyl groups cleaved by hydrolysis $\rightarrow$ acetic acid generated
  – Acetic acid can break glycosidic bonds along hemicellulose backbone or amorphous cellulose (especially in steam treatments)

Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

• HWs have higher mass loss compared to SWs
  – HW hemicellulose more acetylated (7Ac per 10Xy)
  – SW hemicellulose less acetylated (1Ac per 4Glc)
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

• Removal of ‘water of constitution’
• Loss of hydroxyl (-OH) groups

![Diagram showing chemical reactions and degradation products]

Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

• Degrade into furfural, hydroxymethylfurfural, and subsequent degradation products

Acids = equipment corrosion

Furfural also responsible for ‘smoky’ odor
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose Summary

- **Deacetylation**
  - Acetyl groups removed
- **Dehydration**
  - Loss of water of constitution
- **Depolymerization**
  - Glycosidic bonds broken along xylose chain
- **Reduced hygroscopicity**
  - Loss of hydroxyl bonding sites
  - Residual degradation products (furfural, hydroxymethylfurfural) less hydrophilic

Thermal Treatment Stage <260°C (<500°F) Effects on Cellulose Summary

- **Crystalline regions unchanged**
  - Stable to 300°C
- **Amorphous region degraded**
  - Less so compared to hemicelluloses
- **Degree of crystallinity increases**
  - Crystalline remains, amorphous degraded
  - No amorphous regions are converted
Lignin is thermoplastic
  – Will plasticize and physically flow, rearrange
    • $T_g = 150^\circ C$

Condensation reactions, cross-linking
  – Lignin structure condenses within itself
  – Degradation products of hemicellulose condense onto lignin macrostructure
  – Contributes to color changes

Softwood lignin more modified
  – SW lignin less condensed, HW S and G type lignin,
    SW predominantly G type lignin
Reduced hygroscopicity – Hemicellulose and amorphous cellulose regions degraded, fewer available bonding sites (–OH) – Residual degradation products (furfural, hydroxymethylfurfural) less hydrophilic

Mechanical properties reduced – Cellulose remains largely intact, crystalline regions not affected by thermal conditions – Hemicellulose degradation prevents transfer of stress from rigid cellulose to amorphous lignin

Wood becomes more brittle

Thermal Treatment Effect on Wood Properties

Embrittlement

Modulus of Elasticity=stiffness Modulus of Rupture=strength

Green at start of thermal treatment vs dry at start of thermal treatment
Thermal Treatment Process Variables

• Open versus closed system
  – Closed systems will result in higher mass loss due to the concentration of acids released from wood
  – Closed systems also result in higher pressure due to dissolved degradation products
• Wet versus dry systems
  – Wet systems result in higher mass loss
    • More protons more hydrolysis
• Air versus shielding gases
  – Thermal treatment in air results in greater mass loss as result of oxidation reactions
• Temperature and time
  – Longer times and higher temperatures result in greater mass loss
• Dimensions and species of boards
  – Initial MC, density, heat transfer

Thermal Treatment Summary

• Chemical changes during thermal treatment result in reduced hygroscopicity resulting in desirable EMC reduction, increased durability, and improved dimensional stability

• Chemical changes during thermal treatment result in decreased mechanical properties
Weathering of Thermally Modified

Fig. 1. Visual appearance of tangential surfaces of birch, untreated and heat-treated at different temperatures during weathering: (a) untreated, (b) heat-treated at 105°C, (c) heat-treated at 205°C, (d) heat-treated at 215°C.
Making Matters Worse

- Average relative humidity varies greatly
  - So EMC does as well

<table>
<thead>
<tr>
<th>Product</th>
<th>Final MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pallet stock</td>
<td>18% to green</td>
</tr>
<tr>
<td>Bending stock, severe bends</td>
<td>25% to 28%</td>
</tr>
<tr>
<td>Bending stock, mild bends</td>
<td>15% to 18%</td>
</tr>
<tr>
<td>Lumber to be pressure treated</td>
<td>20% to 30%</td>
</tr>
<tr>
<td>Lumber for framing in construction</td>
<td>10% to 19%</td>
</tr>
<tr>
<td>Lumber for export to Europe</td>
<td>10% to 13%</td>
</tr>
<tr>
<td>Lumber for export to Eastern Asia and tropical areas</td>
<td>12% to 16%</td>
</tr>
</tbody>
</table>