Surface Modification versus Bulk Wood Modification – Properties and Challenges

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Content of presentation

Wood modification
- Why and how (principles)
- Status quo industrial applications
- Bulk treatment versus surface treatment
- Challenges and limitations

Photos: BASF, Titanwood
Wood: material of the future

- Ecological
- Sustainable
- Renewable
- Esthetical
- Energy efficient
- End-of-life: energy
- Traditional and modern

Wood, not just perfect...

Maintenance problems of wood due to:

- Moisture sensitive
- UV-stability
- Dimensional movements
- Resistance against fungi
- Soft surface

Photos: Grosser, Evans, Mitz
What is wood modification?

History of wood modification

- 1930’s: Acetylation etc. (Stamm et al., USA)
- 1970’s: heat treatment production plant FWD (Giebeler et al., D)
- 1990’s:
  - Heat treatment processes (TMT)
    - Plato
    - Thermowood
    - French processes
  - Acetylation with acetic anhydride
    - R. Simonson (Chalmers, SE)
    - H. Militz (SHR, NL)
Thermo treatment (TMT, Thermowood)
- no chemicals
- temperature 180° C to 220° C
- many wood species used
- difference between producers:
  - technology used

ThermoWood® process

Photos: Plato process

Modification technology based on liquids

- Belmadur® Technology
  - (DMDHEU)
- Kebony® Technology
  - (Furfurylation)
- Accoya® Titanwood
  - (Acetylation)
- Silanes/ Silicones
Kebony® production

Autoclave: 13 m length, 3.25 m diameter (0.1 - 13 bar)

Production plant, Arnhem, NL
Use class 1-2 (EN 335)
(Photos by Mitteramskogler/Austria)

Use class 3 (EN 335)
(Photos by Thermowood Association, Finland)
Use class 3 (EN 335)
(Photos by Mitteramskogler/ Austria)

Kebony® Products
Accoya® products

Wood modification in research phase

- Silicones/ siloxanes
- Aldehydes
- Phenols
- Anhydrides
- Others…

- See several presentations during conference
Wood properties gained with modification treatment

- Improved durability against decay
- Reduced equilibrium moisture content
- Color?
- Improved stability
- Thermal conductivity?
- Strength properties?
- Resin removed
- UV stability?

Surface modification

Challenges and limitations

- material properties
- applications
Wood properties gained with surface modification

- Reduced equilibrium moisture content
- Improved durability against decay?
- Thermal conductivity: no effect
- Resin removed: no effect/ limited
- Color? Just on surface
- Improved stability?
- UV stability?
- Strength properties? limited...

Sorption properties changed
(Tjeerdsma, Boonstra 1990’s)

Scotch pine

- Heat-treated adsorption
- Heat-treated desorption
- Non-treated adsorption
- Non-treated desorption

Equilibrium Moisture Content (%) vs. Relative Humidity (%)
Swelling/ shrinkage

Swelling/ Shrinkage [%]

Teak  Oak  Meranti  Beech  Pine

Belmadur® Wood

Swelling/ shrinkage: improvement of surface?

• Any effect of a solid/ building part because of thin layer?

• Possible effect on performance of a coating or adhesive?
Water repellency (Weigenand 2004)

![Graph showing water uptake over time for different samples.]

- ASE 8730
- ASE 8730
- ASE 8730
- ASE 8130
- ASE 8130
- ASE 8130
- Control

Moisture content variation in field tests

- Photographs of equipment used in field tests.
Moisture content in field tests (pine)

Moisture content in field trials (PhD A. Gellerich)

<table>
<thead>
<tr>
<th>treatment</th>
<th>m.c. above &gt;30%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pine</td>
</tr>
<tr>
<td>Untreated</td>
<td>52</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>5</td>
</tr>
<tr>
<td>Siloxan</td>
<td>0</td>
</tr>
<tr>
<td>Waterglas</td>
<td>10</td>
</tr>
</tbody>
</table>
Surface roughness and waviness
(Xie et al. 2008)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water-borne / acrylic</th>
<th>Oil-based</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Roughness ($R_a$) [µm]</td>
<td>Waviness [µm]</td>
</tr>
<tr>
<td>Untreated</td>
<td>6.0 (0.8)</td>
<td>164.8 (15.3)</td>
</tr>
<tr>
<td>Treated</td>
<td>1.0 (0.0)</td>
<td>17.5 (2.6)</td>
</tr>
</tbody>
</table>

'1: very few cracks; 2: few cracks; 3: moderate cracking; 4: considerable cracking; 5: many cracks

Water related properties

- Reduced liquid (water) uptake
  - Positive effect on end product
  - Negative effect on raw/ semi-product
    - Glueability?
    - Paintability?

(Tingaut et al., 2005)
Resistance against degrading fungi (brown rot, white rot, soft rot) in EN 113, Env 807, EN 252

![Graph showing weight gain after reaction for different treatments]

- Interface Treatment "A"
- Interface Treatment "B"
- Interface Treatment "C"

Coriolus versicolor, Beech

Silicones

Polydimethylsiloxane

Silicone Quats

Functional groups:
- \( \text{CH}_2/\text{OCH}_3 \)
- \( \text{(CH}_2)_2 - \text{NH}_2 \)
- \( \text{(CH}_2)_2 - \text{NH}^+ \)
- \( \text{(CH}_2)_2 - \text{NH}_2 \)

\( \phi < 2 \text{nm} \)
### Growth reducing activity (Ghosh et al. 2004)

- **Coniophora puteana**
  - 0.05, 0.1, 0.2, 0.4, 1% QSMiE with control after 7 days
- **Trametes versicolor**
  - 0.05, 0.1, 0.2, 0.4, 1% ASMaE with control after 7 days

### Type of fungi in field test with Pine (Gellerich 2009)

<table>
<thead>
<tr>
<th>fungi</th>
<th>Untreated</th>
<th>Siloxan</th>
<th>Waterglas</th>
<th>DMDHEU</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Trichoderma</em> sp.</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td><em>Epicoccum</em> sp.</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td><em>Aureobasidium pullulans</em></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Lewia</em> sp.</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td><em>Chaetomium</em> sp.</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td><em>Fusarium</em> sp.</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- - x
Outside weathering of uncoated wood (Xie et al. 2008)

Effect of UV-degradation/weathering of surfaces (photos by P. Evans)
**Change in Klason-Lignin content due to weathering of spruce veneers**
(by P. Evans)

<table>
<thead>
<tr>
<th>Exposure</th>
<th>% Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 days (control)</td>
<td>26.2</td>
</tr>
<tr>
<td>4 h</td>
<td>25.0</td>
</tr>
<tr>
<td>1 day</td>
<td>24.3</td>
</tr>
<tr>
<td>2 days</td>
<td>20.6</td>
</tr>
<tr>
<td>3 days</td>
<td>19.9</td>
</tr>
<tr>
<td>5 days</td>
<td>18.0</td>
</tr>
<tr>
<td>10 days</td>
<td>16.0</td>
</tr>
<tr>
<td>20 days</td>
<td>11.4</td>
</tr>
<tr>
<td>30 days</td>
<td>10.0</td>
</tr>
</tbody>
</table>

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**FTIR Infrared-Spectroscopy** (Xie et al. 2005)

Absorption at 1505 cm\(^{-1}\) representative for lignin
Effect of DMDHEU on performance outside (22 months) (Xie et al. 2008)

- After 144 h artificial weathering (QUV)

Micro veneers after weathering (Xie et al. 2005)
SEM (cross cut) of weathered veneers (Xie et al. 2005)

A
B
C
D
E
F
G
H
I

Untreated
10% DMDHEU
50% DMDHEU

0h
48h
144h

SEM (radial) of weathered veneers (Xie et al. 2005)

Before QUV
After QUV
After QUV

Untreated
30% DMDHEU
Process of bulk wood modification

- Wood
- Treatment
- Curing
- Modified wood

Solution

Room temperature
Temperature > 100 - 140°C

Processes of surface modification

- Easier than bulk because thin layers only...but...
- Application?
  - Batch?
  - Run through?
  - Atmospheric pressure/ vacuum/ over pressure?

- Reaction conditions?
  - Reaction speed?
  - Temperature?
  - Catalysts?
  - Other conditions? (N, UV-curing? Plasma?)

Photos: BASF

HOLZ
Plasma treatment of wood

Improved wetting and spreading

untreated

Plasma treated
**X-ray-Photoelectron-Spectroscopy (XPS)**


**Creation of electronegative groups**


**Improvement of adhesion**

Testing of adhesion forces with peel-off test

**WPC and wood composites: improved surface adhesion of glues and paints**

**Improvement of adhesion**

<table>
<thead>
<tr>
<th>Schälkraft / N</th>
<th>Spanplatte</th>
<th>Faserplatte</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing comparison between untreated and plasma-treated samples.](image)
Processes of surface modification

• Easier than bulk because thin layers only…but...

  • Penetration depth/ treated zone is just some nm-mm!!

  • How to handle raw/ sawn/ semi-planed surfaces?

  • How to treat complex shapes?

Future research

• Basic research on chemicals/ processes to improve wood surfaces
  - UV-stability
  - water related properties
  - hardness/ scratch resistance
  - dimensional stability
  - biological resistance

• Applied research and process development

• Include researchers from wood modification/ chemistry/ wood coatings research
Good forum for discussion: COST FP 1006!

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- Carsten Mai
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- Phil Evans
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