Dimensional stability of wood modified by citric acid using different catalysts

Stabilnost dimenzija drva modificiranoga limunskom kiselinom uz različite katalizatore

Original scientific paper · Izvorni znanstveni rad
Received – prispjelo: 13. 1. 2009.
Accepted – prihvaćeno: 25. 2. 2009.
UDK: 630*812.23; 630*841.61

ABSTRACT • Small wooden samples of fir (Abies alba Mill.) and beech (Fagus sylvatica L.) were chemically modified by citric acid (CA) as non-formaldehyde cross-linking system reagent and cured by convection heating at three different temperature regimes. Two different CA solutions were used, one with NaH₂PO₂ and the other with NaH₂PO₄ as a catalyst. The dimensional stability of the modified wood was determined by the anti-swelling efficiency (ASE) using the water soak/oven dry method. Almost equally large improvement of dimensional stability of wood was attained using NaH₂PO₄ as when NaH₂PO₂ was applied as a catalyst.

Keywords: dimensional stability of wood, beech wood, fir wood, chemical modification, citric acid, NaH₂PO₂, NaH₂PO₄

SAŽETAK • Mali drveni blokovi jelovine i bukovine kemijski su modificirani neformaldehidnim sustavom za umrežavanje – limunskom kiselinom (CA), u trima različitim temperaturnim režimima. Upotrijebljene su dvije otropoline limunskake kiseline. U jednoj je katalizator bio NaH₂PO₂, a u drugoj NaH₂PO₄. Stabilnost dimenzija modificiranog drva određena je tzv. učinkom smanjenja bubrenja (ASE) metodom potapanja u vodi i sušenja do apsolutno suhog stanja. Upotrebom NaH₂PO₄ postignuto je gotovo jednako poboljšanje stabilnosti dimenzija kao i primjenom NaH₂PO₂.

Ključne riječi: stabilnost dimenzija drva, jelovina i bukovina, kemijska modifikacija, limunskuka kiselina, NaH₂PO₂, NaH₂PO₄

1 INTRODUCTION

1 UVOD

Dimensional stability of wood is often an important factor that limits its usage. It is caused by shrinking and swelling of wood. Shrinkage of the cell wall occurs when water molecules escape from between long-chain cellulose and hemicellulose molecules while swelling is a reverse process. There are several options as to how to overcome this issue, and one of the most promising is wood modification. One of the main aims of wood modification was to improve its dimensional stability. Since

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wood consists of approximately 50% of cellulose there are many similarities with cotton textiles, which mainly consist of cellulose - up to 98%. For that reason the agents that have shown good results in textile finishing applications can be applied in chemical modification of wood as well. Textile or wood is usually impregnated with emulsions or solvents of the applied agents. The reaction of chemicals and wood usually occurs at higher temperatures. Cross-linking chemicals reacting with hydroxyl groups reduce the hygroscopicity of wood and the tendency to swell or shrink (Rowell et al., 1988; Rowell 1991; Yasuda and Minato, 1994; Ashaari et al., 1990). One of the reactants often applied is DMDHEU (1.3-dimethylol 4.5-dihidroxy ethylene urea). At higher temperature the N-methylole reactants form ether linkages accelerated with Lewis acid catalyst (MgCl2). Wood modified by DMDHEU showed great improvement in wood stability, while tensile strength was reduced (Militz, 1993; Xie et al., 2005). One of the problems that limit its usage is formaldehyde release at higher temperatures which can be toxic, potentially carcinogen and cause dermatitis (Soljačić and Katović, 1988).

In late 80s the research for non-formaldehyde finishes in cotton textiles focused on polycarboxylic acids (PCA). Welch and Andrews (1988) reported that 1,2,3,4-butanetetracarboxylic acid (BTCA) is an effective cross-linking agent for cotton cellulose. NaH2PO2 proved to be the best catalyst (Bischof Vukusic et al., 2002; Schramm et al., 2002). The mechanism involved is a two-step esterification. In the first step anhydride is formed, while in the second, this cyclic anhydride reacts with hydroxyl groups (Figure 1).

Bischof Vukusic et al. (2006) showed that CA and BTCA crosslink with wood and reduce swelling and shrinking of wood. They also showed that the dimensional stability of wood achieved in this way is comparable to that achieved with DMDHEU. In this study NaH2PO2 was used as a catalyst in CA and BTCA solutions, because it already proved to be the best catalyst in CA modification of cotton cellulose (Bischof Vukusic et al., 2002; Schramm et al., 2002).

This research was aimed at establishing the effect of replacing one costly catalyst (NaH2PO2) with a less expensive one (NaH2PO4) on dimensional stabilisation of wood. The second aim was to shorten the time of curing while achieving comparable anti swelling efficiency (ASE) of wood.

2 MATERIALS AND METHODS

The samples with dimensions 20×20×10 mm (T×L×R) were cut from quarter-sawn air dried boards of fir (Abies alba) and beech wood (Fagus sylvatica). They were signed in succession from one end for different treatments according to Figure 2. There were 10 replicates of samples for each treatment. After air drying and conditioning at 20 °C and 65% relative humidity, the samples to be modified (T, S and Z) were impregnated with the specific CA solution, and control samples (KT and KZ) were impregnated with distilled water. CA solutions were water solutions of 6.9% of CA and 6.5% catalyst. One solution catalyst contained NaH2PO2 and the other NaH2PO4. The impregnation cycle consisted of a 5-minute initial vacuum of 2 kPa. The vacuum vessel was then filled with specific treating solution (control distilled water) and maintained under the same vacuum for 3 hours, followed with an 18-hour soaking at atmospheric pressure. The samples were then drained.
measured and left to air dry at 20 °C and 65% relative humidity to constant mass. One portion of samples (T) was then cured at 140 °C for 5 hours, the second portion (S) at 160 °C for 5 hours, and the third portion (Z and KZ) at 180 °C for 2 hours. Controls marked KT were then simply dried at 100 °C to constant mass.

For lower temperatures of treatment, as shown previously, the influence of temperature itself on the volumetric swelling coefficient is insignificant compared to the influence of the CA modification (Katović et al., 2004). It explains why the same control (KT) was compared to the sample modified by CA at 140 °C (T) and to the one modified by CA at 160 °C (S). However, samples modified by CA at 180 °C (Z) were compared to the water impregnated controls (KZ) that were air dried at 20 °C and 65% relative humidity to constant mass and then exposed to 180 °C for 2 hours.

Dimensional stability was quantified by comparing the total volumetric swelling of treated and control samples. After modification and air drying all samples including controls were oven dried at 100 °C to a constant mass and then vacuum impregnated with distilled water and allowed to soak for 24 hours. The total volumetric swelling (\(V_v\)), reduction in water absorption (\(R\)), and anti-swelling efficiency (\(ASE\)) were calculated by Eq. (1):

\[
\begin{align*}
\alpha_v (\%) &= 100 \left( \frac{V_{\text{max}} - V_{\text{min}}}{V_{\text{min}}} \right); \\
R (\%) &= 100 \left( \frac{w_c - w_t}{w_c} \right); \\
ASE (\%) &= 100 \left( \frac{\alpha_v c - \alpha_v t}{\alpha_v c} \right).
\end{align*}
\]

Where \(V_{\text{max}}\) is the volume, at a moisture content greater than the saturation point of the cellular walls of wood, \(V_{\text{min}}\) is the volume, after drying at 103 °C, \(w_c\) - the moisture content, \(c\) - control, \(t\) - treated.

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Impregnation solution / Otopina za impregnaciju</th>
<th>Curing temperature, °C / time, h</th>
<th>Weight percent gain / Dotika mase, %</th>
<th>(R^1) %</th>
<th>ASE(^2) %</th>
<th>CV(^3) %</th>
<th>Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech wood</td>
<td>6.9% CA + 6.5% NaH(_2)PO(_2)</td>
<td>140/5</td>
<td>9.6</td>
<td>19</td>
<td>39</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160/5</td>
<td>9.7</td>
<td>19</td>
<td>45</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180/2</td>
<td>7.8</td>
<td>15</td>
<td>41</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>6.9% CA + 6.5% NaH(_2)PO(_4)</td>
<td>140/5</td>
<td>6.8</td>
<td>16</td>
<td>43</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160/5</td>
<td>6</td>
<td>16</td>
<td>40</td>
<td>20</td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td>180/2</td>
<td>6</td>
<td>16</td>
<td>40</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Fir wood</td>
<td>6.9% CA + 6.5% NaH(_2)PO(_2)</td>
<td>140/5</td>
<td>17.9</td>
<td>22</td>
<td>57</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160/5</td>
<td>15.1</td>
<td>20</td>
<td>51</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180/2</td>
<td>14.9</td>
<td>19</td>
<td>54</td>
<td>8</td>
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</table>

\(^1\)reduction in water absorption (smanjenje apsorpcije vode); \(^2\)anti-swelling efficiency (učinak smanjenja bubrenja); \(^3\)coefficient of variation (koeficijent varijacije)

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

The improvement in dimensional stabilisation of beech and fir wood modified by citric acid with NaH\(_2\)PO\(_2\) or NaH\(_2\)PO\(_4\) as a catalyst cured at three different regimes are presented in Table 1.

Total volumetric swelling of untreated fir wood was around 16% and total volumetric swelling of beech wood was between 9.6% and 9.7%.
wood was around 20%. The difference can be explained mainly with lower density of fir wood (0.46 g/cm³) compared to beech wood (0.76 g/cm³).

The effect of CA modification on dimensional stabilisation of wood was almost equal using either of catalysts applied. For the same treatment conditions ASE was always greater in modified fir wood (over 50%) than in modified beech wood (around 40%) probably due to higher wood percent gain in fir wood. The ASE improvement in both wood species was about 54% in fir wood and about 40% in beech wood. The ASE achieved at 180 °C for 2 hours. The application of both acid solutions using three different curing regimes revealed more favourable results in ASE improvement compared to DMDHEU application (Bischoff Vukušić et al, 2006; Katović et al, 2004). These results further emphasise possible use of CA as a non-formaldehyde cross-linking system reagent.

Although it was not the object of investigation colour change was observed particularly in samples modified at 180 °C. In accordance with the ASE and weight percent gain values water absorption was also reduced more in modified fir wood (20%) than in modified beech wood (16%), and it does not differ much between modes of modification applied.

The quantity of CA cross-linkages to wood achieved by application of different modification regimes is still not known. Further research of leaching of modified wood is needed to prove the strength of cross linkages to wood. Thus the prevailing effect of CA on dimensional stability of wood would be tested, i.e. it would be determined whether it is cross-linking or bulking.

4 CONCLUSION
4. ZAKLJUČAK

Heating temperature, modification period, and catalyst type and amount are limiting factors for successful chemical wood modification.

With the application of CA as a non-formaldehyde agent using NaH₂PO₄ as a catalyst, the average ASE was about 54% in fir wood and about 40% in beech wood. The ASE improvement in both wood species was similar when NaH₂PO₄ was applied as a catalyst. The price of NaH₂PO₄ is lower compared to NaH₂PO₄.

Comparable ASE results can be achieved either by shortening the curing time and/or by increasing the curing temperature.

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DRVNA INDUSTRIJA 60 (1) 23-26 (2009)