

# Dimensional stability of wood modified by citric acid using different catalysts

## Stabilnost dimenzija drva modificiranoga limunskom kiselinom uz različite katalizatore

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**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  $\text{NaH}_2\text{PO}_2$  and the other with  $\text{NaH}_2\text{PO}_4$  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  $\text{NaH}_2\text{PO}_4$  as when  $\text{NaH}_2\text{PO}_2$  was applied as a catalyst.

**Keywords:** dimensional stability of wood, beech wood, fir wood, chemical modification, citric acid,  $\text{NaH}_2\text{PO}_2$ ,  $\text{NaH}_2\text{PO}_4$

**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 otopine limunske kiseline. U jednoj je katalizator bio  $\text{NaH}_2\text{PO}_2$ , a u drugoj  $\text{NaH}_2\text{PO}_4$ .

Stabilnost dimenzija modificiranog drva određena je tzv. učinkom smanjenja bubrenja (ASE) metodom potapanja u vodi i sušenja do apsolutno suhog stanja. Upotrebom  $\text{NaH}_2\text{PO}_4$  postignuto je gotovo jednako poboljšanje stabilnosti dimenzija kao i primjenom  $\text{NaH}_2\text{PO}_2$ .

**Cljučne riječi:** stabilnost dimenzija drva, jelovina i bukovina, kemijska modifikacija, limunska kiselina,  $\text{NaH}_2\text{PO}_2$ ,  $\text{NaH}_2\text{PO}_4$

### 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-dihydroxy ethylene urea). At higher temperature the N\_methylol reactants form ether linkages accelerated with Lewis acid catalyst ( $MgCl_2$ ). 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.  $NaH_2PO_2$  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  $NaH_2PO_2$  was used as a catalyst in CA and BTCA solutions, because it already proved to be the best catalyst for PCA 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 ( $NaH_2PO_2$ ) with a less expensive one ( $NaH_2PO_4$ ) 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

### 2. MATERIJALI I METODE

The samples with dimensions  $20 \times 20 \times 10$  mm ( $T \times R \times L$ ) were cut from quarter-sawn air dried boards of fir (*Abies alba* Mill.) and beech wood (*Fagus sylvatica* L.). 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  $20^\circ C$  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  $NaH_2PO_2$  and the other  $NaH_2PO_4$ . 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,

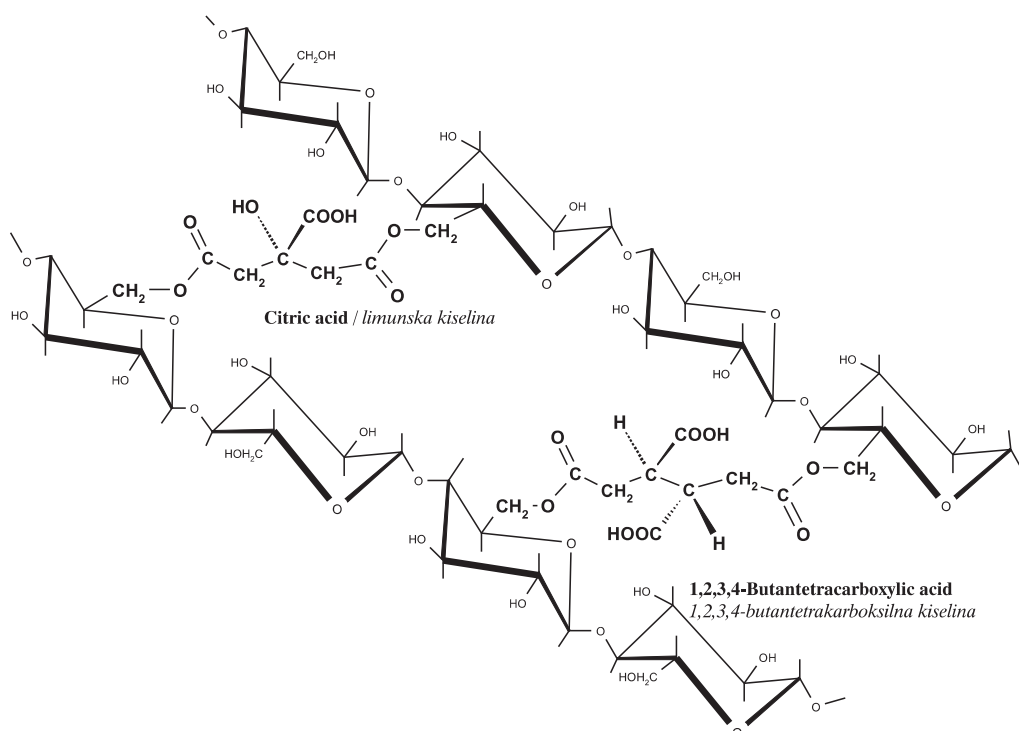


Figure 1 Cross-linking via ester linkages of CA and BTCA with cellulosic chains (Schramm, 1999a).

Slika 1. Umrežavanje CA i BTCA s lancima celuloze preko esterskih veza (Schramm, 1999a)

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 ( $\alpha_v$ ), reduction in water absorption (R), and anti-swelling efficiency (ASE) were calculated by Eq. (1):

$$\alpha_v (\%) = 100 (V_{\max} - V_{\min}) / V_{\min};$$

$$R (\%) = 100 (w_c - w_t) / w_c,$$

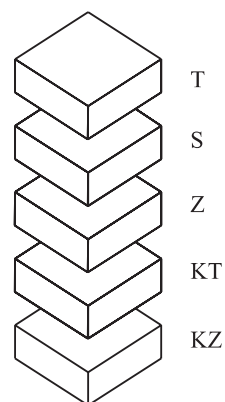
$$ASE (\%) = 100 (\alpha_{v,c} - \alpha_{v,t}) / \alpha_{v,c}$$

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

**Table 1** Dimensional stability of beech and fir wood achieved using two different chemical treatments and three curing regimes  
**Tablica 1.** Stabilnost dimenzija bukovine i jelovine postignuta primjenom dviju različitih otopina za impregnaciju i uz tri različita režima zagrijavanja

Species <i>Vrsta drva</i>	Impregnation solution / Otopina za impregnaciju	Curing temperature, °C / time, h / Temperatura zagrijavanja, °C/ vrijeme, h	Weight percent gain / Dobitak mase, %	R <sup>1</sup> %	ASE <sup>2</sup> %	CV <sup>3</sup> %	Replicates <i>Broj ponavljanja</i>
Beech wood ( <i>Fagus sylvatica</i> L.) <i>bukovina</i>	6.9% CA + 6.5% NaH <sub>2</sub> PO <sub>2</sub>	140/5	9.6	19	39	18	10
		160/5	9.7	19	45	13	10
		180/2	7.8	15	41	10	10
	6.9% CA + 6.5% NaH <sub>2</sub> PO <sub>4</sub>	140/5	7.6	15	43	13	10
		160/5	6.8	16	43	14	10
		180/2	6	16	40	20	10
Fir wood ( <i>Abies alba</i> Mill.) <i>jelovina</i>	6.9% CA + 6.5% NaH <sub>2</sub> PO <sub>2</sub>	140/5	17.9	22	57	13	10
		160/5	15.1	20	51	10	10
		180/2	14.9	19	54	8	10
	6.9% CA + 6.5% NaH <sub>2</sub> PO <sub>4</sub>	140/5	17.1	20	54	19	10
		160/5	14.6	20	56	17	10
		180/2	14.8	20	57	18	10

<sup>1</sup>reduction in water absorption ( *smanjenje apsorpcije vode*); <sup>2</sup>anti-swelling efficiency ( *učinak smanjenja bubrenja*); <sup>3</sup>coefficient of variation ( *koeficijent varijacije*)



**Figure 2** Succession of wood samples in quarter sawn boards  
**Slika 2.** Redosljed uzimanja uzoraka iz četvrtača  
T - samples impregnated by CA solutions and cured at temperature of 140 °C / *uzorci impregnirani otopinama CA i zagrijavani pri temperaturi 140 °C*  
S - samples impregnated by CA solutions and cured at temperature of 160 °C / *uzorci impregnirani otopinama CA i zagrijavani pri temperaturi 160 °C*  
Z - samples impregnated by CA solutions and cured at temperature of 180 °C / *uzorci impregnirani otopinama CA i zagrijavani pri temperaturi 180 °C*  
KT - control samples cured at temperature of 100 °C / *kontrolni uzorci zagrijavani pri temperaturi 100 °C*  
KZ - control samples cured at temperature of 180 °C / *kontrolni uzorci zagrijavani pri temperaturi 180 °C*

### 3 RESULTS AND DISCUSSION

#### 3. REZULTATI I RASPRAVA

The improvement in dimensional stabilisation of beech and fir wood modified by citric acid with NaH<sub>2</sub>PO<sub>2</sub> or NaH<sub>2</sub>PO<sub>4</sub> 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 around 20%. The difference can be explained mainly with lower density of fir wood ( $0.46 \text{ g/cm}^3$ ) compared to beech wood ( $0.76 \text{ g/cm}^3$ ).

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 (Table 1). It is known that ASE increases directly with the amount of chemicals remained in the wood after modification (Rowell *et al*, 1976). The results of a previous experiment (Bischoff Vukušić *et al*, 2006) showed similar ASE values for curing at  $140 \text{ }^\circ\text{C}$ , but in double curing time (10 hours). Curing at  $160 \text{ }^\circ\text{C}$  for 5 hours resulted also with ASE comparable to that achieved at  $140^\circ\text{C}$ , and even to the ASE achieved at  $180 \text{ }^\circ\text{C}$  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 (Bischof Vukušić *et al*, 2006; Katović *et al*, 2004). These results further emphasise possible use of CA as non-formaldehyde cross-linking system reagent.

Although it was not the object of investigation colour change was observed particularly in samples modified at  $180 \text{ }^\circ\text{C}$ . 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 important limiting factors for successful chemical wood modification.

With the application of CA as a non-formaldehyde agent using  $\text{NaH}_2\text{PO}_2$  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  $\text{NaH}_2\text{PO}_4$  was applied as a catalyst. The price of  $\text{NaH}_2\text{PO}_4$  is lower compared to  $\text{NaH}_2\text{PO}_2$ .

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

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