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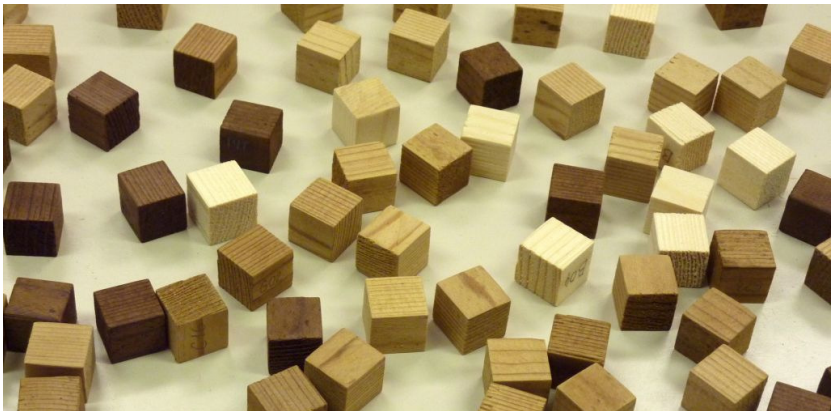

The Sixth European Conference on Wood Modification

PROCEEDINGS

Ljubljana, Slovenia
17-18 September 2012

University of Ljubljana
Biotechnical Faculty
Department of Wood Science and Technology

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Bringing new functions to wood through surface modification

Edited by D. Jones, H. Militz, M. Petrič, F. Pohleven, M. Humar and M. Pavlič

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Optimisation of Modification of Beech Wood by Citric Acid

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Keywords: anti swelling efficiency (ASE), biological durability, compression strength (CS), leachability coefficient of gained mass (LCM), mass loss caused by leaching (MLL), weight percentage gain (WPG)

ABSTRACT

Different concentration of chemicals in solution, temperature and curing period were used for common beech wood modification with Citric acid (CA). In distilled water (at 60 °C) extracted specimens were impregnated with citric acid (CA) water solutions of different concentrations with phosphate catalyst. After impregnation, specimens were air-dried and then cured at elevated temperatures using different regimes. The effects of different modification regimes were assessed through the values of weight percentage gain (WPG), anti swelling efficiency (ASE), mass loss caused by leaching (MLL) and leachability coefficient of gained mass (LCM). Optimal combination of modification parameters was chosen for each of mentioned properties and then only one optimal combination of modification parameters was selected. Compression strength parallel to the grain and biological durability of beech wood after modification by optimal regime were researched and data presented.

INTRODUCTION

Chemical modification implicates etherification, esterification or acetylation between some chemical and OH groups of cellulose, hemicelluloses and lignin. Important parameters for successful modification by some chemical are chemical concentration in dilution, temperature and processing time, type of catalyst and wood species.

One of the most researched wood modifying chemical is DMDHEU (1,3-dimethylol-4,5-dihidroxyethylene urea). Wood modified by DMDHEU has increased dimensional stability for up to 50 – 60 %. Pine, Asian cedar and beech wood modified by DMDHEU have increased durability against several *Basidiomycetes*, although this modification does not comply with many available preservatives). Lignocellulosic materials modified by DMDHEU have a problem of formaldehyde release caused by the hydrolytic destruction of N-methylol groups at higher modification temperatures. Because of the formaldehyde problem, scientists are introducing new non-formaldehyde chemicals.

One non-formaldehyde chemical is cyclic alcohol furfural which can be easily produced from agricultural biomass. Wood furfurylation can result with huge WPG. Furfurylated wood has very good biological durability and dimensional stability. On one hand furfural, as a cyclic chemical is capable of modifying lignin while many other wood

modifying chemicals mainly modify holocellulose. On the other hand the main problem of this chemical is that it is susceptible to self-polymerisation.

Although wood acetylation has been developed to the large scale production, there are still lots of problems with this process.

Other non-formaldehyde chemicals are polycarboxylic acids (PCA). By application of three-carboxylic acids, first anhydride arises from two neighbouring carboxyl groups for first bond creation, and the second anhydride arise from other two neighbouring carboxyl groups. This possibility of bonding the second anhydride with hydroxyl groups of wood ensures cross-linking, bond stability and durability (Bischof Vukušić *et al*. 2006). Several persons (Katovic *et al.* 2004, Bischof Vukusic *et al.* 2006, Hasan *et al.* 2006, 2007, Despot *et al.* 2008 and Šefc *et al.* 2009, 2012) have esterified a range of wood species with citric acid (CA) and gained very good dimensional stability and biological durability, while micro tensile strength decreased for 30 %, and compression strength parallel to the grain stayed unchanged.

The aim of this article is to show the optimisation process of beech wood modification with citric acid (CA) and to present selected wood properties after modification by optimal regime.

MATERIALS AND METHODS

Home-grown beech wood (*Fagus sylvatica* L.) was used for this research. Wood lattices close to bark were sawn from the air-dried and afterwards kiln-dried radial planks. All specimens for modification optimisation were cut out of selected lattices (R×T×L: 20×20×10 ± 0.1 mm), successively axially selected, marked and prepared according to DIN 52 184 (1979) (Table 1). For biological durability and compression strength parallel to the grain tests specimens were prepared according to HRN EN 113 (1996) (R×T×L: 15×25×50 ± 0.1 mm) and according to HRN D. A1.045 (R×T×L: 20×20×40 ± 0.1 mm; Table 2).

Chemicals, solutions, modification and leaching procedures

Water solution of different concentrations of CA and catalyst were prepared for modification. At 60 °C extracted specimens were full-cell impregnated with prepared solutions (Despot *et al*., 2008). Afterwards specimens were slowly air dried and oven dried till constant mass and then thermocondensed at different temperatures for different times (Table 1).

Specimens prepared for extraction and leaching were conditioned at standard climate, and then leached (full-cell impregnated with distilled water and heated in oven at 60 °C for 48 hours). Every 12 hours the water was changed. Then the specimens were again air-dried and oven-dried to constant mass. After modification and after first and second cycle of leaching weight percentage gain (WPG), anti swelling efficiency (ASE), mass loss caused by leaching (MLL), leachability coefficient of gained mass (LCM) were measured in order to define optimal modification parameters (Table 1).

After choosing the optimal modification regime, groups of specimens were modified according to optimal regime and compression strength parallel to the grain (CS) and

biological durability against brown-rot fungus *Poria placenta* were researched (Table 2).

Table 1: Combinations of chemicals concentrations, temperature and time of thermocondensation, number of specimens

Modification Treatment Code	Chemicals concentrations [%]		Number of specimens	Thermocondensation	
	CA	Catalyst		Temperature [°C]	Time [h]
1A	7.0	5.0	30	140	10
2A	7.0	6.5	30		
3A	7.0	8.0	30		
4A	10.5	7.5	30		
5A	10.5	9.75	30		
6A	10.5	12.0	30		
1B	7.0	5.0	30	160	10
2B	7.0	6.5	30		
3B	7.0	8.0	30		
4B	10.5	7.5	30		
5B	10.5	9.75	30		
6B	10.5	12.0	30		
1C	7.0	5.0	30	180	2.5
2C	7.0	6.5	30		
3C	7.0	8.0	30		
4C	10.5	7.5	30		
5C	10.5	9.75	30		
6C	10.5	12.0	30		

Table 2: Type of test, modification paramethers and number of specimens

Type of test	Modification Treatment Code	Modification paramethers				Number of specimens
		Chemicals concentration [%]		Thermocondensation		
		CA	Catalyst	Temperature [°C]	Time [h]	
Compression strength	MCA	10.5	7.5	140	10	30
	AHT	-	-	140	10	30
	Control	-	-	-	-	30
Biological durability	MCA	10.5	7.5	140	10	14
	AHT	-	-	140	10	14
	Control	-	-	-	-	28

WPG, ASE, MLL and LCM determination

Weight percentage gain of modified specimens (WPG) was calculated as a ratio of difference of oven-dried mass after modification (m_2) and oven-dried mass before modification (m_1) and m_1 (Eqn. 1).

$$WPG = \frac{m_2 - m_1}{m_1} \times 100[\%] \quad (1)$$

Dimensional stability of non-leached and leached specimens was quantified by comparing the volumetric swelling coefficients (α_V; Eqn. 2) of treated and control specimens. After modification and air-drying all specimens including controls were oven dried at 103 °C to a constant mass and then full-cell impregnated with distilled

water following atmospheric soak for 24 hours. The volumetric anti-swelling efficiency (ASE) could also be calculated (Eqn. 3):

$$\alpha_V = \frac{(V_S - V_O)}{V_O} * 100[\%] \quad (2)$$

$$ASE = \frac{(\alpha_{VC} - \alpha_{VT})}{\alpha_{VC}} * 100[\%] \quad (3)$$

where: V is the volume, indexes: S represents water-saturated, O oven dried at 103 °C, C control, T treated (modified).

Mass loss of specimens caused by leaching (*MLL*) was calculated by dividing the difference of oven-dried mass of specimens after modification-before leaching (m_2) and oven dry mass of specimens after leaching (m_3) and mass of specimens before leaching (m_2) (Eqn. 4).

$$MLL = \frac{m_2 - m_3}{m_2} * 100[\%] \quad (4)$$

Leachability coefficient of mass gained by modification (LCM) was calculated by dividing the difference of oven-dried mass of specimens after modification-before leaching (m_2) and oven dry mass of specimens after leaching (m_3) and difference of oven dry mass of specimens after modification-before leaching (m_2) and starting mass (m_1) (Eqn. 5).

$$LCM = \frac{m_2 - m_3}{m_2 - m_1} \quad (5)$$

Compression strength parallel to the grain and Biological durability tests

Compression strength (CS) measurements parallel to the grain were performed according to HRN D. A1.045 using a Wolpert universal machine for the determination of mechanical properties. Before CS testing specimens were conditioned in standard climate for 2 weeks.

Determination of biological durability was done according to EN 113 (1996). Brown-rot, fungus *Poria placenta* (Fries) Coke sensu J.Erikson was chosen. Mass loss of specimens caused by fungal decay (MLF) was calculated by dividing the difference of oven-dried mass of specimens after decay (m_4) and starting mass (m_2) with starting mass (Eqn. 6).

$$MLF = \frac{m_2 - m_4}{m_2} * 100[\%] \quad (6)$$

This percentage of mass loss MLF [%] is the unit which shows the durability – as the MLF is smaller as the wood is more-durable.

RESULTS AND DISCUSSION

Either by increasing the concentration of citric acid or a catalyst, WPG is constantly increasing at each thermocondensation temperature. WPG of specimens cured at 140 °C is significantly higher than of those cured at 160 °C while specimens cured at 180 °C had the smallest WPG for all chemicals concentrations. This can be explained by partially catalyst evaporation and partially evaporation of thermally destroyed wooden components during thermocondensation. Combinations 1, 2 and 3 represent

concentration of CA of 7.0 % and combinations 4, 5 and 6 represent concentration of CA of 10.5 %. It is visible that the greatest increase in WPG occurs when greater concentration of CA is introduced than when greater catalyst concentration is introduced. Therefore, for all temperatures, as the optimal combination of chemicals concentrations, combination 4 was selected. Since specimens cured at 140 °C had the greatest WPG, combination 4A was selected as the best combination for WPG property (Figure 1).

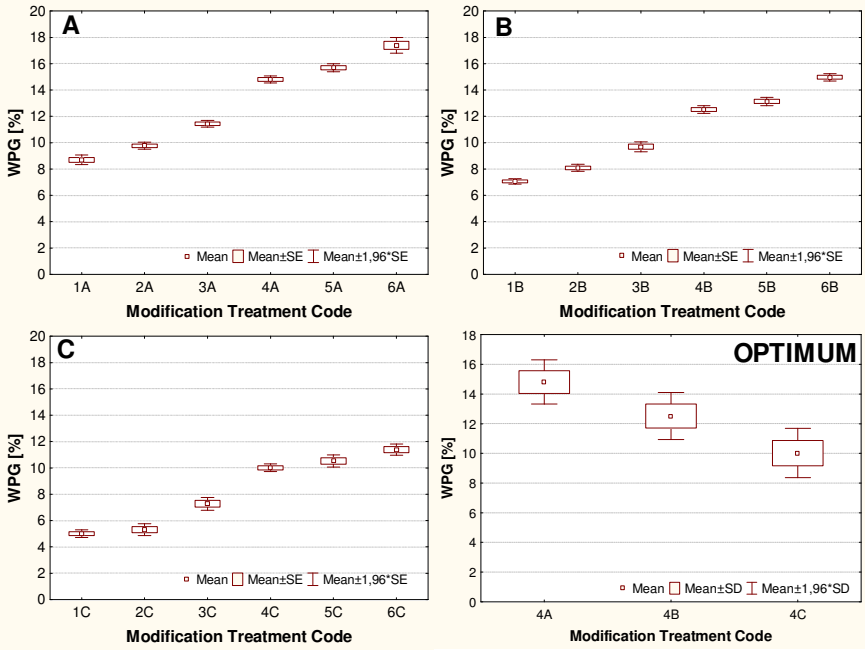

Figure 1: Weight percentage gain (WPG) of specimens thermo-condensed at: A= 140 °C, 10h; B= 160 °C, 10 h and C= 180 °C, 2.5 h

It was expected that higher temperature would lead to smaller MLL since this regularity is present at WPG. The greatest MLL had specimens thermocondensed at 140 °C for most chemicals combinations, while the smallest MLL had specimens thermocondensed at 160 °C. When comparing MLL of first and second leaching cycle it is visible that the smallest difference in MLL between first and second leaching cycle had specimens thermocondensed at 180 °C. Furthermore it was expected that greater concentrations of catalyst ensures greater amount of CA bonded to wood cell wall compounds, but the results of MLL stand in contrast to that. That could be explained with greater density of catalyst than of CA and at catalyst concentration increase MLL also increased at all thermocondensation temperatures. All mentioned led to the conclusion that combination 1 led to the smallest MLL the same as the temperature of 160 °C. For MLL, the optimal combination of modification parameters was 1B (Figure 2).

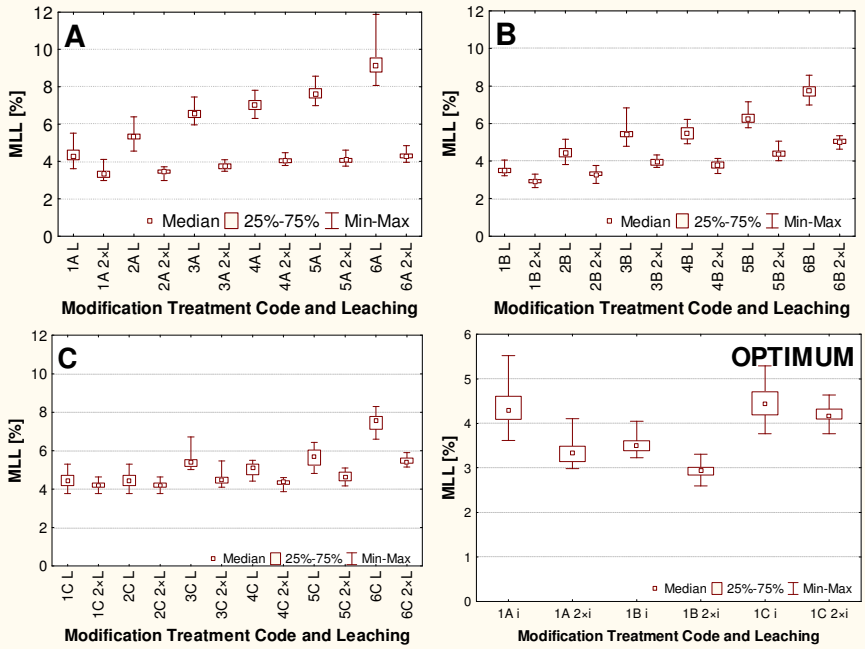

Figure 2: Mass loss caused by leaching (MLL) of specimens thermo-condensed at: A= 140 °C, 10 h; B= 160 °C, 10 h; C= 180 °C, 2.5 h, after first and second leaching

For each CA concentration, LCM is almost constant with very slight increase as the concentration of catalyst increased. That is a pure proof that the catalyst after thermocondensation was leached out of the specimens. Greater concentration of CA resulted in smaller LCM which confirms that greater concentration of CA resulted in greater esterification. Therefore the combination 4 of chemicals concentrations is optimal for LCM. No significant difference in LCM between specimens thermocondensed at 140 and 160 °C was determined for almost all combinations of chemicals concentrations. Thermocondensation temperature of 180 °C resulted in the greatest LCM which is logical due to thermal degradation of thermally unstable wood cell wall compounds which were leached out of the specimens. Modification parameters combination 4A resulted in the smallest LCM after both cycles of leaching and it is optimal for CLM (Figure 3).

Dimensional stability of beech wood modified by CA was improved for 35 to 45 %. ASE significantly decreased after leaching. Statistically the greatest ASE had specimens modified at 140 °C and the smallest ASE had specimens modified at 180 °C. At increasing the concentration of CA, ASE significantly increased while at increasing concentration of catalyst, ASE significantly decreased for all thermocondensation temperatures. According to all mentioned optimal regime for ASE was 4A (Figure 4).

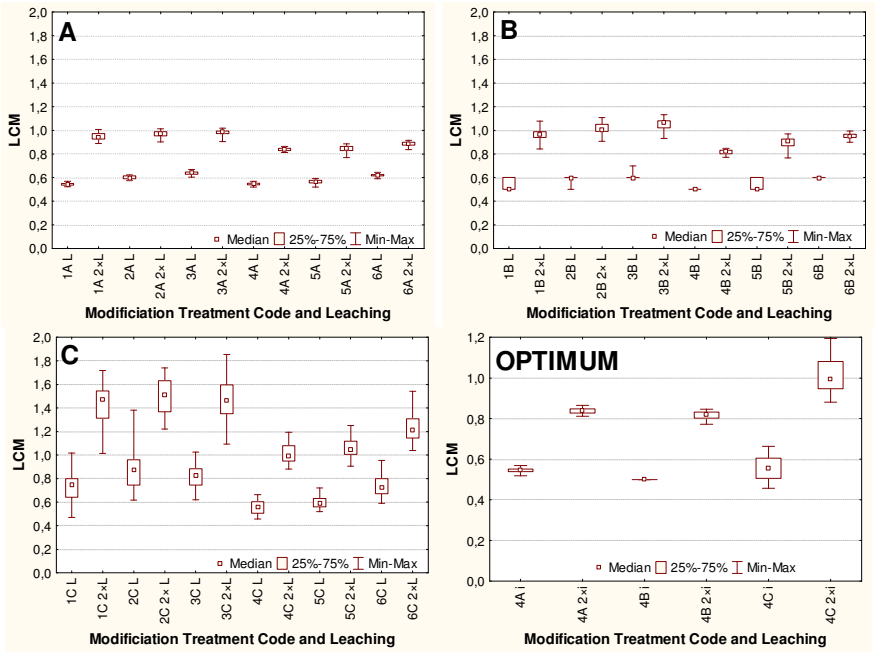

Figure 3: Coefficient of leachability of beech-wood specimens thermo-condensed at: A= 140 °C, 10 h; B= 160 °C, 10 h; C= 180 °C, 2.5 h, after first and second leaching

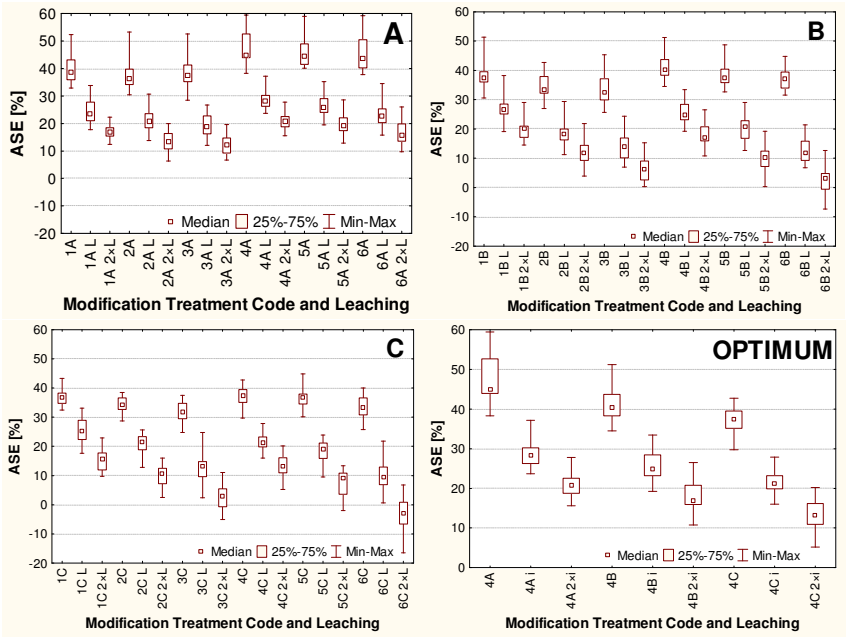

Figure 4: Anti-swelling efficiency (ASE) of specimens modified at: A= 140 °C, 10h; B= 160 °C, 10h; C= 180 °C, 2.5h, before and after first and second leaching

After summarising all optimal combinations of modification parameters it can be concluded that between investigated parameters optimal combination is 4A (Table 3).

CS due to modification by CA very slight and insignificant increased. This slight improvement could be explained by CA bonding to cellulose chains forming stronger cell walls. Air heat treated (AHT) specimens had the same CS as control ones. (Figure 5 A). MLF of specimens modified by CA (MCA) was significantly the smallest while pure air heat treatment (AHT) had no influence on MLF caused by tested fungus. Beech wood modification by CA significantly increased biological durability against the

fungus *Poria placenta* for more than eight times in comparison to unmodified controls (Figure 5 B).

Table 3: Summary of optimal modification parameter combination for researched properties

Researched property of modified wood	Optimal Parameter combination
WPG	4A
MLL	1B
LCM	4A/4B*
ASE	4A
OPTIMAL COMBINATION	4A

*4A was chosen due to lover temperature (140 °C instead of 160 °C)

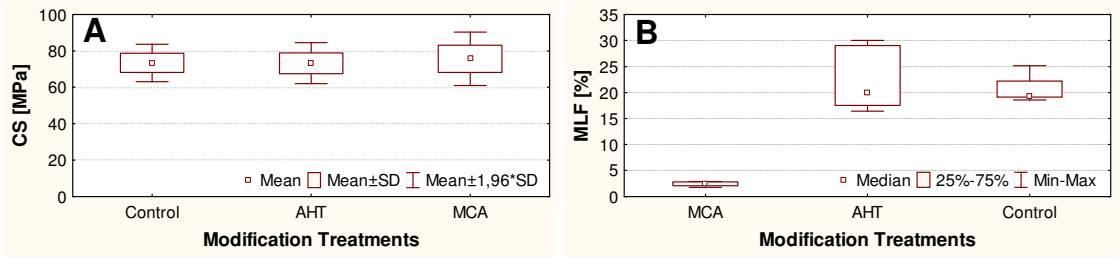

Figure 5: Selected properties of beech wood after modification by optimal regime: A – Compression strength(CS) parallel to the grain, B – Mass loss (MLF) caused by fungus Poria placena

CONCLUSIONS

On the basis of weight percentage gain, mass loss caused by leaching, leachability coefficient of gained mass and anti swelling efficiency optimal regime for beech wood modification by citric acid was chosen (c(CA)=10.5 %, c(catalyst)=7,5 %, t=140 °C, τ=10 hours). Although the optimum regime of the wood modification by CA was assessed, it is necessary to continue the examination of other favourable parameters combinations for measured properties regardless on the regime.

Results showed increased durability of modified wood to be 8.3 times greater than non-modified, while thermal treatment itself did not give significant durability improvement. Average compression strength parallel to the grain of wood was retained after modification. The results indicated that wood modified by citric acid may be considered for the purposes where compression strength properties are equally important as improved durability and dimensional stability of wood.

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