Radovan Despot, Marin Hasan, Matija Jug, Bogoslav Šefc[1]

Biological durability of wood modified by citric acid

Biološka otpornost drva modificiranoga limunskom kiselinom

Original scientific paper · Izvorni znanstveni rad
Received – prispjelo: 22. 2. 2008.
Accepted – prihvaćeno: 5. 6. 2008.
*UDK: 630*841.112; 630*841.6*

ABSTRACT • *This paper presents the results of measurement of durability of beech wood (Fagus sylvatica) modified by Citric Acid (CA) against brown rot fungus Poria placenta according to EN 113. Modification was performed by impregnation with 7.0% CA and 6.5% sodium-hypophosphite (SHP) water solution and 10-hour curing at 140 °C. The influence of thermal treatment on durability was also researched. Weight percentage gain (WPG) caused by modification, moisture content (MC) and mass loss of wood (dm) after fungal nutrition were measured. WPG of modified beech wood was 6.1% and that of thermally treated wood was -0.3%. The results showed increased durability of modified wood to be 8.3 times greater than non-modified, while thermal treatment did not give significant durability improvement. These results indicate modification by CA as a promising alternative, but further research on optimisation of modification parameters is needed to achieve improvement of wood properties.*

Key words: *chemical modification of wood, esterification, citric acid, biological durability, Poria placenta, beech wood*

SAŽETAK • *U radu su prezentirani rezultati biološke otpornosti limunskom kiselinom modificiranog drva obične bukve (Fagus sylvatica) protiv gljive Poria placenta, a prema EN 113. Modifikacija je izvedena termokondenziranjem drvenih uzoraka impregniranih vodenom otopinom 7-postotne limunske kiseline (CA) i 6,5-postotnog natrij-hipofosfita (SHP) pri 140 °C. Tijekom prvih pet minuta impregnacije uzorci su vakuumirani, a potom je u operacijski cilindar puštena otopina. Za cijelo vrijeme impregnacije primijenjen je apsolutni tlak od 2 kPa pri temperaturi od 20 °C. Navedeni uvjeti održavani su tri sata, nakon čega je slijedilo potapanje uzoraka u trajanju 18 sati pri atmosferskom tlaku. Uzorci su potom prosušeni u standardnoj klimi tijekom 48 sati, a zatim zagrijavani (termokondenzirani) u sušioniku na temperaturi 140 °C deset sati. Dodatno je kontroliran i sam utjecaj temperature na biološku otpornost. Mjereno je povećanje mase (WPG) zbog modifikacije, sadržaj vode (MC) i gubitak mase (dm) nakon djelovanja gljive. WPG bukovine modificirane limunskom kiselinom iznosio je 6,1%, a samo zagrijanih uzoraka -0,3%. Rezultati su pokazali čak 8,3 puta veću biološku otpornost bukovine modificirane limunskom kiselinom dok samo zagrijavanje nije imalo statistički značajan utjecaj na biološku otpornost. Nakon djelovanja gljiva uzorci modificirani limunskom kiselinom imali su najveći, a kontrolni uzorci najmanji sadržaj vode. Rezultati pokazuju da je modifikacija limunskom kiselinom obećavajuća alternativna metoda u zaštiti drva, no potrebna su daljnja istraživanja optimiranja koncentracija CA i SHP-a u vodenoj otopini, vremena i temperature termokondenzacije radi poboljšavanja željenih svojstava drva.*

Ključne riječi: *kemijska modifikacija drva, esterifikacija, limunska kiselina, biološka otpornost, Poria placenta, obična bukva*

[1] Autori su, redom, izvanredni profesor, znanstveni novak, znanstveni novak i viši asistent Drvnotehnološkog odsjeka Šumarskog fakulteta Sveučilišta u Zagrebu, Hrvatska.
[1] The authors are associated professor, young scientist, young scientist and senior assistant at Wood Technology Department, Faculty of Forestry, University of Zagreb, Croatia.

1 INTRODUCTION
1. UVOD

Research on wood modification mostly deals with the improvement of wood properties i.e. elimination or reduction of limitations of wood as a raw material. Modified wood is expected to be more dimensionally stable, more durable against bluestain and rot fungi, and more resistant to UV radiation in comparison to unmodified wood. Mechanical properties should be unchanged. Ecological and economic feasibility of modification processes and chemicals must also be provided.

Thermal modification is a process where the wood cell wall polymers (especially hemicellulose, less lignin) are destructed to the radicals that repolymerise with OH groups of wood cell wall compounds only by heating. It is mostly conducted in operating cylinder at the temperature between 150 and 260 °C without the presence of oxygen (Rapp and Sailer, 2001; Rep and Pohleven, 2001; Yildiz *et al.*, 2003). Type of heating medium, period of heating, final temperature and wood species are the most important parameters of modification processes (Mitchell, 1988). Dimensional stability and durability against rot-fungi are improved with this type of modification, but some mechanical properties are degraded (Bengtsson *et al.*, 2002; Ladner and Halmschlager, 2002; Hasan and Despot, 2003; Britschke and Rapp, 2004). Thermal modification in vegetable oil has shown to be much better than modification in air atmosphere. In-air-atmosphere thermally-modified wood did not increase biological durability in comparison to non-modified wood. Increased retention of oil in modified wood increases its durability. Durability against moulds and bluestain increases at enhancing modification degree. Paucity of bluestain and mould's mycelium on the surface of modified wood ensures reduced discoloration. The amount of simple carbohydrates decreases and chemical structure of parenchyma cells contents changes during modification so fungal enzymes cannot recognise new structure and became less effective (Feist and Sell, 1987).

Chemical modification implies etherification, esterification or acetylation between some chemical and OH groups of wood. The 1.3 dimetilol 4.5 dihidroksietilen urea (DMDHEU) combined with an adequate catalyst reacts with OH groups of cellulose forming cross-linking between cellulose chains. Important parameters for successful modification by these chemical are temperature, processing time, type of catalyst and wood species. Dimensional stability of wood modified by DMDHEU is increased by 50 to 60% (Militz, 1993; Yusuf *et al.*, 1995). Increased durability is recorded in Pine wood, Asian cedar and Beech wood modified by DMDHEU against *Coniophora puteana*, *Tyromyces palustis* i *Coriolus versicolor* and some other rot fungi. Increased durability is also retained after one circle of leaching (Yusuf *et al.*, 1995). Militz (1993) reported that DMDHEU modification does not comply with other modern preservatives.

Modification by DMDHEU has a problem with releasing formaldehyde from N-methylol bonds by hydrolytic destruction at higher modification temperatures. Because of this problem, scientists are introducing new non-formaldehyde chemicals.

One group of such chemicals is polycarboxylic acids (PCA). The possibility of bonding PCA anhydride with OH groups of lignocelluloses ensures cross-link reaction, good bond stability and durability (Fang *et al.*, 1999). Esterification is a cross-linking reaction between cellulose and PCA. Citric Acid (CA) is widely spread in the nature and it completely satisfies strict ecological and economic requirements.

Šefc *et al.* (2006) have modified fir wood and beech wood by CA. Wood modified by CA and cured by temperature or by microwaves showed improved dimensional stability. Improved dimensional stability significantly decreased after leaching. Beech wood modified by DMDHEU showed similar improvement of dimensional stability as the one modified by CA. Fir and beech wood modified by CA had unchanged compression strength parallel to the grain while micro-tensile strength decreased by 30%. Wood modification by DMDHEU resulted in a 50 to 70% decrease of micro-tensile strength (Šefc, 2006; Xiel *et al.*, 2007). Hasan *et al.* (2006, 2007) reported multiple increasing of biological durability of pine sapwood modified by CA against some rot fungi.

Both of these chemical modifications have the same goal – to improve dimensional stability and biological durability with unchanged mechanical properties. Some studies on the influence of CA modification on physical and mechanical properties of wood have been already done. This paper presents some preliminary results on the weight percentage gain (*WPG*) and improvement of biological durability in lab conditions of beech wood modified by CA.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Beech wood (*Fagus sylvatica* L.) was used for this research. Beech is commercially the most important wood species in Croatia and due to its very low-durability it is used as a reference wood species in European norms.

Lattices were sawn from wood close to bark of one air-dried and afterwards kiln-dried beech board. All specimens were cut, selected and marked axially and successively according to EN 113 (1996) (R×T×L = 25×15×50 [±0.2 mm]) (Tab. 1).

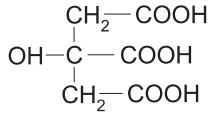
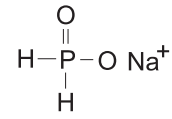
2.1 Chemicals, solutions and modification parameters
2.1. Sredstva, otopine i parametri modifikacije

7.0% water solution of CA with 6.5% sodium-hypophosphite monohydrate (SHP) as a catalyst was prepared for modification. Structural formulas of chemicals used in modification are presented in Table 2. Concentration of CA and SHP were optimised for cellulose modification in textile (Katović *et al.*, 2000)

Table 1 Type of modification, fungus species and number of specimens
Tablica 1. Vrsta modifikacije, vrsta gljive i broj uzoraka

Fungus species *Vrsta gljive*	**Modification type** *Vrsta modifikacije*	**No. of specimens** *Broj uzoraka*
Poria placenta (Fries) Coke sensu J. Erikson	modification by CA (MCA)	7
	Control 1	7
	Air Heat Treatment (AHT)	7
	Control 2	7

Table 2 Structural formulas of chemicals used for modification
Tablica 2. Strukturne formule sredstava upotrijebljenih za modifikaciju

Citric Acid (CA) *Limunska kiselina*	**Sodyum HypoPhosphite monohydrate (SHP)** *Natrij-hipofosfit monohidrat*
	

and applied in this research. Group of specimens was only air heat treated at the thermo-condensation temperature (ATM) and used as the control of possible influence of temperature on biological durability.

2.2 Wood impregnation and modification procedures
2.2. Postupak impregnacije i modifikacije drva

Oven-dried samples (103 ± 2 °C, up to constant mass) were weighed on lab balance (0.1 mg), conditioned at standard climate (20 °C and 65% relative humidity) up to moisture content of 12%. The impregnation cycle consisted of a 5-min initial vacuum of 2 kPa. The vacuum vessel was then filled with the CA+SHP solution and a vacuum of 2 kPa was maintained for 3 h, followed by 18 hours soaking at atmospheric pressure.

MCA and AHT specimens were air-dried at standard climate for 48 hours and afterwards cured at 140 °C for 10 hours in an oven.

2.3 WPG, MC and durability determination
2.3. Određivanje *WPG*, MC i biološke otpornosti drva

WPG of modified specimens 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 (1).

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

Determination of biological durability of CA modified wood was done according to EN 113 (1996). Brown rot fungus *Poria placenta* (Fries) Coke sensu J. Erikson was chosen. "Potato dextroze agar (PDA)" by OXOID was used as a nutrient medium.

Moisture content (MC) of wood after fungal degradation was calculated as a ratio of difference of wet mass after exposure to fungi (m_3) and oven-dried mass after exposure to fungi (m_4) and m_4 (2).

$$MC = \frac{m_3 - m_4}{m_4} \cdot 100\ [\%] \qquad (2)$$

Mass loss of samples caused by fungal nutrition (dm) was calculated by dividing the difference of oven-dried mass of specimens after fungal nutrition (m_4) and starting mass (m_2) with starting mass (3).

$$\mathrm{d}m = \frac{m_2 - m_4}{m_2} \cdot 100\ [\%] \qquad (3)$$

This mass loss percentage dm [%] is the unit that shows the durability – as the dm decreases with the increase of wood durability.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

It is interesting to observe *WPG* of different wood species after the same modification procedures with CA. After the same modification procedure, fir-wood had the highest *WPG*, while the beech-wood had the lowest *WPG*. These data suggest that *WPG* depends on wood density. Air heat treatment (AHT) resulted in almost the same average mass loss of pine and beech wood (Tab. 3).

On one hand, according to Rapp and Sailer (2001), the increase of wood mass loss caused by oil heat treatment (OHT) results in the increase of biological durability of OHT wood. On the other hand, (Rapp and Sailer (2001) and Hasan *et al.* (2006) reported no difference in biological durability between the AHT wood and non-modified controls.

Results of this study confirm no significant difference in biological durability between AHT and control specimens. These results indicate that statistically high significant difference in biological durability of MCA specimens is exclusively the result of cross linking of CA on OH groups of pine sapwood components (Fig. 1).

Table 3 *WPG* of different wood species after modification
Tablica 3. *WPG* različitih vrsta drva nakon modifikacije

Modification type *Vrsta modifikacije*	**Mean value of *WPG*** *Srednja vrijednost WPG-a, %*	**Source** *Izvor*
MCA* Fir	17.9	Šefc (2006)
MCA* Pine	12.43	Hasan *et al.* (2006, 2007)
AHT** Pine	-0.30	
MCA* Beech	6.11	
AHT** Beech	-0.33	

* MCA = 7% CA + 6.5% SHP, 140 °C, 10 hours
** AHT = 140 °C, 10 hours

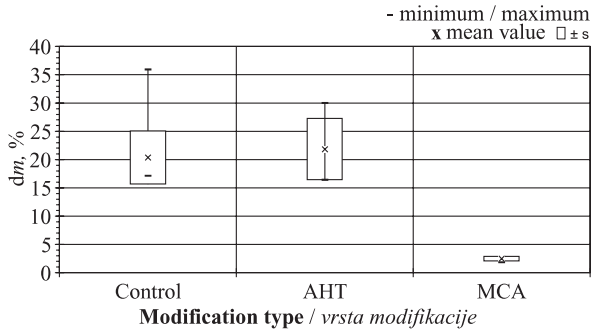


Figure 1 Mass loss (d*m*) of differently modified specimens after 16 weeks of exposure to *Poria placenta* (*n* = 14 for controls, *n* = 7 for AHT and MCA).
Slika 1. Gubitak mase (d*m*) različito modificiranih i kontrolnih uzoraka nakon 16 tjedana izlaganja gljivi *Poria placenta* (*n* = 14 za kontrolne, *n* = 7 za AHT i MCA)

Significant difference in MC between control, AHT and MCA specimens was determined. MC of MCA specimens was the highest. MC of AHT specimens was higher than controls but lower than MCA specimens. Due to influence of thermo-condensation temperature of 140°C thermo unstable hemicelluloses depolymerised. The concentration of simpler sugars increased and the fungus needed more water to attenuate incurred simpler sugars (Fig. 2).

While CA modification of pine sapwood resulted in *WPG* of 12.4% and 5.3 times greater biological durability against some rot fungus (Hasan *et al.*, 2006), MCA beech wood had 8.3 times greater biological durability regardless of the fact that *WPG* of beech wood was twice smaller than *WPG* of pine wood.

Durability against brown rot fungi of beech wood modified with CA and cured at only 140 °C seemed to be better than the OHT pine heated at the temperatures between 180 and 200 °C (Fig. 3).

At increasing *WPG* during chemical modification, biological durability also increases. It is to be expected that *WPG* will increase by optimising parameters of wood modification by CA. In this way biological durability of wood modified by CA could be even more improved.

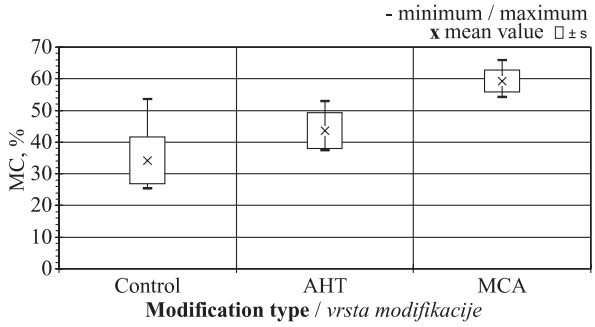


Figure 2 Moisture content (MC) of differently modified and control specimens after 16 weeks of exposure to *Poria placenta* (*n* = 14 for controls, *n* = 7 for AHT and MCA).
Slika 2. Sadržaj vode u drvu (MC) različito modificiranih i kontrolnih uzoraka nakon 16 tjedana izlaganja gljivi *Poria placenta* (*n* = 14 za kontrolne, *n* = 7 za AHT i MCA)

Figure 3 Appearance of specimens after 16 weeks of exposure to fungus *Poria placenta* (MCA = beech wood modified by CA, Control = unmodified beech wood).
Slika 3. Izgled uzoraka nakon 16 tjedana izlaganja gljivi *Poria placenta* (MCA - bukovina modificirana limunskom kiselinom, Control - nemodificirana kontrola)

4 CONCLUSION
4. ZAKLJUČAK

Biological durability of beech wood modified by citric acid (CA) is significantly increased. Weight percentage gain (*WPG*) of 6.1% resulted in an eight time increase of biological durability against brown rot fungus *Poria placenta* in comparison to unmodified controls.

Combining the concentrations of citric acid and catalyst in water solution and by optimisation of impregnation procedure, temperature and time of thermo-condensation it would be possible to optimise the desired wood properties.

5 REFERENCES
5. LITERATURA

1. Bengtsson, C.; Jermer, J.; Brem, F. 2002: Bending strength of heat-treated spruce and pine timber. The International Research Group on Wood Preservation, Document No.: IRG/WP 02/40242.

2. Bischof Vukušić, S.; Katović, D.; Schramm, C.; Trajković, J.; Šefc, B. 2006: Polycarboxylic acids as non-formaldehyde anti-swelling agents for wood. Holzforschung 60(4):439-444.
3. Britschke, C.; Rapp, A.O. 2004: Investigation of the suitability of silver fir (*Abies alba* Mill.) for thermal modification. The International Research Group on Wood Preservation, Document No.: IRG/WP 03/10457.
4. Fang, G.Z.; Li, J.; Liu, Y.X. 1999: Effect of pH value on cross linking reaction between wood and polycarboxilic acid. Chemistry and Industry of Forest Products, 19(1):28-32. abstract from TREECD 1973-1999/10.
5. Feist, W. C.; Sell, J. 1987: Weathering Behavior of Dimensionally Stabilized Wood Treated by Heating under Pressure of Nitrogen Gas. Wood and Fiber Science 19(2):183-195.
6. Hasan, M.; Despot, R. 2003: *Thermal modified wood – nowadays material.* Les-*Wood* 55(3):342-345. [*in Croatian language*].
7. Hasan, M.; Despot, R.; Trajković, J.; Šefc, B. 2006: Role of modification processes at increasing biological durability of wood. International conference European Union – Challenges and perspectives for the wood-processing industry, Zagreb, October 13th, Proceedings, pp. 153-158.
8. Hasan, M.; Despot, R.; Katović, D.; Bischof Vukušić, S.; Bogner, A.; Jambreković, V. 2007: Citric Acid – Promising Agent for Increased Biological Durability of Wood. 3rd European Conference on Wood Modification, Cardiff UK, October 15-16th, Proceedings, pp. 275-278.
9. Katović, D.; Bischof Vukušić, S.; Štefanić, G. 2000: Investigations of esterification of policarboxide acids with cellulosic materials. Tekstil, 49(10):551-554. [*in Croatian language*].
10. Ladner, C.; Halmschlager, E. 2002: Dauerhaftigkeit von modifiziertem Holz gegenüber holzzerstörenden Pilzen. poglavlje u knjizi: Modifiziertes Holz: Eigenschaften und Märkte, Lignovisionen Band 3, September 2002, pp.191-219.
11. Militz, H. 1993: Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability. Wood Science and Technology 27:347-355.
12. Mitchell, P. H. 1988: Irreversible Property Changes of Small Loblolly pine Specimens Heated in Air, Nitrogen or Oxygen. Wood and Fiber Science 20(3):320-355.
13. Rapp, A. O.; Sailer, M. 2001: Oil-heat-treatment of wood – process and properties. Drvna industrija, 52(2):63-70.
14. Rep, G.; Pohleven, F. 2001: Wood modification – a promising method for wood preservation. International Conference: Wood in construction industry: Tradition and future, Zagreb, Croatia, 25 April 2001, pp.27-38.
15. Šefc, B. 2006: Wood properties when treated by citric acid, Disertation, Faculty of Forestry Zagreb, pp.92. [*in Croatian language*].
16. Xiel, Y.J.; Krause, A.; Militz, H.; Turkulin, H.; Richter, K.; Mai, C. 2007: Effect of treatments with 1,3-dimethylol-4,5-dihydroxy-ethyleneurea (DMDHEU) on the tensile properties of wood. Holzforschung. 61(1):43-50.
17. Yildiz, S.; Yildiz, Ü.; Çolakolu, G.; Derya, E.; Temýz Ali G. 2003: The Effects of heat Treatment on the specific Gravity of Beech and Spruce Wood. IRG 34th Annual Meeting in Brisbane, Australia, IRG/WP 03 – 40254.
18. Yusuf, S.; Imamura, Y.; Takahashi, M.; Minato, K. 1995: Weathering properties of Chemically Modified Wood with Some Cross-Linking Agents and Its Decay Resistance after Weathering. Mokuzai Gakkaishi, 41(8):785-793.

Corresponding address:

Associate Prof. RADOVAN DESPOT, PhD

Department for Wood Science
University of Zagreb, Faculty of Forestry
Svetošimunska cesta 25, P.O. Box 422
10002 Zagreb
Croatia
E-mail: despot@sumfak.hr