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Comparative Study on Dimensional Stability and Biological Durability of Poplar Wood Modified by Chemical and Heat Treatment

Usporedna studija dimenzijske stabilnosti i biološke trajnosti kemijski i toplinski modificirane topolovine

ORIGINAL SCIENTIFIC PAPER

Izvorni znanstveni rad

Received – prispjelo: 24. 3. 2023.

Accepted – prihvaćeno: 27. 9. 2023.

UDK: 630*84; 674.04

https://doi.org/10.5552/drvind.2024.0097

ABSTRACT • *The fast-growing species of Populus deltoides is of significant commercial importance to the Indian wood merchants. Despite its abundant availability and better treatability, the use of P. deltoides is limited due to its perishable nature. Heat treated and chemically modified Populus deltoides L. was thus explored for dimensional stability and biological durability to commercialise its use. Chemical modification was performed using a combination of citric acid and sodium hypophosphite. Heat treatment was done in a laboratory oven in air at 140 °C for 8h. Both chemically modified and heat-treated samples exhibited improvements in dimensional stability and biological durability in comparison to the untreated control sets. Chemical modification resulted in better dimensional stability. Anti-swelling efficiency of Populus deltoides was 2-2.5 times more for the chemically modified set compared to heat treatment in both radial and tangential directions. Chemically modified set became significantly more resistant to biodeterioration showing 5 times less mass loss by termites, whereas controls and heat-treated sets returned loss percentages which were comparable. Soil block bioassay with Trametes versicolor (TV) exhibited mass loss of 9.46 % for chemically modified samples, 40.26 % for heat treated samples and 50.02 % for the untreated controls, respectively. Rhodonia placenta (OP) followed a similar trend with mass loss of chemically modified set being 5.72 % and heat-treated set being 37 %, respectively, with the controls showing 43.85 % mass loss. Mass loss exhibited by the heat-treated samples were less than the controls, but the values suggested that heat treatment at 140 °C for 8 h failed to impart any substantial resistance against rotting fungi and termites.*

KEYWORDS: *biological durability; chemical modification; dimensional stability; heat treatment*

SAŽETAK • *Brzorastuća vrsta Populus deltoides ima veliku komercijalnu važnost za indijske trgovce drvom. Unatoč velikoj dostupnosti i dobroj obradivosti, upotreba drva P. deltoides ograničena je zbog njegove slabe trajnosti. Stoga je radi bolje komercijalizacije drva Populus deltoides L. istražen utjecaj toplinske i kemijske modifikacije na njegovu dimenzijsku stabilnost i biološku trajnost. Kemijska modifikacija provedena je kombinacijom*

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limunske kiseline i natrijeva hipofosfita. Toplinska modifikacija u trajanju od osam sati obavljena je u laboratorijskom sušioniku pri 140 °C, uz prisutnost zraka. Kemijski i toplinski modificirani uzorci drva pokazali su bolju dimenzijsku stabilnost i biološku trajnost od nemodificiranih kontrolnih uzoraka. Kemijska modifikacija rezultirala je i većom dimenzijskom stabilnošću. Učinkovitost u sprečavanju bubrenja drva Populus deltoides bila je 2 – 2,5 puta veća u kemijski modificiranih uzoraka nego u toplinski modificiranih uzoraka, i to u radijalnome i tangencijalnom smjeru. Kemijski modificirani uzorci drva postali su znatno otporniji na biološko propadanje i pokazali su pet puta manji gubitak mase pri djelovanju termita nego toplinski modificirani i nemodificirani uzorci. Test s Trametes versicolor (TV) pokazao je gubitak mase od 9,46 % za kemijski modificirane uzorke, 40,26 % za toplinski modificirane uzorke i 50,02 % za nemodificirane uzorke. Za test s Rhodonia placenta (OP) uočen je sličan trend gubitka mase, koji je za kemijski modificirane uzorke iznosio 5,72 %, za toplinski modificirane uzorke 37 %, a za nemodificirane uzorke 43,85 %. Gubitak mase toplinski modificiranih uzoraka drva bio je manji od gubitka mase nemodificiranih uzoraka, ali su vrijednosti pokazale da se toplinskom modifikacijom pri 140 °C tijekom osam sati nije uspjela postići značajna otpornost protiv gljiva truležnica i termita.

KLJUČNE RIJEČI: *biološka trajnost; kemijska modifikacija; dimenzijska stabilnost; toplinska modifikacija*

1 INTRODUCTION
1. UVOD

The use of wood is abundant in modern life and is often promoted due to its natural origin, aesthetic appeal, and ability to sequester carbon in service. Despite being preferred over other construction materials, the use of wood is often limited due to its inherent properties like bio deterioration, poor dimensional stability (DS) and fire susceptibility, which are highly undesirable in service (Hom *et al*., 2020a). Treating wood with several chemicals can make its performance more acceptable and enhance its durability. However, these may contain some biocides often associated with environmental concerns and health hazards. With the level of environmental pollution from other sources reaching extremes, restrictions on the use of such chemicals have been proposed by the environmentalists. Many countries have already banned the use of formulations containing chromium, arsenic and pentachlorophenol, which has resulted in intensified research on more eco-friendly practices (Hill 2006; Ganguly, 2018; Ganguly *et al*., 2020)

Wood modification is a new approach to overcome one or more such disadvantages associated with wood by means of altering the physical and chemical properties of the material to enhance its performance and durability in service (Rowell, 2006; Sandberg *et al*., 2017; Samani *et al*., 2019; 2020; Ganguly *et al*., 2021). Chemical modification (CM) of wood offers a viable good alternative to conventional wood preservation. Chemically modified wood is expected to be more dimensionally stable, more durable against blue stain and rot fungi, and more resistant to UV radiation than unmodified wood (Hom *et al*., 2020b). Chemical modification of wood is an efficient way to improve dimensional stability (DS), Biological Durability (BD) and UV resistance, which is particularly interesting in service. This has been established through various studies using different chemicals, and their negative impacts on wood and the environment were also discussed at length (Singh *et al*., 1979; Rowell, 1982; Kumar and Agarwal, 1983; Kumar and Kohli, 1985; Matsuda, 1987; Kumar *et al*., 1991; Donath *et al*., 2004; Hansmann *et al*., 2005; Hom *et al*., 2020b). Acetic Anhydride was found to be the most suitable reagent for chemical wood modification through acetylation (Singh *et al*., 1992; Mantanis, 2017), although most of the researchers reported a net loss of more than 50 % of the reagent due to formation of acetic acid, which may affect the strength of wood and increase corrosiveness to metal fittings. Chemical modification by DMDHEU (1, 3-dimethylol-4, 5-dihydroxyethyleneurea) had reportedly increased dimensional stability of wood up to 50-60 % (Despot *et al*., 2008) and increased durability of modified wood (Videlov, 1989; Ashaari *et al*., 1990; Militz, 1993; Yusuf *et al*., 1994), although formaldehyde release is an associated problem (Katović and Soljačić, 1988). Heat Treatment (HT) is also known to impart dimensional stability to wood but varies from species to species (Militz, 2002) and is different in different directions. The dimensional stability, thus induced, is primarily due to the reduced hygroscopicity and subsequent decreased Equilibrium Moisture Content (EMC) of heat treated wood (Esteves and Pereira, 2009). Tjeerdsma *et al*. (1998) mentioned a possibility of the loss of methyl radicals of some guiacylic and syringylic units of lignin leading to the increase of phenolic groups and proportion of free ortho positions, which results in the increased dimensional stability of heat-treated wood.

Inhibiting wood affinity towards water should be the fundamental step in protecting it against rapid decay and subsequent distortion. This is highlighted in the research on wood modification, which sheds light on non-biocidal modes of action, such as water exclusion efficacy (Winandy and Morrell, 2017), anti-swelling efficiency (ASE) and dimensional stability (Hom *et al*., 2020b). CM is known to improve decay resistance of wood (Hill *et al*., 2005; Hill, 2006; Rowell *et al*., 2008). The use of citric acid (CA) for wood preservation and chemical modification is well known and can be traced back to the first part of the last decade. Wood modified by CA and cured by temperature or by microwaves showed improved dimensional stability. As a raw material, CA is easily affordable and adheres to strict ecological and environmental requirements. Water is used as a solvent during CM of wood with CA, which also makes it a cost-effective alternative to wood preservatives. CA modified wood was reported for its enhanced BD (Hasan *et al*., 2006, 2007; Despot *et al*., 2008; Šefc *et al*., 2009; Treu *et al*., 2020). Heat treatment of wood at higher temperatures has also been reported to become significantly durable by Dirol and Guyonnet (1993). Kim *et al*. (1998) further concluded that heat treatment at higher temperatures and longer duration imparts more resistance to fungal decay than it does at lower temperatures and exposure durations.

The fast-growing species of *Populus deltoides* (PD) is of significant commercial importance to the Indian wood merchants due to its rapid use for various purposes and is an integral part of the agroforestry system in the country. Previous studies of this species ascertained that the wood of poplar is of non-durable nature and is susceptible to the attack of *Trametes versicolor* (Casado-Sanz *et al*., 2019).

Keeping in mind the above cited literatures, the present study was conducted on highly perishable poplar wood in order to assess and evaluate the impact of chemical modification and heat treatment on its dimensional stability and biological durability, which may give an indication to its performance in service in both indoor and outdoor conditions. The primary aim of this study was to commercialise the use of poplar, a secondary timber species in Indian wood sector by making it more durable and less prone to damage due to moisture induced movements in wood.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Sample preparation and treatments
2.1. Priprema uzoraka i tretmani

Logs of *Populus deltoids* of 183 cm in length were procured from the Forest Range office of Forest Research Institute, Dehradun, India. Logs were converted into planks of full length. The dimensions of the planks were 182 cm × 25.4 cm × 9 cm. Samples of dimensions of 50 mm × 50 mm × 50 mm for dimensional stability test and 19 mm × 19 mm × 19 mm for soil block assay were prepared from seasoned planks. For termite mound test (TeMoT), the sample size was maintained as 100 mm × 25 mm × 6 mm. Defect free samples were chosen for the study and samples were prepared parallelly from the same part of the board. In total 3 sets of samples were prepared, with each set having 6 replicates for DS, SBA and TeMoT (Table 1). The first set (T1) was treated with CA (6.9 %) and SHP (6.5 %). The samples were treated by giving an initial vacuum of 30 mm of Hg (4kPa) for 10 min, and then the vessel was filled with the treating solution. Samples were maintained under the same vacuum for 3 h. Vacuum was released after 3h and samples were allowed to remain soaked in the solution for 18 h under atmospheric pressure (Despot *et al*., 2008). After completion of impregnation cycle, samples were removed from treating solution, air dried for 48h at room condition and kept in the laboratory oven at 140 °C for 8 h. The second set (T2) was kept in the oven at 140 °C for 8 h to see the effect of heat treatment. This was done to explore a cost-effective potential solution to an otherwise cumbersome method of heat treatment. The third set (T3) was made of control samples without any treatment (Table 1).

2.2 Weight percent gain (*WPG*)
2.2. Povećanje mase (*WPG*)

The weight percent gain (*WPG*) of the specimens after chemical modification and heat treatment (Loss) was calculated by:

$$WPG = (W_t - W_o) / W_o \times 100 \qquad (1)$$

Where, W_o and W_t are oven dried (OD) weights of unmodified and chemically modified and heat-treated samples, respectively.

2.3 Water immersion
2.3. Uranjanje u vodu

2.3.1 Dimensional stability (DS)
2.3.1. Dimenzijska stabilnost (DS)

DS was determined by comparing the total volumetric swelling (*VS*) of treated and control samples. The

Table 1 Chemical treatments and sample distribution
Tablica 1. Kemijski tretmani i distribucija uzoraka

S. No.	Treatment *Tretman*	Chemical reagents *Kemijski reagensi*	Species: PD / *Vrste: PD*						Total *Ukupno*
			DS	SBA	TMT	RS	TS	VS	
1	T1 (CA 6.9+SHP 6.5)	Citric acid (6.9 %) and sodium hypophosphite (6.5 %) *limunska kiselina (6,9 %) i natrijev hipofosfit (6,5 %)*	6	6	6	6	6	6	36
2	T2 (Heat)	Heat treatment 140 °C for 8 h *toplinska modifikacija pri 140 °C tijekom 8 h*	6	6	6	6	6	6	36
3	T3 (Control)	Control / *kontrolni uzorak*	6	6	6	6	6	6	36
Total / *ukupno*			18	18	18	18	18	18	108

R – Radial, T – Tangential, V – Volumetric, S – Swelling coefficient (e.g., RS – radial swelling coefficient)
R – radijalno, T – tangencijalno, V – volumetrijski, S – koeficijent bubrenja (npr. RS – radijalni koeficijent bubrenja)

samples of all sets were oven dried at (103±2) °C for 24 h, and oven dried weight and initial dimensions were recorded. Swelling was determined by a water immersion test. All samples were submerged in distilled water and kept under vacuum (30 mm Hg/ 4 kPa) for 30 minutes and allowed to soak for 24 h under atmospheric pressure (Šefc *et al*., 2009). Weight and dimensions of saturated samples were recorded. Swelling coefficient (S) was calculated using the following Eq.

$$S\,(\%) = (V_s - V_o)/V_o \times 100 \quad (2)$$

Where, V_s is the volume of soaked sample and V_o is the volume of oven dried sample.

$$ASE\,(\%) = (S_u - S_m) / S_u \times 100 \quad (3)$$

Where, S_u and S_m are swelling coefficients of unmodified and modified wood samples, respectively.

2.3.2 Water exclusion efficiency (*WEE* %)
2.3.2. Učinkovitost odbojnosti drva prema vodi (*WEE* %)

WEE was calculated using the following method:

$$WEE\,(\%) = (W_c - W_t)/ W_c \times 100 \quad (4)$$

Where, W_c is water absorbed by untreated controls in g and W_t is water absorbed by treated samples in g.

2.4 Soil block bioassay (SBA)
2.4. Ispitivanje biološke trajnosti (SBA)

2.4.1 Test fungi and specimens
2.4.1. Ispitne gljive i uzorci

One brown rot, *Rhodonia placenta* (Fr.) Niemelä, K.H. Larss. & Schigel (OP) (FRI Culture No. 180) and one white rot, *Trametes versicolor* (L.) Lloyd (TV) (FRI Culture No. 651) fungi were selected for the SBA study (IS 4873:2008). Fresh cultures of the fungi were obtained from the collection of Forest Pathology Discipline of Forest Research Institute, India for research purposes. The test blocks of size 19 mm ×19 mm ×19 mm and the feeder blocks of size 4 mm ×19 mm ×35 mm were prepared along the length of grain. The feeder blocks were prepared from sapwood of *Bombax ceiba*. The test blocks were oven dried at (103±2) °C for 24 h and then conditioned at 75 % *RH* till constant weights (W_1) were achieved. W_1 was considered as the weight before incubation.

2.4.2 Preparation of soil culture bottles
2.4.2. Priprema posuda s hranjivom podlogom

Sieved, air-dried garden soil (125 g), having pH 5.0-7.0, was filled (compacted by tapping) in screw capped bottles. Distilled water (44 ml) was added to the bottles to obtain 130 % of water holding capacity of soil in test bottles. Two feeder blocks of size 4 mm × 19 mm × 35 mm were placed directly on the surface of the soil. The prepared bottles with caps loosened were sterilized in an autoclave at a pressure of 98066.5 Pa for 30 min prior incubation.

2.4.3 Preparation of test culture
2.4.3. Priprema ispitne kulture

Sterilized culture bottles were cooled and the fungus inoculum from freshly grown culture, approximately 8-10 mm in diameter, was placed on the edge of the feeder blocks in culture bottles. The inoculated bottles were incubated in B.O.D. (Biochemical oxygen demand) with slightly loosened lids at (25±2) °C and (70±4) % relative humidity (*RH*) for approximately 3 weeks, till the feeder blocks were completely covered by the test fungi.

2.4.4 Incubation of test blocks in culture bottles
2.4.4. Inkubacija ispitnih blokova u posudama s kulturama

Two blocks were placed on feeder blocks in contact with mycelium along the cross-section face in each culture bottle. The bottles containing the test blocks were incubated for a period of 12 weeks in the incubator maintained at (25±2) °C and a *RH* of about (70±4) %. At the end of the incubation period the blocks were removed from the culture bottles, cleaned off from the adhering mycelium with a soft tissue and dried at room temperature for 3-4 days. Subsequently the blocks were again dried in a hot air oven at (103±2) °C for 24 h and then conditioned at 75 % *RH* till the constant weights (W_2) were obtained.

2.5 Calculation of mass loss (*ML*)
2.5. Izračun gubitka mase (*ML*)

ML (%) was calculated from the conditioned weight of the blocks before and after SBA.

$$ML\,(\%) = (W_1 - W_2)/W_1 \times 100 \quad (5)$$

Where, W_1 is the conditioned weight of the blocks before test, and W_2 is the conditioned weight of the blocks after test.

2.6 Termite mound test (TeMoT)
2.6. Ispitivanje otpornosti drva na djelovanje termita (TeMoT)

TeMoT was conducted as per Shukla (1977). CM, HT and control blocks were buried at different places inside a termite mound of *Odontotermes obesus* (rambur) at the beginning of the month of May. Blocks were removed from the mound in November when the activity of termites almost ceased due to fall in temperature. The blocks were examined for termite attack and reinstalled in next May to have exposure to termites for two successive termite seasons. Blocks were cleaned of mud and debris and evaluated visually to ascertain and quantify damage by termites. Efficacy of treatments in terms of protection against termites was evaluated by *ML* % (wood consumed) as reported by previous researchers (Shukla, 1977; Kumar and Dev, 1993) (Table 2).

Table 2 Classification of wood into various resistance classes after TeMoT
Tablica 2. Klasifikacija drva u različite klase otpornosti prema TeMoT-u

ML, %	Termite resistance class *Klasa otpornosti na termite*
0-6	Very resistant (Class I) / *vrlo otporno (klasa I)*
7-16	Resistant (Class II) / *otporno (klasa II)*
17-30	Moderately resistant (Class III) *srednje otporno (klasa III)*
31-50	Poorly resistant (Class IV±) *slabo otporno (klasa IV+)*
51 and above	Perishable (Class IV-) / *neotporno (klasa IV-)*

2.7 Statistical analysis
2.7. Statistička analiza

Statistical analysis was done using SPSS (Version 16) software package (IBM, Chicago, USA). The mean, standard deviation and standard error of mean (SE) were calculated, and ANOVA was performed. Duncan Analysis was performed further to compare the means statistically at 95 % significance level.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The results of the overall study are presented in Table 3 and 4 and Figures 1, 2 and 3. Chemical modification (CM) showed better dimensional stability and biological durability over heat-treated (HT) and control samples. *WPG* of chemically modified samples were satisfactory and comparable with previous studies and provided enough resistance to fungi and termites (Larnøy *et al.*, 2018) The treatment methods chosen might have added to the modification as CA cured better when it was followed by curing at high temperatures (Larnøy *et al.*, 2018). For HT samples, a cheap alternative was explored by trying to modify the samples in oven at a relatively lower temperature. Heat treatment (HT) by this method was fairly successful and HT sets performed marginally better, but the performance was not up to the mark and further research should be carried out.

3.1 Dimensional stability (*DS*)
3.1. Dimenzijska stabilnost (*DS*)

A 12 % increase in weight observed by CM was due to substitution of OH groups of the cell wall by citric acid cross linking (Lee *et al.*, 2020), while HT causes a loss in weight. Similar weight loss (1.5 % at 180 °C for 4 h) was observed in previous studies (Alén *et al.*, 2002). Stamm, (1956) showed that wood heated in the presence of oxygen causes degradation of wood more rapidly than wood heated in an oxygen-free atmosphere, which was also reported by Mitchell (1988). Weight loss occurs to a higher extent in hardwoods as compared to softwoods (MacLean, 1951, 1953; Hills, 1975; Hill *et al.*, 2021). Mass loss was 2-3 % higher in hardwoods than softwoods treated under identical conditions (Zaman *et al.*, 2000).

The *WEE* observed for CM was higher as compared to HT. Citric acid modification resulted in 24 % while HT caused 16 % *WEE*. Previous studies have stated that the molecular volume of the substituted group along with a degree of substitution of the hydroxyl groups influences *WEE* of modified wood (Chang and Chang, 2002). The data of *WEE* for CM was similar to that observed by Rowell and Banks, (1985) of 20 % and 25 % for Acetic Anhydride and Butylene Oxide.

From Table 3 and Figure 1, it can be clearly deduced that both CM and HT have significantly reduced the swelling of PD wood as compared to control. It was observed that the swelling coefficient was lowest for CM (CA 6.9+SHP 6.5) as compared to T2 or T3 for radial, tangential and volumetric samples. The swell-

Table 3 Mean of weight percent gain/loss due to treatment and swelling in water immersion test of PD (Standard Error (*SE*) Values are in parenthesis)
Tablica 3. Srednja vrijednost povećanja/gubitka mase zbog tretmana i rezultati testa bubrenja uranjanjem uzoraka drva *Populus deltoides* u vodu (vrijednosti standardne pogreške *SE* navedene su u zagradama)

Treatment *Tretman*	WPG	**Radial swelling coefficient** *Koeficijent radijalnog bubrenja*	**Tangential swelling coefficient** *Koeficijent tangentnog bubrenja*	**Volumetric swelling coefficient** *Koeficijent volumnog bubrenja*	***WEE*, %**
T1 (CA 6.9+SHP 6.5)	11.76 (±0.82)	2.11 (±0.07)a	4.50 (±0.07)m	7.13 (±0.40)x	24.34 (±1.17)p
T2 (Heat)	-0.31 (±0.16)	3.25 (±0.07)b	6.23 (±0.15)n	10.20 (±0.61)y	16.12 (±0.79)q
T3 (Control)	-	4.18 (±0.15)c	7.35 (±0.11)o	13.36 (±0.45)z	-

Note: Different alphabets denote different homogeneous groups as per Duncan Analysis. Duncan Analyses were performed separately for all above parameters and reported accordingly. a, b, c denote different groups for radial swelling; m, n, o denote different groups for tangential swelling and x, y, z denote different groups for volumetric swelling, p and q represent the same for *WEE*.
Napomena: Različita slova označavaju različite homogene skupine prema Duncanovoj analizi, koja je provedena za svaki parametar naveden u tablici zasebno, a rezultati su prikazani u skladu s tim. Pritom a, b, c označavaju različite skupine za radijalno bubrenje; m, n, o obilježavaju različite skupine za tangentno bubrenje; x, y, z predočuju različite skupine za volumno bubrenje, a slova p i q predstavljaju isto to za WEE.

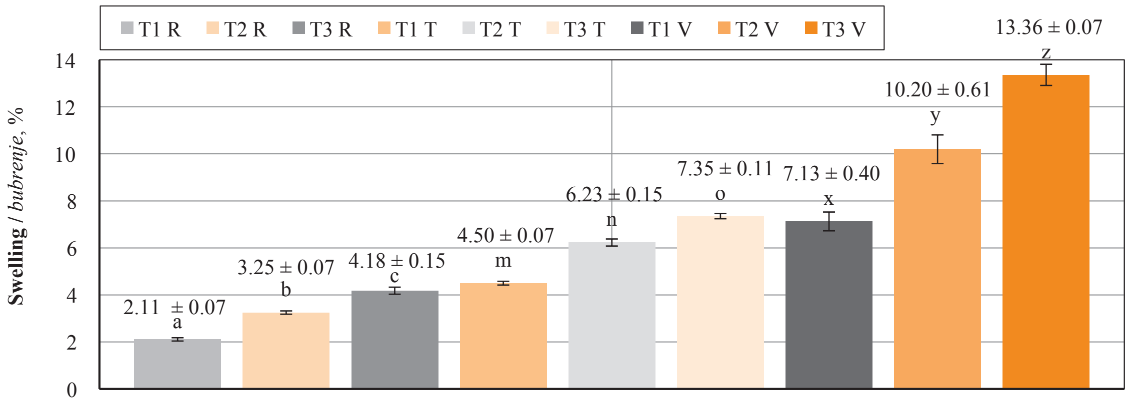

Figure 1 Swelling coefficient (*S*) after different treatments in radial (R) and tangential (T) direction and volumetric swelling coefficient (*V*) (T1 – chemical modification, T2 – heat treatment, T3 – control)
Slika 1. Koeficijent bubrenja (*S*) nakon različitih tretmana u radijalnome (R) i tangencijalnom (T) smjeru te koeficijent volumnog bubrenja (*V*) (T1 – kemijska modifikacija, T2 – toplinska modifikacija, T3 – kontrola)

Table 4 Anti swelling efficiency (*ASE*) of modified PD wood (*SE* values in parenthesis)
Tablica 4. Učinkovitost smanjenja bubrenja (*ASE*) modificiranog drva *Populus deltoides* (*SE* vrijednosti su u zagradi)

Treatment / *Tretman*	*ASE* radial	*ASE* tangential	*ASE* volumetric
T1 (CA 6.9+SHP 6.5)	49.44 (±0.84)	38.79 (±1.02)	45.10 (±0.63)
T2 (Heat)	22.16 (±0.76)	15.26 (±0.95)	20.23 (±1.4)

ing for non-modified samples ranged between 4.18-13.36, while the *S* observed for T1 was between 2.11-7.12, which was significantly lower than T2 having *S* ranging between 3.25-10.20. The *S* obtained from T2 treatment was similar to that obtained by CM of radiata pine using acetic anhydride by combination of 689 kPa pressure for 30 mins followed by 137 kPa pressure and curing at 120 °C for 30 mins (Hom *et al*., 2016). Heat treated wood is hydrophobic in nature and hence reduces shrinkage and swelling due to decrease in the hydroxyl groups and decomposition of a large portion of the hemicelluloses in the wood cell wall (Boonstra, 2008; Korkut and Kocaefe, 2009).

The *ASE,* calculated for CM from *S*, was observed to be higher as compared to HT for all the samples. Radial samples showed highest *ASE* followed by volumetric and minimum for tangential samples. The *ASE* was between 39-49 % for CM, while HT resulted in 15-22 %. The *ASE* for CM was similar to that of *Fagus sylvatica* when modified with 7.0 % water solution of CA with 6.5 % SHP as a catalyst when cured at 140 °C causing *ASE* of 43 % (unleached) and 30 % (leached) (Šefc *et al.,* 2009). Similarly, the *ASE* observed by CM using CA is comparable to the values reported by previous researchers with maleic anhydride with *ASE* of 35-45 % (Essoua Essoua *et al*; 2016).

3.2 Soil block bioassay (SBA)
3.2. Ispitivanje biološke trajnosti (SBA)

Figure 2 shows that *ML* reduced significantly after both CM and HT, with CM returning excellent biological durability against both brown rot and white rot

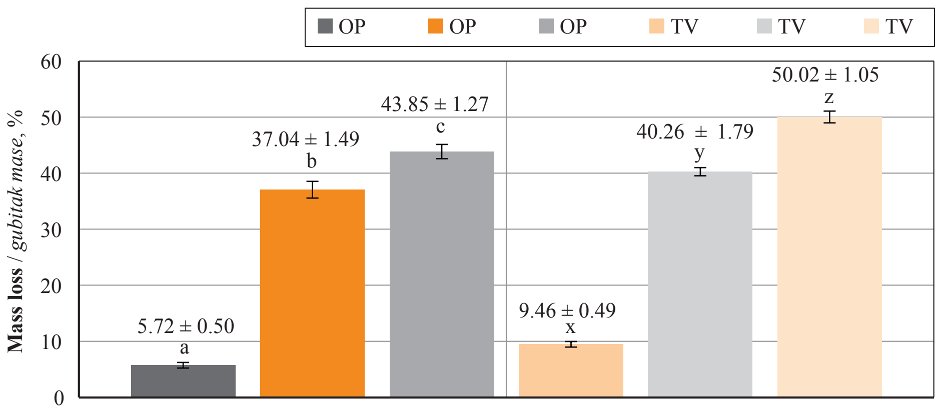

Figure 2 Mean mass loss (*ML*) percentage in PD after SBA against OP and TV (*SE* values are mentioned after ± and different alphabets (a, b, c for OP and x, y, z for TV) denote different homogeneous subsets as per Duncan analysis)
Slika 2. Srednji postotni gubitak mase (*ML*) uzoraka drva *Populus deltoides* nakon SBA s obzirom na OP i TV; vrijednosti *SE* prikazane su nakon znaka ±, a različita slova (a, b, c za OP i x, y, z za TV) označavaju različite homogene podskupove prema Duncanovoj analizi

fungi. Several authors reported higher rot resistance of HT wood when not in direct contact with ground (Esteves and Pereira, 2009). After HT, several wood polymers, like hemicellulose, degrade and release acetic acid, which may result in some chemical modification of wood compounds (Esteves and Pereira, 2009; Hill *et al.*, 2021). The primary reason for increased durability against rotting fungi was reported to be the formation of several molecules after HT, like furfural, which reticulates with lignin in wood and becomes unrecognisable by the decaying fungi (Weiland and Guyonnet, 2003). Additionally, reduced *EMC* after HT and lower FSP also adds to protection of wood against decay. In the present study, HT reduced biodeterioration but not to a greater extent. A mere 7 % reduction in *ML* % against brown rot OP was observed in the HT sets with respect to the untreated control sets. For white rot, HT set performed slightly better as it resulted in *ML* % of 40.26 %, which was about 10 % less than *ML* observed in the control set (50.02 %). These findings are in conformity with the results of previous studies, where 35 % to 65 % rot resistance was reported for heat treated wood at different temperatures and time durations (Kim *et al.,* 1998), and the researchers highlighted that BD increased with increasing temperature and treatment time after HT. It can be said that, for highly perishable species like PD, HT at such low temperature level might not provide the required resistance to wood, and that wood may remain somewhat susceptible to fungal attack if no additional treatment is applied. CM however showed remarkable improvement in BD against both white and brown rot fungi and exhibited 6-8 times less reduction in mass against untreated samples exposed to TV and OP, respectively. This enhanced durability can be attributed to the cross linking of CA on -OH groups of cell wall components (Larnøy *et al.*, 2018) of PD wood, which made it quite unrecognisable as a food source to the decaying fungi. Another possible reason could be the leaching of treating solution in the culture jars with higher *MC,* which might have reduced the virulence of test fungi with time.

3.3 Termite mound test (TeMoT)
3.3. Ispitivanje otpornosti drva na termite (TeMoT)

From Figure 3 it can be inferred that CM using CA and SHP has imparted a very high level of biological resistance to an otherwise perishable poplar (PD) wood. After two successive termite seasons, the control samples were almost destroyed, which is evident as their *ML* was 69.27 %. The biological durability (BD) is often attributed to the presence of toxic chemicals in wood, but the *ML* observed in case of PD in the present study indicates that PD is poor in terms of inherent natural durability, which is obvious as it has a very limited range of use in the Indian woodworking sector. Susceptibility of several Poplar species to biodeterioration, especially fungi, was previously reported (Karimi *et al.*, 2013; Casado-Sanz *et al.*, 2019). The chemically modified set of PD exhibited 6 times less ML and elevated the perishable PD species, which normally belonged to class IV, to class II and established it as resistant to termite decay. Decay resistance by CA treated wood were also reported before (Lee *et al.*, 2020; Treu *et al.*, 2020). Treu *et al.* (2020) highlighted in their study that the primary reason for such results was the potential leaching of the chemicals (CA+Sorbitol) due to changes in wood-water relations after modification, along with higher mortality rate of the termites. Another possible explanation of such enhanced BD against termites can be the decreased level of protozoa in certain termite species after being exposed to acetylated wood, which leads to starvation after one or two weeks as highlighted by Duarte *et al.* (2017). BD of the HT sets of PD was comparable with the control set as the HT set exhibited a ML of 65.46 %, which was marginally less than the control set. Esteves and Pereira (2009) highlighted the possibilities of

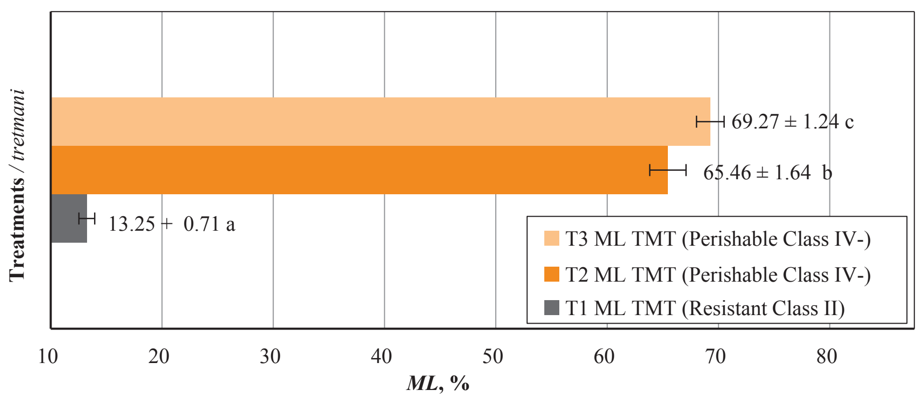

Figure 3 *ML* % and corresponding durability class for different treatments with TeMoT (*SE* values are mentioned after ± and different alphabets denote different homogeneous subsets)
Slika 3. Postotak *ML*-a i odgovarajuća klasa trajnosti za različite tretmane s TeMoT-om (vrijednosti *SE* prikazane su nakon znaka ±, a različita slova označavaju različite homogene podskupove)

an esterification of cellulose after degradation of hemicelluloses as the reason for enhanced biological durability of heat-treated wood, which produces substances that are not recognisable as food materials to decaying agents. Additionally, the *FSP* of HT wood is lower than untreated wood, which is a desirable property to impart better resistance against biological degradation. Further change of hemicelluloses from hydrophilic and easily digestible to hydrophobic molecules may also play some part (Esteves and Pereira, 2009). From the study, it can be concluded that HT at such lower modification temperature is not enough to ascertain sufficient BD to PD. The findings are in line with previous work by Nunes *et al.* (2004), where the researchers also reported insignificant improvement in biological durability against termites for heat treated wood.

4 CONCLUSIONS
4. ZAKLJUČAK

From the present study, it can be concluded that chemical modification of wood using Citric Acid with Sodium Hypophosphite as catalyst, is an eco-friendly modification process and resulted in better overall performance of modified wood in comparison to the heat-treated wood. Both the modification methods exhibited enhanced properties of dimensional stability and improved resistance to bio deterioration with respect to the untreated controls and improved durability class of treated wood against termites. Chemically modified wood with CA and SHP showed excellent resistance to both white and brown rot fungi as well as termites. This should further be investigated for threshold concentrations including additional test sites with varying climate and more decaying agents to further elucidate on the mode of action. The concentrations of the chemicals may be varied in order to establish an optimum combination for best output. These studies may provide valuable inputs to establish this mode of chemical modification as a cost effective alternative and further establish its use in the niche domain of wood science.

Acknowledgements – Zahvala

The authors acknowledge the contribution of ICFRE, Dehradun, India for funding the research.

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