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Physical and Mechanical Properties and Decay Resistance of Poplar Modified with mDMDHEU

Fizička i mehanička svojstva te otpornost na propadanje topolovine modificirane mDMDHEU-om

ORIGINAL SCIENTIFIC PAPER
Izvorni znanstveni rad
Received – prispjelo: 21. 4. 2021.
Accepted – prihvaćeno: 13. 12. 2021.
UDK: 582.681.82; 630*84
https://doi.org/10.5552/drvind.2022.2118

ABSTRACT • *Chemical modification as a non-biocidal treatment is an effective method to improve physical and biological properties of wood. Poplar is a fast growing species but has poor dimensional stability and durability in addition to low mechanical properties. Low molecular weight Dimethylol dihydroxyethyleneurea (mDMDHEU) was used to improve the properties of poplar mainly dimensional stability and decay resistance. Results indicated high anti-swelling efficiency (ASE), but low variation between both concentrations of mDMDHEU. Tangential swelling was greatly reduced by mDMDHEU treatment during the water immersion period. Untreated poplar samples were severely decayed as compared to modified samples. Modified samples showed lower bending strength unlike to compression strength. Ester peak at 1720 cm^{-1} revealed chemical reaction between chemical reagent and wood cell wall components. Control samples exhibited considerably higher thermal degradation when compared to the samples modified with mDMDHEU.*

KEYWORDS: *wood modification; mDMDHEU; dimensional stability; MOR; FTIR; TGA; decay resistance*

SAŽETAK • *Kemijska modifikacija kao postupak bez biocida učinkovita je metoda za poboljšanje fizičkih i bioloških svojstava drva. Topolovina je drvo vrste koja brzo raste, ali ima slabu dimenzijsku stabilnost i prirodnu trajnost te slaba mehanička svojstva. Za poboljšanje svojstava topolovine, prije svega dimenzijske stabilnosti i otpornosti na propadanje, upotrijebljena je dimetilol dihidroksietilenurea male molekularne mase (mDMDHEU). Rezultati su pokazali visoku učinkovitost kemijske modifikacije u smislu sprječavanja bubrenja topolovine (ASE), ali s malom varijacijom među dvjema primijenjenim koncentracijama mDMDHEU-a. Tangencijalno bubrenje uzoraka topolovine tijekom uranjanja u vodu uvelike je smanjeno mDMDHEU modifikacijom. Nemodificirani uzorci topolovine bili su vrlo truli u usporedbi s modificiranima. Modificirani su uzorci, pak, pokazali manju čvrstoću na savijanje u usporedbi s tlačnom čvrstoćom. Vrh vrpce na 1720 cm^{-1} otkrio je kemijsku reakciju između kemijskog reagensa i spojeva u staničnoj stijenci drva. Na kontrolnim je uzorcima nastala znatno veća toplinska degradacija nego na uzorcima modificiranima mDMDHEU-om.*

KLJUČNE RIJEČI: *modifikacija drva; mDMDHEU; dimenzijska stabilnost; MOR; FTIR; TGA; otpornost na propadanje*

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1 INTRODUCTION
1. UVOD

Numerous studies have been performed to improve dimensional stability, decay and insect resistance of wood. This can be done by modifying the reactive sites of cell wall components in wood (Militz, 1993). Nowadays, wood properties such as low dimensional stability and biological durability are improved by various non-biocidal treatments, e.g. thermal or chemical, and such methods extend the service life of the modified wood. These methods present environmentally friendly processes that have no toxic effects on nature and do not cause disposal problem after service life.

Chemical modification of wood is described as a reaction between wood cell wall components (cellulose, hemicelluloses and lignin) and chemical reagent, resulting in the formation of a stable chemical bond (Rowell, 1983; Hill, 2006; Sandberg *et al*., 2017). A wide range of chemical reagents such as acetic anhydride, carboxylic acids, isocyanates, epoxides, aldehydes were studied for chemical modification of wood; phenol formaldehyde, dimethylol dihydroxyethyleneurea (DMDHEU), furfuryl alcohol and silicon-containing compounds were used for impregnation modification (Hill, 2006). However, acetylation, heat treatments, furfurylation and DMDHEU have been introduced to the market since these methods were found to be successful (Militz and Lande, 2009). Although modifications of wood and veneers with DMDHEU were developed on a pilot scale, modified products with the first generation of DMDHEU have not been in the market. However, modified wood based on the second generation of DMDHEU is underway due to little or lack of formaldehyde (Brischke, 2018).

1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) is a water-soluble glyoxal resin, acting as cross-linking agent and mostly used in textile industry for wrinkle resistance; it also found application in the field of wood modification (Emmerich *et al*., 2019). DMDHEU can make crosslinking with the wood cell wall polymers by reacting with the hydroxyl groups, and also can deposit within the cell walls leading to bulking of the cell wall (Xie *et al*., 2010). Magnesium chloride and zinc nitrate are the most commonly used catalysts for accelerating the cross-linking reaction of DMDHEU (Schindler and Hauser, 2004). In an early study on DMDHEU modification with different catalysts, like citric or tartaric acid, Militz (1993) improved anti shrink efficiency (ASE) up to 75 % and improved decay resistance with beech wood. Weight percentage gain (WPG) affects the performance of DMDHEU treated wood. Mass loss below 3 % against decay fungi was obtained with 15 % WPG in beech and 10 % WPG in pine against decay fungi (Verma *et al*., 2009). Differential scanning calorimetry (DSC) demonstrated that DMDHEU reduced the pore size in wood by filling the void space in the cell wall (Dieste *et al*., 2009). Infrared spectroscopy and scanning electron microscopy analyses showed that high WPG (48 %) stabilized lignin to some extent in wood veneers modified with DMDHEU, which effectively prevented the degradation of the wood cell wall during artificial weathering (Xie *et al*., 2005). Despite the improvements in physical and biological properties by DMDHEU modification, some mechanical properties are decreased. The loss in bending strength of DMDHEU modified wood was previously reported by some authors (Nicholas and Williams, 1987; Ashaari *et al*., 1990). Modification with mDMDHEU decreased the abrasion resistance in Scots pine (Brischke *et al*., 2019). According to Bollmus *et al*. (2020), DMDHEU increases the decay resistance, dimensional stability, compressive strength, and hardness, whereas it reduces the tensile and impact bending strength in modified wood. Pore size in wood was reduced by the filling effect of DMDHEU, resulting in the mechanical support to the cell wall that led to the preventing of strength loss in treated wood at lower curing temperatures, e.g. 90 ˚C. However, when curing was performed at the temperature as high as 150 °C, the bending strength of DMDHEU-treated wood greatly decreased (Yuan *et al*., 2013). Impact strength was decreased by DMDHEU treatment, while hardness and compression strength parallel and perpendicular to grain increased (Jiang *et al*., 2014).

Many studies related to chemical modification of DMDHEU have been carried out with Scots pine and beech, since both species displayed improved material properties. Then, various authors gave particular focus on permeable wood species such as Rubber wood, Slash pine, Radiata pine, Albizzia hardwood, Ponderosa pine, Maritime pine and Balsam poplar (Emmerich *et al*., 2019).

Poplar is a fast growing species, but has poor physical and durability properties. However, Poplar wood can be used in various places depending on the market and industrial technology. It is generally used for the production of wood based boards, packaging, pulp and biomass for energy (Castro and Zanuttini, 1991). In addition, modified poplar is produced according to thermal modification process, which improves the dimensional stability and decay resistance of wood. On the other hand, poplar is a proper species for impregnation modification as it shows good permeability. The treatability of poplar sapwood is classified as 1, which indicates that it can be easily treated according to EN 350-2 standard. However, natural resistance of poplar wood against decay fungi is classified as 5, which means that it is not durable according to that standard.

The objective of this study is to impregnate poplar wood by mDMDHEU with low molecular weight to improve dimensional stability and decay resistance. There is little research on poplar modification with DMDHEU compared to other wood species. In addition, modified DMDHEU with low molecular weight was used in this study at the curing temperature that was a bit higher than in a wide range of studies dealing with DMDHEU.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Poplar (*Populus euramericana*) with 28 cm in diameter was provided from the sawmill producing wooden pallets in the Bartin province. The logs were cut vertically in four pieces and were left to the air drying before sizing of the specimens. Specimens were prepared from the sapwood section according to the dimensions specified in the experiments. All of the samples were oven dried at 103 °C before treatment.

Modified DMDHEU with low molecular weight (130 g/mol) was provided from Latro Chemistry (Istanbul, Turkey). It was diluted with distilled water to the concentrations of 15 % and 30 % (w/w), respectively. Magnesium chloride ($MgCl_2$) was added as a catalyst at a rate of 5 % of the total solution amount. Impregnation was carried out according to full cell process with 30 min vacuum (0.08 MPa) and 1 h air pressure (0.5 MPa), subsequently one-week air conditioning and curing at 130 °C for 48 h. Weight change in the samples after the modification was calculated as the percentage according to Eq. 1:

$$WPG(\%) = \left[\frac{M_m - M_u}{M_u}\right] \cdot 100 \quad (1)$$

Where M_m is the oven-dry mass of modified wood, M_u is the oven-dry mass of unmodified wood.

2.1 Physical tests
2.1. Ispitivanje fizičkih svojstava

Samples with dimensions of 20 mm × 20 mm × 10 mm (tangential × radial × longitudinal) were prepared for water related properties with six replicates. Oven-dry weight of the modified and unmodified samples was recorded and the lengths in the longitudinal, radial and tangential directions were measured by digital calliper for measuring the volumetric change. All samples were immersed in distilled water for 2, 4, 6, 24, 48, 72 h, 240 h and 360 h.

Leaching rate (*LR*) was obtained based on the oven dried weights after modification and water immersion as given below:

$$LR(\%) = \left[\frac{M_0 - M_1}{M_0}\right] \cdot 100 \quad (2)$$

Where M_0 is the oven dried weight of wood before immersion and M_1 is the oven dried weight of wood after immersion.

Bulking coefficient (*BC*), swelling coefficient (*S*), anti-swelling efficiency (*ASE*), tangential swelling (*TS*) were calculated as follows:

$$BC(\%) = \left[\frac{V_m - V_u}{V_u}\right] \cdot 100 \quad (3)$$

Where V_u is the volume of the unmodified wood sample and V_m is the volume of the modified wood sample

$$S(\%) = \left[\frac{V_{ws} - V_{od}}{V_{od}}\right] \cdot 100 \quad (4)$$

Where V_{ws} is the water-swollen volume of the wood sample and V_{od} is the oven-dry volume of the wood sample

$$ASE(\%) = \left[\frac{S_u - S_m}{S_u}\right] \cdot 100 \quad (5)$$

Where S_u is the swelling coefficient of unmodified wood and S_m is the swelling coefficient of modified wood

$$TS(\%) = \left[\frac{T_1 - T_0}{T_0}\right] \cdot 100 \quad (6)$$

T_0 and T_1 is the tangential length for oven dried wood and water-swollen wood, respectively.

2.2 Mechanical tests
2.2. Ispitivanje mehaničkih svojstava

Bending strength and modulus of elasticity, as well as compression strength, were performed on the control and modified samples. Three points bending measurements were performed according to TS 2474. Bending samples with 10 mm × 10 mm × 200 mm (tangential × radial × fibers direction) in size were used for each treatment with 15 replicates. The samples were air-conditioned for an equal moisture content level prior to the bending experiment.

Bending strength (*MOR*) was determined according to Eq. 7:

$$MOR = \frac{3 \cdot P_{max} \cdot L}{2 \cdot b \cdot h^2} \quad \left(\frac{N}{mm^2}\right) \quad (7)$$

Where P_{max} is the maximum load at failure of the samples, *L* is the span, *b* and *h* are the width and height of the specimen.

Modulus of elasticity (*MOE*) was determined according to Eq. 8:

$$MOE = \frac{\Delta F \cdot L^3}{\Delta f \cdot 4 \cdot b \cdot h^3} \quad \left(\frac{N}{mm^2}\right) \quad (8)$$

Where ΔF is the difference in load in the elastic deformation area, Δf is the deflection in the bending area, *L* is the span, *b* and h are the width and height of the specimen.

For the compression strength parallel to the fibers, wood samples were prepared in the dimensions of 20 mm × 20 mm × 30 mm (tangent × radial × fiber direction) according to TS 2595. Compression strength was determined according to Eq. 9:

$$\sigma\beta = \frac{F_{max}}{A} \quad (\frac{N}{mm^2}) \tag{9}$$

Where F_{max} is the maximum compressive force and A is surface area.

2.3 Fourier transform infrared spectroscopy (FTIR)
2.3. Fourierova transformacijska infracrvena spektroskopija (FTIR)

Measurements were carried out using the Shimadzu IR Affinity-1 FTIR spectrophotometer device equipped with an attenuated total reflectance probe (Shimadzu Corp., Kyoto Japan). Using the Pike ATR Diamond/ZnSe accessory compatible with the Shimadzu model, measurements were taken from the surface without causing any damage to the samples. The spectra of each sample were at a resolution of 4 cm^{-1} and a wavenumber range of 700-4000 cm^{-1}. 32 scans were obtained on the surface of untreated control and modified samples.

2.4 Thermogravimetric analysis (TGA)
2.4. Termogravimetrijska analiza (TGA)

Thermogravimetric analysis (TGA) of the samples was performed using a Netzsch TG 209 F1 Iris instrument (NETZSCH Group Selb, Germany). A sample of about 2 mg of wood was placed on an alumina crucible bowl (17 mm diameter), then heated from 25 °C to 500 °C at a heating rate of 20 °C (min^{-1}) per minute under nitrogen atmosphere.

2.5 Decay test
2.5. Ispitivanje propadanja

White rot fungus *Trametes versicolor* was selected for decay test for the mini-block samples of 30 mm × 15 mm × 5 mm in size used for each treatment with 10 replicates. For growth culture, 48 g of Malt extract agar (Merck) was diluted with 1 liter of distilled water, sterilized in the autoclave at 121 °C for 10 min. Control and treated samples were placed in the petri dishes completed with mycelium development and subjected to decay test for 8 weeks at 25 °C and 80 % of relative humidity. At the end of the decay test, the samples were taken from the petri dishes and the micelles on the surface were cleaned by brush and kept in the oven until the constant weight at 103 °C. Mass loss was calculated based on the weight differences at oven-dried state before and after decay test.

2.6 Statistical analysis
2.6. Statistička analiza

A descriptive analysis was developed (mean and standard deviation) for samples. ANOVA was applied to verify the effect of treatment with the mDMDHEU. Duncan's test was set at 99 % confidence level to determine the statistical difference between the means.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Weight percentage gain (*WPG* %)
3.1. Postotak povećanja mase (*WPG* %)

Weight percentage gain (*WPG* %) of the modified samples was calculated after curing at 130 °C for 48 hours on the water uptake, decay test, bending strength and compression strength samples (Table 1). The calculation was based on difference of oven-dry weights of the samples before and after impregnation.

Table 1 indicates that *WPG* results varied according to the concentration of mDMDHEU, and type of experiment, since samples were of different size in each experiment. Impregnation with 30 % of mDMDHEU resulted in approximately twofold *WPG* compared to those with15 %. This was due to the higher amount of mDMDHEU.

Generally, *WPG* values ranged from 15 % to 30 % in all experiments. The reasons for the differences in weight increase rates can be explained in two ways: The first and main reason is the difference in dimensions according to the radial, tangential and longitudinal directions of the samples for each experiment and the probability of the evaporation of some resins during the curing process at 130 °C. Our results on *WPG* are consistent with the findings of Yuan *et al*. (2013) who found the values of more than 15 % and lower than 25 % when the curing process was performed at 120 °C for DMDHEU treatment. Similarly, Li *et al*. (2019) obtained the WPG between 17.9 % to 29.3 % after modification of Masson and Camphor pine with 50 % DMDHEU catalyzed by acrylic acid. However, Li *et al*. (2020) found the highest WPG as 9.5 % with the bamboo modified with 50 % DMDHEU under cur-

Table 1 *WPG* values of wood samples impregnated with mDMDHEU
Tablica 1. *WPG* vrijednosti uzoraka drva impregniranoga mDMDHEU-om

Experiments *Istraživanje*	**mDMDHEU**	***WPG*, %**
Water uptake *primitak vode*	% 15	$15.22^{a} \pm 0.46$
	% 30	$29.1^{b} \pm 2.44$
Decay test *ispitivanje propadanja*	% 15	$25.18^{a} \pm 3.51$
	% 30	$30.87^{a} \pm 3.80$
Bending strength *čvrstoća na savijanje*	% 15	$15.63^{a} \pm 2.09$
	% 30	$28.92^{b} \pm 3.08$
Compression strength *čvrstoća na tlak*	% 15	$16.58^{a} \pm 0.96$
	% 30	$25.95^{b} \pm 0.65$

[a]The letters indicate Duncan's homogeneity groups in the column.
[a]*Slova označavaju Duncanove grupe homogenosti unutar stupca.*

Table 2 Weight and volumetric changes of wood samples due to water soaking
Tablica 2. Promjena mase i volumena uzoraka drva zbog namakanja u vodi

Treatment *Tretman*	**Density, g/cm³** *Gustoća,* g/cm³	***LR*, %**	***BC*, %**	***S*, %**	***ASE*, %**
Control / *kontrolni uzorci*	0.35^{a}±0.00	0.68^{a} ± 0.43	-	16.81^{c} ± 0.80	-
15% mDMDHEU	0.38^{b}±0.00	9.34^{b} ± 0.27	4.08^{a} ± 0.51	6.53^{b} ± 0.34	61.16^{a} ± 2.01
30 % mDMDHEU	0.43^{c}±0.02	11.13^{c} ± 0.80	6.44^{b} ± 0.29	5.74^{a} ± 0.38	65.88^{ab} ± 2.27

[a]The letters indicate Duncan's homogeneity groups in the column
[a]*Slova označavaju Duncanove grupe homogenosti unutar stupca.*

ing at 95 °C for 3 h. Poplar modified with 10 % DMDHEU resulted in 16.50 % *WPG* in another study (Cai *et al*., 2018).

3.2 Dimensional stability
3.2. Dimenzijska stabilnost

After two weeks of water soaking, bulking value of the samples due to the impregnation (ΔV %), Leaching rate (*LR* %), maximum swelling (S_{max} %) and anti-swelling efficiency (*ASE* %) are given in Table 2.

According to Table 2, impregnation with mDMDHEU increased the bulking coefficient of the wood samples. As expected, this value was increased by the increasing of the resin concentration.

Xie *et al*. (2010) referred that the positive relationship between *WPG* and bulking, meaning high *WPG,* may increase the bulking effects due to the deposition of DMDHEU in the cell walls by reducing the space within the cell walls where the water molecules enter.

At the end of the soaking experiment, the samples treated with 30 % of mDMDHEU showed slightly higher *LR* than 15 % of mDMDHEU due to water leaching.

Table 2 indicates that control samples displayed very high swelling compared to the treated samples. The difference in swelling was found to be low between the concentrations of the resin treatments. The similar result was obtained with the *ASE*, which slightly increased with the increasing of the resin amount. Cai *et al*. (2018) reported lower swelling (3.29 %) and lower *ASE* (52.45 %) than our results when poplar wood was modified with 10 % DMDHEU.

In an early report on DMDHEU, it was reported that permanent *ASE* was achieved up to 70 % as a function of wood species, chemical reagent, applied concentration (*WPG*), catalyst and hardening temperature (Militz, 1993).

In the industrial scale production (superheated steam process) with suitable concentrations (30 % DMDHEU, catalyst $MgCl_2$), 45-50 % of *ASE* in Scots pine (Schaffert, 2006) and 30-35 % in beech were reported (Bollmus, 2011). According to Van der Zee *et al*. (1998), catalysts added to the reagent significantly improved the dimensional stability of the modified wood. In our experiments, $MgCl_2$ as a catalyst at 5 % was used to increase the *ASE*. $MgCl_2$ was proposed as the most suitable catalyst for wood applications in terms of high fixation of DMDHEU, high dimensional stability and resistance to decay fungi. In addition, optimized concentration of $MgCl_2$ is suggested to be 5 % (Emmerich *et al*., 2019).

Volumetric ASE was found to be 47.8 % for Masson pine and 51.2 % for Camphor pine, respectively, as a result of DMDHEU modification catalyzed by acrylic acid (Li *et al*., 2019). It varied between 18 - 42 % in bamboo modified with DMDHEU catalyzed by maleic anhydride (Li *et al*., 2020).

Based on Table 2, it can be said that mDMDHEU improved the dimensional stability of poplar wood. However, there was little difference between the concentrations of 15 % and 30 % of mDMDHEU with regard to *ASE*, although there was a marked difference between the mDMDHEU treatments in relation to WPG. This may be due to the evaporation of mDMDHEU at high temperature or due to the interaction of mDMDHEU with cell wall. Some authors stated that the reaction mechanism between wood cell wall and DMDHEU is still not clear (Hill, 2006; Larsson-Brelid, 2013).

Tangential swelling of the control and modified samples during the two-week period is given in Figure 1.

Figure 1 shows that tangential swelling values of the control samples considerably increased during the water uptake. However, impregnation with mDMDHEU exhibited a great reduction in tangential swelling. When comparing rates of mDMDHEU, both concentrations showed almost similar behavior in tangential swelling. For control samples, swelling increased particularly between 2 h and 24 h of soaking, followed by a relatively stabilized period, and reached over 10 %. Swelling behavior of the samples treated with mDMDHEU showed increasing over 4 % for 2 h, but then remained at approximately the same level for later periods.

3.3 Mechanical properties
3.3. Mehanička svojstva

Impregnation of poplar with mDMDHEU significantly reduced the *MOR* compared to control samples as shown in Table 3.

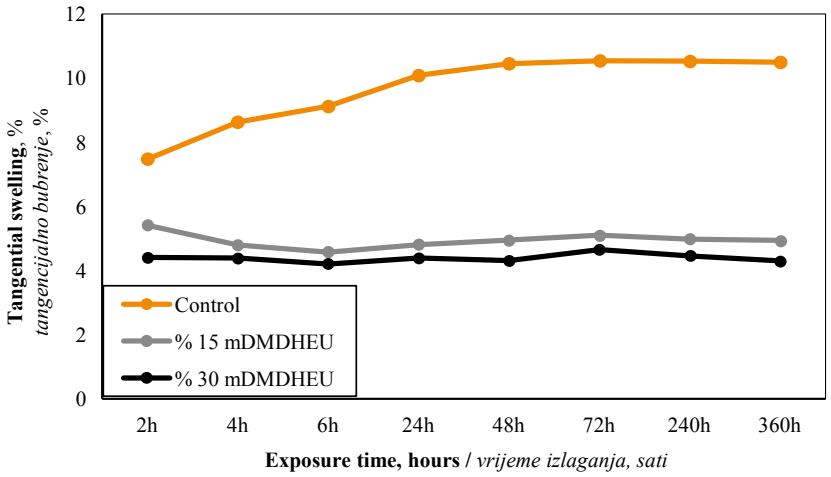

Figure 1 Tangential swelling of control and mDMDHEU modified samples depending on exposure time
Slika 1. Tangencijalno bubrenje kontrolnih uzoraka i uzoraka modificiranih mDMDHEU-om ovisno o vremenu izlaganja

Table 3 Strength values of control and modified samples
Tablica 3. Vrijednosti čvrstoće kontrolnih i modificiranih uzoraka

Modification *Modifikacija*	***MOR*, N/mm²**	**Change in *MOR*, %** *Promjena MOR-a, %*	***MOE*, N/mm²**	**Change in *MOE*, %** *Promjena MOE-a, %*	**Compression strength (*CS*), N/mm²** *Čvrstoća na tlak (CS), N/mm²*	**Change in *CS*, %** *Promjena čvrstoće na tlak, %*
Control / *kontrolni uzorci*	59.7 ± 3.9	-	4791 ± 477	-	31.2 ± 1.5	-
mDMDHEU (15 %)	40.4 ± 6.3	-32	4686 ± 377	-2	30.6 ± 2.9	-2
mDMDHEU (30 %)	39.9 ± 9.2	-33	4513 ± 615	-6	37.2 ± 2.3	19

On the other hand, there was no significant difference between the *MOR* values of the samples impregnated at 15 % concentration and at 30 %. This means that increasing in the concentration of resin had no apparent impact on the *MOR*.

MOE was found to be the highest in the control samples, followed by 15 % mDMDHEU and 30 % mDMDHEU, respectively. However, *MOE* results showed less difference.

In contrast to the *MOR*, the reduction in *MOE* in treated samples was not considerably lower than that of control.

Reduction in strength properties with regard to DMDHEU modification was previously reported by some authors. According to Yuan *et al*. (2013), decreasing in bending strength may be due to the hydrolysis effect of the catalyst, which accelerates the degradation of wood, and this effect would be different according to the type of catalyst.

Jiang (2014) found that DMDHEU with the concentration of 30 % improved the MOE, but decreased the *MOR*, the concentration being associated with the *WPG*. Lopes *et al*. (2013) reported the reduction in *MOR* up to 25 % in maritime pine regardless of the level of modification with DMDHEU. The variation in bending strength due to the DMDHEU modification varies depending on the wood species. DMDHEU increased the *MOR* at a rate of 2.8 % in Masson pine, whereas it decreased 25 % in Camphor pine compared to untreated wood (Li *et al.* 2019). It was stated that *MOR* of untreated bamboo was 145.6 MPa, whereas that of DMDHEU-modified bamboo ranged between 94.5 - 121.5 MPa. 30 % DMDHEU cured at 105 °C for 5h exhibited the lower impact on *MOR* of bamboo. In addition, modulus elasticity of modified bamboo changed less (Li *et al*., 2020).

The notable result in the mechanical properties was that the compression strength was not affected by chemical modification. Poplar samples modified with mDMDHEU at 30 % concentration was even remarkably higher than that of the control samples. This confirms that there is a positive relationship between *WPG* and compression strength.

Table 3 indicates that no significant difference was found between the control samples and the samples modified with 15 % of mDMDHEU. Increase in compression strength by DMDHEU modification was reported by previous authors (Schaffert, 2006; Bollmus, 2011; Derham *et al*., 2017). Winandy and Rowell (2005) reported 65 % increase in compression strength in DMDHEU-modified beech wood catalyzed by $MgCl_2$. Li *et al*. (2020) achieved the highest compression strength in bamboo modified with 50 % DMDHEU, cured at 95 °C for 5h.

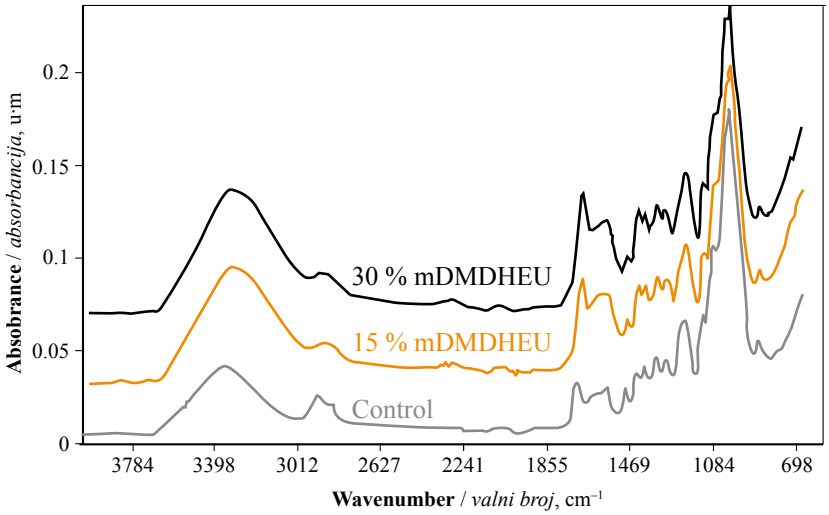

Figure 2 FTIR spectra of control and treated samples at different mDMDHEU level
Slika 2. FTIR spektri kontrolnih uzoraka i uzoraka tretiranih mDMDHEU-om različitih koncentracija

3.4 FTIR analysis
3.4. FTIR analiza

Change in the FTIR spectra of untreated control and treated samples is displayed in Figure 2 depending on the wavelength on the x-axis.

As can be seen in Figure 2, a broad peak around 3300 cm^{-1} shows the increasing of OH groups in samples modified with mDMDHEU. This can be attributed to the OH content in mDMDHEU. In this band region, OH stretching vibration was reported by previous authors (Pandey, 1999; González-Peña and Hale, 2011; Chen *et al*., 2017).

Ester peak due to the carbonyl content was revealed at 1720 cm^{-1}, which confirms the chemical reaction between wood cell wall components and mDMDHEU. A similar result was found by Xie *et al.* (2005), who reported that, as the WPG of DMDHEU increased, the carbonyl content increased (1707 - 1733 cm^{-1}), this increase in absorption resulting from the carbonyl groups in DMDHEU. Correspondingly, the increase in the carbonyl content (1709 and 1726 cm^{-1}) was attributed to the carbonyl groups in DMDHEU (Pfeffer *et al*., 2012).

The peak of 750 cm^{-1} demonstrated the cis occurring, increasing of crystallinity, and resulting in more regular formation for molecules.

Ether peaks are shown at the bands of 1030, 1060, 1100 and 1240 cm^{-1}, the large breaking in ether peaks in treated samples occurred between 1030 and 1060 cm^{-1}. Control samples displayed the strongest peak in this region due to the high ether content. Yuan *et al*. (2013) obtained the highest band at 1050 cm^{-1} and stated that this resulted from the reaction between cellulose and DMDHEU. In addition, absorbance maxima at 1475 cm^{-1} and 1236 cm^{-1} corresponded to CH_2 deformation and C-O stretch vibration, respectively.

Breaking of long chain ether peaks increased the ratio of short chain ether peaks, which was shown at 1230 cm^{-1}. According to Pfeffer *et al*. (2012), absorbance maxima at 1237 cm^{-1} and 1232 cm^{-1} for Scots pine and beech, respectively, were associated with the C–O stretch vibration in the N-methylol group of DMDHEU.

3.5 Thermogravimetric analysis
3.5. Termogravimetrijska analiza

Figure 3 shows the weight changes due to the increased temperature in untreated and treated samples by thermogravimetric analysis.

According to the results obtained from the TG curve, the weight loss in control samples between 30 °C and 200 °C was 7 %, while it was 12 % for 15 % of mDMDHEU and 13 % for 30 % of mDMDHEU, respectively. Evaporation of moisture and initial decomposition of cellulose and hemicellulose up to 200 °C were associated with the initial weight loss (Doh *et al*., 2005). Shebani *et al*. (2008) referred the low weight loss below 100 °C to the evaporation of water, the apparent distinct loss between 200 and 400 °C, and approximately 75 % weight loss at 400 °C. They reported that the degradation between 218 °C and 260 °C, which was responsible for the decomposition of hemicelluloses and the slower decomposition of lignin, while the degradation above 350 °C was responsible for the degradation of cellulose.

Hydrolysis process, determined from room temperature up to 223 °C, indicates the releasing of non-combustible products, traces of inorganic compounds and water vapor and dehydration reaction of hemicelluloses as a result of destruction of hydroxyl groups (Shen *et al*., 2010; Okon *et al*., 2018).

In the present study, decreasing in weight loss was more apparent especially over 200 °C. Control

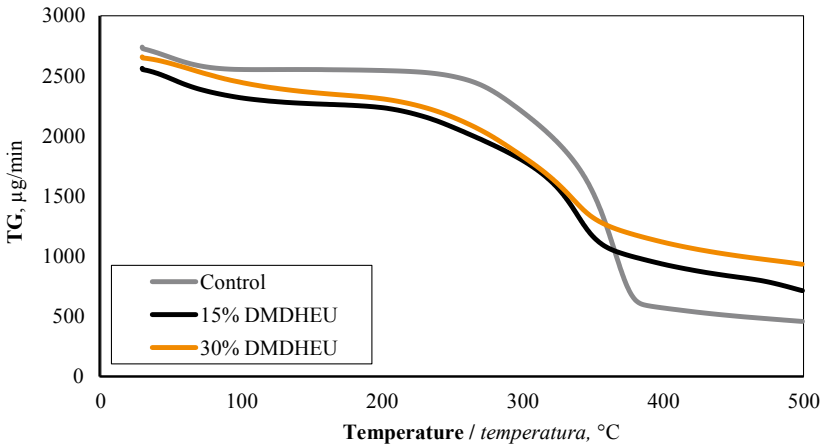

Figure 3 TG curve of control and modified samples at different temperatures
Slika 3. TG krivulja kontrolnih i modificiranih uzoraka pri različitim temperaturama

samples lost 65 % of their weight between 200 °C and 370 °C, while the weight loss was 54 % in the samples treated with 15 % of mDMDHEU and 48 % in samples with 30 % of mDMDHEU, respectively, in this temperature range.

According to Doh *et al*. (2005), cellulose and hemicellulose are major components, decomposed in the temperature range of 200 and 400 °C, and lignin causes the charring over 400 °C. In the last stage of TGA in our study, involving the temperatures range from 370 to 498 °C, weight loss in control samples was 48 %, whereas it was found to be 30 % and 23 % for mDMDHEU (15 and 30 %) treated samples. It was reported that in the last stage of thermal degradation up to 489 °C, decomposition of cellulose is around 80 % (Popescu *et al*., 2013; Okon *et al*., 2018).

It is concluded from Figure 4 that the treatment with mDMDHEU combined with magnesium chloride as a catalyst increased the thermal stability of poplar when compared to control samples. On the other hand, the increase in the *WPG* somewhat lowered the thermal decomposition. Magnesium chloride may have contributed to the improving of thermal stability.

The DTG curve shows the temperature at which the highest mass loss (maximum) occurs per minute for control and treated samples (Figure 4).

According to the DTG curve, the highest weight losses occurred at 366 °C in control samples, at 339 ° C in the samples impregnated with 15% of mDMDHEU, and at 335 °C in the samples with 30 % of mDMDHEU.

Results indicate that control samples were degraded at higher temperature than impregnated samples but resulted in greater weight loss as well. Although modified samples decompose at lower temperatures, their weight losses were less than those of control samples. It was reported that medium or higher concentration of DMDHEU improved the TGA of bamboo (Li *et al*., 2020).

Mass loss at approximately 330-340 °C was found higher in samples treated with 15 % mDMDHEU than with 30 %. Maximum weight loss was observed to be 383 µg in control samples, while it was 194 µg in treated samples with 15 % mDMDHEU and 132 µg with 30 % of mDMDHEU.

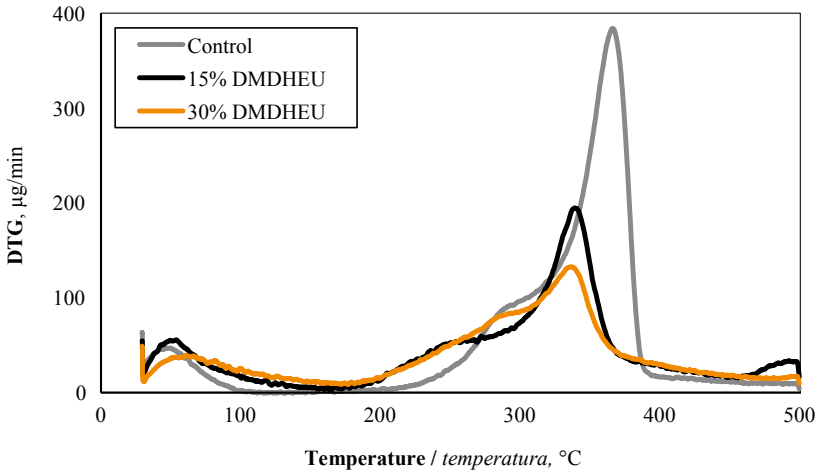

Figure 4 DTG curve of control and modified samples depending on temperature
Slika 4. DTG krivulja kontrolnih i modificiranih uzoraka u ovisnosti o temperaturi

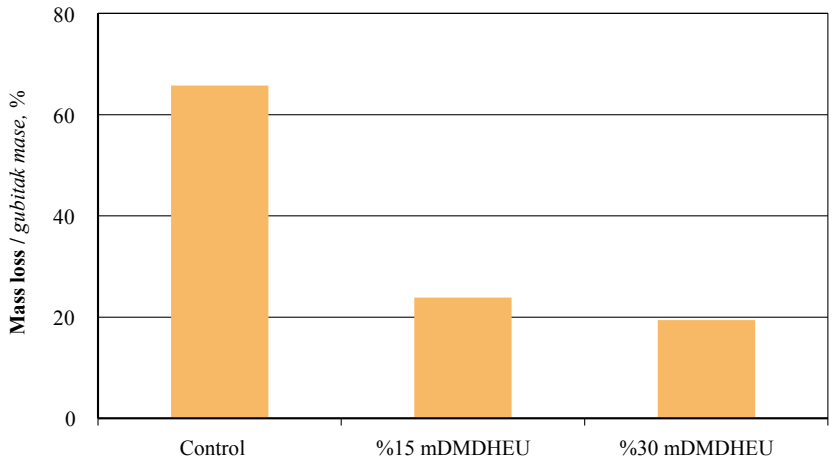

Figure 5 Mass loss of untreated (control) and mDMDHEU treated mini-blocks after 8 weeks of fungal incubation (*T. versicolor*)
Slika 5. Gubitak mase netretiranih (kontrolnih) blokova i miniblokova tretiranih mDMDHEU-om nakon osam tjedana inkubacije gljivom (*T. versicolor*)

3.6 Decay resistance
3.6. Otpornost prema propadanju

Durability of the untreated and treated samples against *T. versicolor* on malt-agar media is displayed in Figure 5.

Figure 5 indicates considerably higher mass loss in control samples than samples modified with mDMDHEU due to the activity of the decay fungus *T. versicolor*. Mass loss in control samples was about three times higher than in the samples treated with 30 % of mDMDHEU.

Mass loss was found lower with 30 % of mDMDHEU than 15 % in the poplar samples. Results reveal that increasing in the concentration of mDMDHEU moderately enhanced the decay resistance. The results of decay resistance was also in accordance with the WPG values of the 15 % mDMDHEU (25.18 % *WPG*) and 30 % mDMDHEU (30.87 % WPG).

Although the decay resistance of the samples treated with mDMDHEU was higher than that of the untreated samples, the mass loss of the treated samples was still above the expected value. It might be assumed that a reason for the loss of weight lies in the fact that some of the chemical reagent leached out during the incubation period. According to Emmerich *et al*. (2021), significant amounts of non-fixated chemicals were removed from the wood treated with DMDHEU and its derivatives when subjected to water leaching that may have affected the mass loss due to the fungal exposure.

In the earlier studies, good protection was achieved by wood modified with DMDHEU at about 10 % *WPG* against decay fungus *Coniophora puteana* in spite of the number of water-leaching cycles (Videlov, 1989). Van Acker *et al*. (1999) found significant reduction in weight loss depending on the treatment parameters rather than retention in their research involving the DMDHEU modification with pine and beech based on the EN113 and ENV807 tests. Verma *et al*. (2009) obtained good results with lower *WPG*, for example 15 % of *WPG* in beech and 10 % in pine, indicating that increasing in *WPG* increased the decay resistance to *T. versicolor* and *C. puteana*.

4 CONCLUSIONS
4. ZAKLJUČAK

Modification of poplar with mDMDHEU considerably improved the dimensional stability and reduced the tangential swelling. Compression strength was not affected by the modification process, even though it was improved with the increasing of mDMDHEU level, despite the decrease in bending strength. FTIR confirmed the chemical modification in the impregnated wood samples. Samples modified with mDMDHEU initially showed higher thermal degradation; however, at higher temperatures above 300 °C they gained thermal stability as compared to control samples. Modified samples showed substantially lower mass loss due to the decay by *T. Versicolor* in comparison to the unmodified wood samples.

Acknowledgements – Zahvala

This study was supported by Bartın University Scientific Research Projects Commission (Project No: 2018-FEN-A-007). The authors gratefully acknowledge the Latro Chemistry (Istanbul, Turkey) for providing chemicals.

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