

Accelerated Weathering of Coated and Uncoated Beech Wood Modified with Citric Acid

Ubrzano izlaganje vanjskim uvjetima bukovine modificirane limunskom kiselinom, neobrađene i obrađene lazurama

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ABSTRACT • Chemical modification of wood can minimize wood drawbacks in exterior application, such as moisture absorption, swelling and shrinkage, susceptibility to photodegradation and microbial attack. We modified a beech wood with 7.0 % water solution of citric acid and 6.5 % sodium-hypophosphite monohydrate (SHP) as a catalyst and investigated the color stability and weathering performance of coated and uncoated wood under accelerated weathering conditions. The modified and unmodified beech wood samples were coated with transparent water-borne stain and transparent solvent-borne stain, and with reference stain. The accelerated outdoor exposure was conducted in a QUV weathering tester (Q-Panel Company) equipped with UVA-340 florescent lamps for 56 days (1344 hours). The surface of samples was examined for color and gloss changes, adhesion and appearance of flaking, cracking, blistering and chalking. The overall color change (ΔE^*) of coated beech wood samples at the end of exposure was smaller in unmodified wood samples. The trend of gloss changes of modified and unmodified wood samples was very similar during the exposure. At the end of exposure unmodified beech wood samples exhibited better weathering performance than modified beech wood samples. In order to achieve the optimal protection of wood modified with citric acid the new type of finishes should be developed.

Key words: chemical modification, citric acid, QUV weathering, wood stain, beech wood

SAŽETAK • Kemijskom modifikacijom mogu se smanjiti nedostaci drva pri vanjskoj uporabi, kao što su upijanje vlage, bubrenje i utezanje, podložnost razgradnji pod utjecajem svjetlosti te pri napadu mikroorganizama. U ovom je istraživanju bukovina modificirana 7,0 %-tnom vodenom otopinom limunske kiseline uz dodatak 6,5% natrij-hidrofosfita monohidrata (SHP) kao katalizatora i istraživana stabilnost boje i postojanost pri ubrzanom izlaganju vanjskim utjecajima tako modificiranoga drva, neobrađenoga i obrađenog lazurama. Uzorci su površinski obrađeni transparentnom vodenom lazurama i transparentnom otapalnom lazurama, te referentnom lazurama. Ubrzano izlaganje vanjskim uvjetima bilo je provedeno u QUV uređaju (tvrtke Q-Panel), opremljenome s UVA-340 fluorescentnim svjetiljkama, u trajanju 56 dana (1344 sati). Na površini uzoraka mjerila se promjena boje i sjaja, određivala adhezija i provjeravala pojava ljuštenja, pukotina, mjehuranja i kredanja. Ukupna promjena boje (ΔE^*) obrađenih bukovih uzoraka na kraju izlaganja bila je manja od promjene na nemodificiranim uzorcima.

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Trend promjene sjaja modificiranih i nemodificiranih uzoraka bio je vrlo sličan tijekom izlaganja. Na kraju ubrzanog izlaganja vanjskim uvjetima nemodificirani su bukovi uzorci bili postojaniji nego modificirani. Kako bi se povećala površinska zaštita modificiranog drva, potrebno je posebno razviti novi tip premaza za drvo modificirano limunskom kiselinom.

Ključne riječi: kemijska modifikacija, limunska kiselina, QUV izlaganje vanjskim uvjetima, lazura za drvo, bukovina

1 INTRODUCTION

1. UVOD

In exterior application wood is susceptible to weathering and attack by microorganisms. Weathering is the general term used to define the slow degradation of materials exposed to the weather (Williams, 2005). The weathering process often results in discoloration, a physical deterioration of the wood surface, and loss of paint-retaining properties. Sunlight (especially UV and visible light) and water play a major role in weathering of wood.

The UV light causes photochemical degradation mainly in lignin polymer in the cell wall. As the lignin is degraded, water leaches out degradation products and washes away loosened surface cellulose fibers, causing a rough surface. Water also causes the wood to swell, and upon drying, checks and cracks develop that expose new material to UV degradation (Feist et al. 1991). Wood can be chemically modified to minimize specific problems such as moisture absorption, swelling and shrinkage, as well as susceptibility to photodegradation and microbial attack. It has been established that chemical modification of wood can also influence the behavior of wood under weathering and improve the performance of coatings (Plackett et al, 1992; Beckers et al, 1998; Evans et al, 2000; Xie et al, 2005, 2006, 2008; Tomažič et al, 2004; Temiz et al, 2007). Modification of fir and beech wood with citric acid has been shown to improve the dimensional stability and biological durability (Bischof Vukušić et al, 2006; Despot et al, 2008; Šefc et al, 2009). The citric acid crosslink with wood and enhance dimensional stability of the modified wood, which might help to improve the coating performance because the coating should be less stressed by movements of the substrate. However, the modification of wood may have an impact on wood wettability and adhesion of coatings (Podgorski et al, 2000; Hakkou et al, 2004; Petrič et al, 2007). The aim of this preliminary research was to investigate the color stability and weathering resistance of coated and uncoated wood modified with citric acid under accelerated weathering conditions.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

This study examined chemically modified (mark: M) and unmodified (mark: U) beech wood (*Fagus sylvatica* L.). Chemical modification was performed with 7.0 % water solution of citric acid and 6.5 % sodium-hypophosphite monohydrate (SHP) as a catalyst. Beech wood panels with radial surfaces and with dimen-

sions of (500x110x21) mm³ were conditioned at 20 °C and 65 % RH and then modified. The chemical modification consisted of impregnation followed by thermal process. The impregnation process was started with initial vacuum of 2 kPa without solution (1h). The vacuum vessel was then filled with the solution followed by pressure of 200 kPa (17h), vacuum of 2 kPa (3h), pressure of 200 kPa (2h), and at the end by vacuum of 2 kPa of samples without solution (0.5h). After impregnation the samples were gradually heated from 50 °C to 200 °C. The curing of the samples was carried out as follows: 50 °C (24 h), 75 °C (24 h), 100 °C (96 h), 110 °C (25 min), 120 °C (25 min), 130 °C (20 min), 140 °C (15 min), 150 °C (10 min), 160 °C (10 min), 170 °C (5 min), 180 °C (5 min), 190 °C (5 min) and 200 °C (5 min). The wood panels were planed and sawed to dimensions of (150x74x18) mm³ and then conditioned at 20 °C and 65 % RH. The average weight percentage grain (WPG) of sixteen modified samples was 5.8 %.

The samples were coated with two commercial wood stains: transparent water-borne stain (mark: W) and transparent solvent-borne stain (mark: S), and with reference stain (mark: R) according to HRN EN 927-3 provided by Belinka Belles d.o.o. All coatings were applied on wood manually by brush in three layers with a 24 hour drying time between layers. The amount of applied water-borne stain was 90 g/m² per layer and of solvent-borne and referent stains 50 g/m² per layer. The average dry film thickness was 50 μm for the water-borne and referent system, and 60 μm for the solvent-borne system. The dry film thickness was measured at five positions on two samples for each coating.

The accelerated outdoor exposure was conducted in a QUV weathering tester (Q-Panel Company) equipped with UVA-340 florescent lamps. Seven panels of each type of coated samples and two panels of uncoated chemically modified and unmodified samples were exposed to UV light directly at the distance of 5 cm for 56 days (1344 hours). The exposure cycle consisted of 24 h condensation period at (45±3) °C followed by 2.5 h UV irradiation period of 0.77 W/m²/nm at (60±3)°C and by 0.5 h water spray period of 6-7 l/min without irradiation. The periods of UV irradiation and water spray were alternately repeated 48 times. It took a whole week to complete the cycle (168 h).

The surface of samples was examined for color and gloss changes, adhesion and appearance of flaking, cracking, blistering and chalking before and after 2, 4, 7, 14, 28, 42 and 56 days of exposure.

Color changes were measured with a portable spectrophotometer Microflash 100d produced by Data-color (d/8° measuring geometry, 10° standard observer, D65 standard illuminate, xenon flash lamp source)

always on the same eight locations. The overall color change ΔE^* was measured using the CIE $L^*a^*b^*$ color measuring system by the following equation:

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \quad (1)$$

where ΔL^* , Δa^* and Δb^* are the differences between the initial and final values (before and after UV irradiation) of L^* , a^* and b^* , respectively.

Gloss changes were measured with a portable glossmeter produced by Erichsen, model 507. The measurements were made at the angle of 60° on the three locations parallel to the wood grain.

The examination of wood samples for appearance of cracking, blistering, flaking and chalking was performed according to HRN EN ISO 4628-2, 4, 5 and 6.

The adhesion of coatings was determined by cross-cut test according to HRN EN ISO 2409 at two positions on the samples.

3 RESULTS AND DISCUSSION 3. REZULTATI I RASPRAVA

The results of color and gloss changes are presented in Figure 1 and 2. As could be expected, the most prominent color changes were in uncoated wood sam-

ples. Modified uncoated wood changed the color more than unmodified uncoated wood during accelerated exposure. This could be expected because modification of wood with citric acid modifies cellulose not lignin, which is susceptible to photodegradation.

At the end of exposure the overall color change (ΔE^*) of coated wood samples was smaller in unmodified wood samples. After 56 days of exposure the samples coated with referent stain exhibited the smallest color change, followed by samples coated with solvent-borne stain, and samples coated with water-borne stain. Referent stain shows the best color stability because it contains pigments that protect wood from UV light. Table 1 shows the initial values of color parameter for all the samples. They were apparently different for modified and unmodified wood, and for coated and uncoated wood. After modification with citric acid, wood changed color due to the high temperature during thermocondensation and the decomposition of citric acid at high temperatures (Katović *et al*, 2005).

The trend of gloss changes of modified and unmodified wood samples was very similar during the exposure as can be seen in Figure 2. The gloss of uncoated modified and unmodified wood samples was basically unchanged during the exposure (Figure 2d).

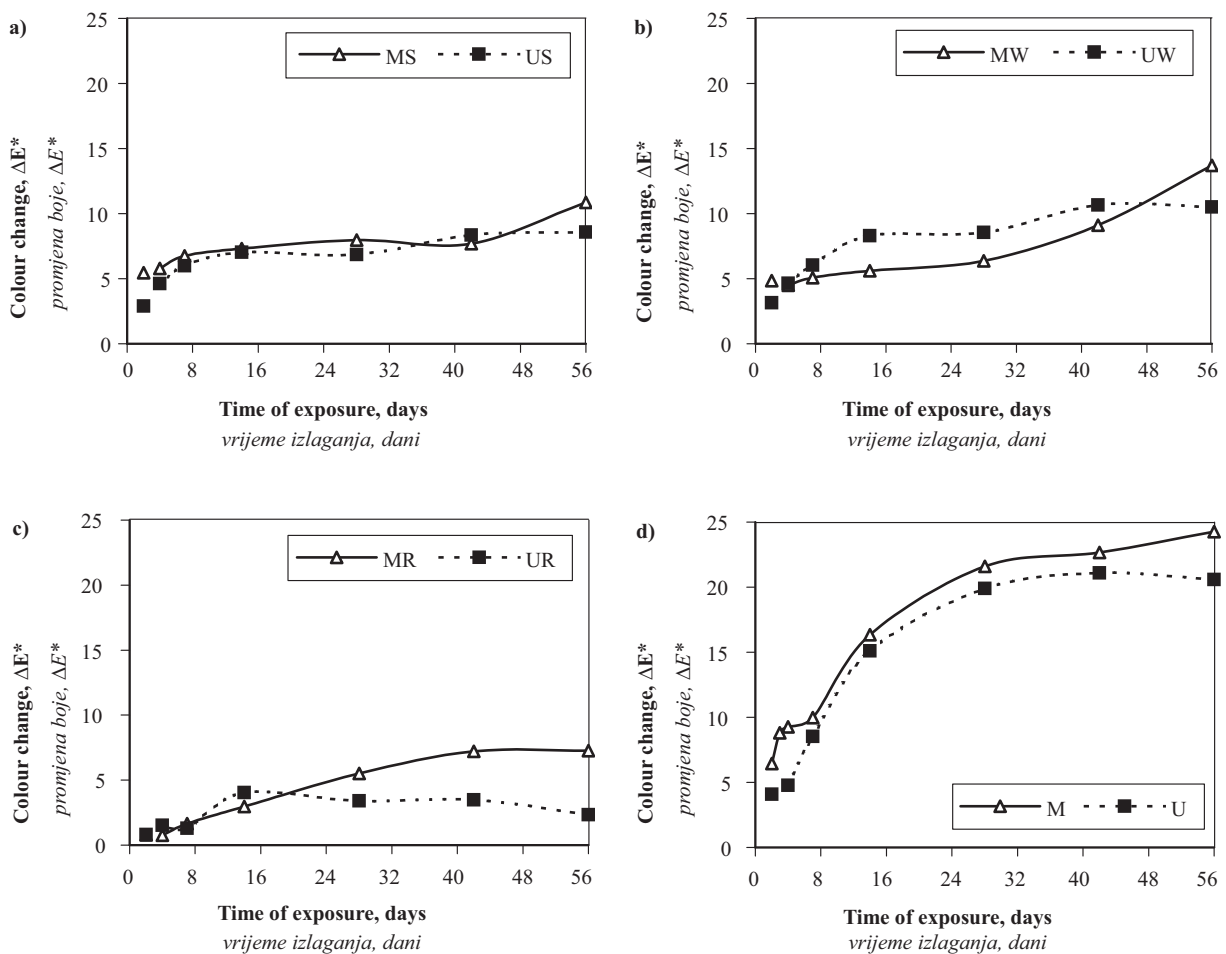


Figure 1 Color changes of beech wood modified with citric acid and coated with solvent-borne stain (a), water-borne stain (b), referent satin (c) and of unmodified and uncoated beech wood (d) during accelerated weathering

Slika 1. Promjene boje bukovine modificirane limunskom kiselinom i obrađene otapalnom lazutom (a), vodenom lazutom (b), referentnom lazutom (c), te nemodificirane, neobrađene bukovine (d)

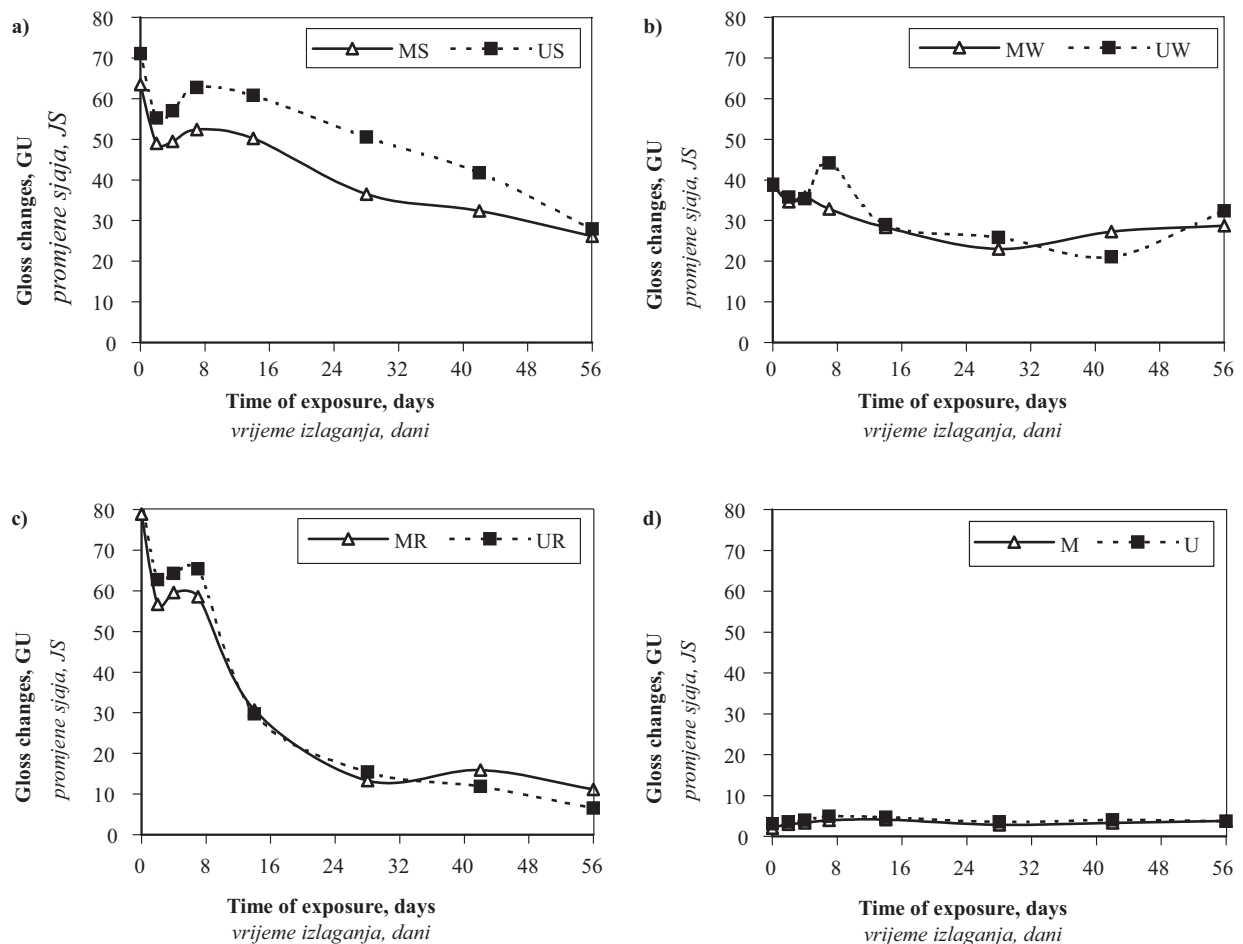


Figure 2 Gloss changes of beech wood modified with citric acid and coated with solvent-borne stain (a), water-borne stain (b), referent satin (c) and of unmodified uncoated beech wood (d) during accelerated weathering
Slika 2. Promjene sjaja bukovine modificirane limunskom kiselinom i obradene otapalnom lazuroom (a), vodenom lazuroom (b), referentnom lazuroom (c), te nemodificirane, neobrađene bukovine (d)

The referent stain exhibited the most prominent gloss change during the exposure (Figure 2c), followed by solvent-borne stain (Fig 2a) and water-borne stain (Figure 2b). The solvent-borne stain exhibited higher gloss changes between unmodified and modified wood samples than other stains.

The results of adhesion and visual assessment of surface properties after accelerated exposure are presented in Table 2.

According to the results presented in Table 2, it can be concluded that unmodified coated beech wood samples exhibited better weathering resistance than

Table 1 Color CIEL*a*b* parameters for beech wood samples before accelerated weathering

Tablica 1. Parametri boje CIEL*a*b* uzoraka bukovine prije ubrzanog izlaganja vanjskim uvjetima

Type of sample / Vrsta uzorka	Color parameters / Parametri boje ^a		
	L*	a*	b*
Uncoated / Neobrađen			
unmodified / nemodificiran	73.10 (3.72)	9.05 (1.82)	20.08 (2.44)
modified / modificiran	55.86 (5.35)	11.25 (0.78)	24.17 (2.10)
Coated with water-borne stain / Obraden transparentnom vodenom lazuroom			
unmodified / nemodificiran	73.69 (1.73)	7.05 (1.01)	22.20 (0.33)
modified / modificiran	59.30 (4.04)	8.32 (0.61)	14.07 (2.78)
Coated with solvent-borne stain / Obraden transparentnom otapalnom lazuroom			
unmodified / nemodificiran	70.00 (5.34)	9.80 (2.72)	26.78 (1.84)
modified / modificiran	47.12 (6.78)	14.22 (1.47)	16.39 (7.99)
Coated with referent stain / Obraden referentnom lazuroom			
unmodified / nemodificiran	37.73 (1.17)	29.02 (2.20)	18.97 (2.00)
modified / modificiran	34.91 (1.16)	21.41 (3.40)	14.20 (2.06)

^a Values in parenthesis are standard deviations. / Vrijednosti u zagradama standardne su devijacije.

Table 2 Determination of adhesion before and after 52-day accelerated weathering and visual assessment of surface properties after 52-day accelerated weathering

Tablica 2. Određivanje adhezije prije i nakon 52 dana ubrzanog izlaganja te vizualna procjena površine nakon 52 dana ubrzanog izlaganja

Type of sample / Vrsta uzorka	Class / Ocjena ^a					
	Before weathering Prije izlaganja	After 52-day weathering / Nakon 52 dana izlaganja				
	Adhesion Adhezija	Adhesion Adhezija	Cracking Pucanje	Chalking Kredanje	Flaking Ljuštenje	Blistering Mjehuranje
Uncoated / Neobrađen						
unmodified / nemodificiran	-	-	5	-	-	-
modified / modificiran	-	-	5	-	-	-
Coated with water-borne stain / Obrađen transparentnom vodenom lazurinom						
unmodified / nemodificiran	2	3	3	1	3	2
modified / modificiran	3	4	5	2	3	3
Coated with solvent-borne stain / Obrađen transparentnom otapalnom lazurinom						
unmodified / nemodificiran	1	1	4	2	2	2
modified / modificiran	2	3	4	1	0	2
Coated with referent stain / Obrađen referentnom lazurinom						
unmodified / nemodificiran	2	1	3	1	1	1
modified / modificiran	1	2	5	1	1	2

^aClass 0 – no changes, class 5 – the greatest changes. / Ocjena 0 – bez promjene, 5 – najveća promjena.

modified coated beech wood samples. During accelerated weathering, the cracking behavior of uncoated modified and unmodified wood samples was very similar. These results suggested that cross-linking reaction between cellulose and citric acid was not sufficient to stop the effects of weathering. At the end of the accelerated exposure the most prominent changes were the changes in adhesion and cracking. Of all tested stains, at the end of accelerated weathering the referent stain showed the best performance, followed by the solvent-borne stain and the water-borne stain. These results are opposite to majority of literature data concerning the weathering of chemically modified wood but there are also results that indicate that some methods of modification do not improve the weathering performance of wood. For example Evans (1998) established that esterification of wood with dicarboxylic acid anhydrides did not increase the resistance of wood to weathering. Podgorski and Roux (1998) showed that acetylation treatment did not improve the coating behavior during artificial weathering. Feist and Rowell (1982) also found that butylenes oxide- or butyl isocyanate-modified southern pine wood performed no better than untreated controls during accelerated outdoor weathering. Unfortunately there is no literature data regarding the coatability of wood modified with citric acid. Modification is generally expected to diminish adhesion by making the wood surface less polar and less porous resulting in worse coating wetting of wood and fewer chemical bonds between the two surfaces (Hunt *et al.*, 2007). Trajković *et al.* (2007) established the decrease of pH value, increase of wettability with water and decrease of total surface free energy after modification of beech wood with citric acid, but which of these properties contributed mostly to change adhesion should be further investigated.

4 CONCLUSIONS

4. ZAKLJUČCI

The modification of beech wood with citric acid did not improve the color stability of neither uncoated nor coated samples during accelerated weathering.

These preliminary results show that wood modification with citric acid and sodium-hypophosphite monohydrate (SHP) as catalyst negatively affects the performances of tested commercial water-borne and solvent-borne wood stains. This indicates that in future research the wood modified with citric acid should require the novel type of finishes developed especially for this type of substrate.

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