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# Effect of Acetylation and Accelerated Weathering of Nigerian Grown Rubberwood (*Hevea brasiliensis,* Müll. Arg.) on Equilibrium Moisture Content and Colour Change

Utjecaj acetilacije i ubrzanog izlaganja vremenskim utjecajima na ravnotežni sadržaj vode i promjenu boje drva kaučukovca uzgojenoga u Nigeriji (*Hevea brasiliensis*, Müll. Arg.)

# **PRELIMINARY PAPER**

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**ABSTRACT** • This study was conducted to investigate the effect of acetylation on equilibrium moisture content (EMC) of Nigerian-grown rubberwood and its effect on colour change in exposure of rubberwood to surface degradation through accelerated weathering. The samples were modified to two levels of acetylation, which yielded weight percent gain (WPG) of 7 % and 10 % after 8hr (8-hr Acetyl) and 48hr of acetylation (48-hr Acetyl), respectively. Accelerated weathering of unmodified (Ref) and acetylated wood was done using QUV-Accelerated Weathering Tester for four weeks. The unmodified and acetylated samples (weathered and unweathered) were oven-dried and conditioned in climate rooms at different relative humidity of 50 %, 65 % and 95 %, with samples being moved to each room after 14 days. Results showed that acetylation led to a significant decrease in equilibrium moisture content of rubberwood. After weathering, there was a decrease in EMC of rubberwood due to removal of hemicelluloses alongside the degraded lignin, and a slight increase in EMC of the acetylated wood. In terms of colour change, photo-bleaching of the acetylated samples was higher (10.46 for 48-hr Acetyl) after four weeks of weathering compared to the unmodified samples (6.43). Hence, the outcome of this study has shown that, although acetylation is effective in minimizing moisture ingress into wood, it resulted in photo-bleaching of the weathered samples. Additional surface coating is recommended to serve as a protective layer, preventing partial washing out of the acetyl groups, minimize photo-bleaching during weathering and prolong the aesthetic value of the wood especially in outdoor applications such as wall cladding and façade.

**KEYWORDS:** *rubberwood; equilibrium moisture content; moisture ratio; acetylation; accelerated weathering* 

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**SAŻETAK** • Ova je studija provedena kako bi se istražio utjecaj acetilacije na ravnotežni sadržaj vode (EMC) i na promjenu boje drva kaučukovca zbog površinske razgradnje prouzročene ubrzanim izlaganjem vremenskim utjecajima. Drvo je uzgojeno u Nigeriji, a uzorci su modificirani acetilacijom u dva stupnja, što je nakon osam sati (8-hr Acetyl) odnosno 48 sati acetilacije (48-hr Acetyl) rezultiralo povećanjem mase (WPG) od 7 i 10 %. Ubrzano izlaganje nemodificiranoga (Ref) i acetiliranog drva vremenskim utjecajima provedeno je u QUV uređaju tijekom četiri tjedna. Nemodificirani i acetilirani uzorci (izlagani i neizlagani) sušeni su u sušioniku i kondicionirani u klimatskim prostorijama pri različitim relativnim vlažnostima zraka, od 50, 65 i 95 %, a uzorci su nakon 14 dana premještani u svaku od prostorija. Rezultati su pokazali da je acetilacija dovela do znatnog smanjenja ravnotežnog sadržaja vode u drvu kaučukovca. Nakon izlaganja vremenskim utjecajima EMC drva kaučukovca smanjio se zbog nestajanja hemiceluloze uz razgradnju lignina, a EMC acetiliranog drva blago se povećao. Kad je riječ o promjeni boje, izbjeljivanje je nakon četiri tjedna izlaganja vremenskim utjecajima bilo veće na acetiliranim uzorcima (10,46 za 48-hr Acetyl) nego na nemodificiranima (6,43). Stoga je ovo istraživanje pokazalo da je acetilacija, iako je učinkovita glede smanjenja prodora vlage u drvo, rezultirala izbjeljivanjem uzoraka ubrzano izloženih vremenskim utjecajima. Stoga se preporučuje primjena površinskog premaza koji će služiti kao zaštitni sloj, sprječavati djelomično ispiranje acetilnih grupa, smanjiti izbjeljivanje tijekom izlaganja drva vremenskim utjecajima i dulje očuvati njegovu estetsku vrijednost, posebice u vanjskim uvjetima, primjerice kad je drvo kaučukovca upotrijebljeno kao zidna obloga ili fasada.

KLJUČNE RIJEČI: drvo kaučukovca; ravnotežni sadržaj vode; omjer ravnotežnog sadržaja vode; acetilacija; ubrzano izlaganje vremenskim utjecajima

# **1 INTRODUCTION**

#### 1. UVOD

Hevea brasiliensis (rubberwood), though previously known as an agricultural product, is fast becoming an acceptable raw material for lightweight constructions and in the furniture industry (de Junior et al., 2015). Although the major aim of establishing rubber tree plantations is for the production of latex, a raw material in the rubber and tyre industries, wood from rubber trees is also an acceptable source of sawn-timber production. After the period of latex production (usually around 25-30 years), rubber tree plantations become unprofitable for the original purpose. At this point, the trees are previously converted to fuelwood or cleared to start a new plantation. Teoh et al. (2012) noted that nowadays, with increasing knowledge about the potentials of rubberwood, the trees are harvested and converted to sawn-timber for various purposes such as construction, furniture production and manufacture of wood-based panel products. In countries such as Malaysia, Indonesia, and Thailand, production of rubberwood has formed a major drive in the success of their wood industries, and this has made a great impact on their economy for several decades (Shigematsu et al., 2011, Shigematsu et al., 2013). However, in Nigeria, the economic and environmental potential of rubberwood is yet to be explored to its maximum capacity. This is due to the dependence on wood supply from the natural forest, whose resource has been overexplored and many durable species are currently becoming or are already endangered.

Rubberwood is a lightweight material with uniform colour that varies from white to pale cream at harvest, but afterwards may change to light straw or light brown. The sapwood is not distinguished from the heartwood, and its texture is homogeneous but varies from moderately coarse to coarse texture (Killmann and Hong, 2000; Lim et al., 2002). The major positive attributes of rubberwood include its ease of sawing, slicing into veneer and turning on lathe machines. On the other hand, rubberwood has quite a number of shortcomings related to its proneness to seasoning defects such as twisting, cupping, bowing and checks; and its non-durability, which makes it susceptible to insects and fungi attacks (Balsiger et al., 2000) and surface degradation due to weathering (Olaniran et al., 2019) when used outdoor. For this reason, rubberwood requires treatments that can minimize its interaction with moisture, thereby making it hydrophobic, and subsequently influence biotic and abiotic agents and enhance its service life. One of the treatments that have been successfully used in improving the hydrophobic properties of wood for decades is the acetylation process. Previous studies have shown that acetylation enhances the hydrophobic properties and improves the durability of several wood species to biological deterioration and weathering (Larsson-Brelid et al., 2000; Chang and Chang, 2001; Mohebby and Militz, 2010).

Acetylation process involves the reaction of acetic anhydride with wood polymers through esterification reactions, where the accessible hydroxyl groups in the wood cell wall undergo a single addition reaction with acetyl groups (Rowell, 1983). This single addition process, where an acetyl group reacts with a hydroxyl group without polymerization (Rowell, 2014), leading to a wood material with higher hydrophobic property and dimensional stability, was compared to the unmodified wood (Gerardin, 2016; Sandberg *et al.*, 2017). Aside from its effect on dimensional stability, acetylation of wood has been reported to lower the photodegradation and weathering of wood. In studies by Pandey and Pitman (2002), and Pu and Ragauskas (2005), acetylation was found to improve the weathering performance of wood. This improvement was made possible by the stabilization of lignin, and reduction of coloured chromophore formation and consequently a reduction in photo-yellowing of wood.

To make rubberwood suitable for outdoor applications such as cladding and facades, its susceptibility to surface degradation due exposure of wood to ultraviolet rays, degradation of lignin on rubberwood surface and subsequent washing away of the degraded lignin from the wood surface by water in form of rain or snow can be minimized by acetylation as previously demonstrated for other species in previous studies. Hence, the purpose of this study is to investigate the role that acetylation method of wood modification can play in minimizing the surface degradation of rubberwood essentially through reduction in equilibrium moisture content of rubberwood. This may further help to prevent the attack of rubberwood by fungi, as the moisture content of the treated wood will become too low to support their growth on the wood surface.

#### 2 MATERIALS AND METHODS 2. MATERIJALI I METODE

The rubber tree used for this study was harvested from a private plantation at Legbogbo village, Ode-Irele Ondo State Nigeria with the following coordinates: Lat. 06.59308°N, Long. 004.89078°E. At the time this study was carried out, the trees in the plantation were well over 30 years old. They yielded no more latex, leading to the abandonment of the plantation. A tree stand was harvested from the plantation at 0.5 m above the buttress, and two boles were selected at diameter at breast height (dbh). The harvested boles were processed into planks of dimension 550 mm × 120 mm × 40 mm, pre-dried in a kiln at 105 °C for three days to lower their moisture content and prepare them for shipping to the laboratory located at Wood Material Science Laboratories at ETH Zurich, Switzerland. On arrival, the wood samples were stacked in the climate room at 65 % relative humidity for a total of 6 months before the commencement of the experiment.

Rubberwood samples were further processed into dimensions of 50 mm  $\times$  15 mm  $\times$  1mm (L-T-R) to produce 180 samples required for the experiment. Thereafter, the samples were grouped into three groups including the unmodified samples (Ref), samples for 8-hr acetylation (8-hr Acetyl) and samples for 48-hr acetylation (48-hr Acetyl). Each of the three groups were further divided into four groups consisting of 15 samples each for the unweathered samples and samples subjected to accelerated weathering for two, three and four weeks.

The process for chemical modification started with drying of the wood samples at 65 °C for 48 hours. Drying at this low temperature was carried out to prevent rapid drying of the samples and occurrence of drying defects such as cracks on the samples. The dried samples were placed in a flask containing dimethylformamide (DMF) and acetic anhydride (50 v/v%). To enhance homogeneous penetration of the reaction chemicals, a vacuum impregnation was performed for 18 hours, and the mixture was heated to a temperature of 70 °C under reflux; the reaction was maintained for 8 hours and 48 hours. After treatment, the acetylated samples were washed in acetone for five days, with the solution being changed twice a day to remove the excess acetic acid. The treated samples were dried at 65 °C for 48 hours and the weight percent gain was determined. The average weight percent gain for the treated samples was 7 % for samples acetylated for 8 hours and 10 % for samples acetylated for 48 hours.

The treated and reference samples were weathered under accelerated conditions with QUV Accelerated Weathering Tester (Q-Lab Miami, USA), equipped with heating compartments, UV-A 340 lamps and water spray. The procedure for weathering followed a single test cycle of 2hr 30 minutes of UV exposure, 30 minutes of water spray, and a panel temperature of 30 °C. Before and after weathering, colour measurements were performed with Chroma Meter (CR-200), Minolta USA. Colour change in the weathered samples was determined according to CIE standard colour space  $L^*a^*b^*$ , and the total colour change was calculated according to Eq. 1:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

Where: *L* is the lightness in the range of 0 - 100;  $+a^*$  and  $+b^*$  are the chromatic indices representing red and yellow, respectively,  $-a^*$  and  $-b^*$  represent green and blue direction, respectively.

The equilibrium moisture content of the weathered and unweathered samples was reached in climate rooms at 50 %, 65 % and 95 % RH after oven-drying the samples to a constant weight at 65 °C for 48 hours. The increase in weight due to moisture sorption in the climate rooms was measured consistently until the samples attained constant weights. After this, the wood samples were moved from one climate room to another after 14 days, and the equilibrium moisture content in each climate room was determined. The moisture ratio of acetylated wood ( $MR_A$ ) was calculated as a ratio of the equilibrium moisture content of the acetylated rubberwood and the unmodified samples (Thygesen *et al.*, 2010). This will help to reveal the percentage of moisture in the unmodified to that in the modified wood, thus revealing the effectiveness of the modifying agent. The data obtained were analysed using the SPSS Software, V20.0 (IBM Corporations, USA) to perform the analysis of variance (ANOVA) and determine the significant differences among the treatments.

## **3 RESULTS AND DISCUSSION**

# 3. REZULTATI I RASPRAVA

#### 3.1 Influence of acetylation on equilibrium moisture content of rubberwood in unweathered state

#### 3.1. Utjecaj acetilacije na ravnotežni sadržaj vode neizloženog drva kaučukovca

The equilibrium moisture content of unmodified and acetylated rubberwood is shown in Figure 1. In the unmodified and unweathered state, the moisture content of rubberwood is 5.3 %, 10.2 % and 17.5 % at the relative humidity of 50 %, 65 % and 95 %, respectively. Subsequently, after 8-hour acetylation (8hr-Acetyl/W0), the moisture content of rubberwood decreased to 2.73 %, 5.39 % and 8.74 %. After 48-hour acetylated rubberwood further decreased to 2.49 %, 5.03 % and 8.35 % at the observed relative humidity (Figure 1b and c). The effect of the level of acetylation and varying level of exposure to relative humidity is significant on the equilibrium moisture content of acetylated rubberwood (Table 1). The goal of the acetylation method is to reduce moisture uptake, thereby improving the dimensional stability and enhancing wood durability (Thygesen et al., 2010), and to decay fungi and non-biological agencts such as the ultra-violet rays and weathering. According to Rowell (2014), through covalent bond formation, acetyl groups are substituted with hydroxyl groups on the sorption sites in the cell wall; this directly blocks the hydroxyl groups from gaining access to moisture. For the modification of rubberwood, acetylation has proved to be effective in reducing the moisture content of rubberwood even at low weight percent gain after treatment. Comparison of moisture ratio  $(MR_{\star})$  of acetylated rubberwood at two levels of WPG showed that the effect on moisture ratio was not significantly different (Table 2). This means that the difference in the WPG of acetylated rubberwood does not significantly influence the moisture ratio (0.53 for 8hr-Acetyl, and 0.5 for 48hr-Acetyl). This  $MR_{A}$  is lower (as shown in Table 3) compared to the previous report on acetylation of Corsican pine reported by Papadopoulos and Hill (2003) with MR in the range of 0.58-0.60, and even at a higher WPG of 15.58 as later reported in the work of Thygesen et al., (2010). Moisture ratio was also estimated by Thygesen et al. (2010) for furfurylated Norway spruce and found that the moisture ratio of furfurylated wood was 0.80, showing that the modified wood can hold as much water as the untreated wood. This indicated that, although a higher WPG can be obtained by furfurylation than by acetylation, the latter is more effective in minimizing moisture

 Table 1 Analysis of variance for equilibrium moisture content of acetylated rubberwood

 Tablica 1. Analiza varijance ravnotežnog sadržaja vode acetiliranog drva kaučukovca

Equilibrium moisture content (EMC) / Ravnotežni sadržaj vode (EMC)							
Source of variation Izvor varijacije	<b>Sum of squares</b> Zbroj kvadrata	df	<b>Mean square</b> Srednja vrijednost kvadrata	F-crit.	<b>p-value</b> p-vrijednost		
Acetylation level stupanj acetilacije	572.308	2	286.153	161.488	0.000*		
Relative humidity relativna vlažnost	966.223	2	483.111	272.640	0.000*		
Error / greška	150.618		1.772				
Total / ukupno	1689.146						

\*significant at *p*-value  $\leq 0.05$  / *značajno pri p-vrijednosti*  $\leq 0.05$ 

**Table 2** Analysis of variance for moisture ratio  $(MR_A)$  of acetylated rubberwood **Tablica 2.** Analiza varijance omjera ravnotežnih sadržaja vode acetiliranoga i nemodificiranog drva kaučukovca

<b>Moisture ratio</b> ( $MR_A$ ) / Omjer ravnotežnih sadržaja vode ( $MR_A$ )							
Source / Izvor	<b>Sum of squares</b> Zbroj kvadrata	df	<b>Mean square</b> Srednja vrijednost kvadrata	<b>F-value</b> <i>F-vrijednost</i>	Significance Značajnost		
Acetylation level (AL) stupanj acetilacije (AL)	0.013	1	0.013	2.614	0.112 ns		
Relative Humidity (RH) relativna vlažnost (RH)	0.008	2	0.004	0.835	0.440 ns		
AL*RH	0.001	2	0.000	0.087	0.916 ns		
Error / greška	0.267		0.005				
Total / ukupno	0.289						

ns - not significant at p-value >0.05 / nije značajno pri p-vrijednosti > 0,05

<b>Table 3</b> Mean values of equilibrium moisture content ( <i>EMC</i> ) and moisture ratio ( $MR_{\lambda}$ ) of acetylated rubberwood				
Tablica 3. Srednje vrijednosti ravnotežnog sadržaja vode (EMS) acetiliranog drva kaučukovca i omjera ravnotežnog sadržaja				
vode $(MR_{A})$ acetiliranoga i nemodificiranog drva kaučukovca				

Acetylation level Stupanj acetilacije	Relative humidity Relativna vlažnost	<i>EMC</i> , %	MR <sub>A</sub>
Unmodified Nemodificirano drvo	50	$5.08 \pm 0.41$	-
	65	$10.03 \pm 0.58$	-
	95	$17.25 \pm 0.36$	-
8hr-Acetyl (7 % WPG)	50	$2.73 \pm 0.38$	$0.54 \pm 0.07$
	65	$5.36 \pm 0.56$	$0.54 \pm 0.07$
	95	$8.76 \pm 0.47$	$0.51 \pm 0.02$
48hr-Acetyl (10 % <i>WPG</i> )	50	$2.57 \pm 0.49$	$0.51 \pm 0.11$
	65	$4.95 \pm 0.49$	$0.49 \pm 0.06$
	95	8.33 ± 0.31	$0.49 \pm 0.02$

interaction with wood. Analysis of variance revealed that  $MR_A$  of acetylated rubberwood among those observed is also not significantly different, and this is consistent with previous studies.

The implication of this result is that sufficient bulking of the cell wall was achieved for acetylated wood by acetyl group despite the low *WPG*, and consequently a significant difference was observed in reduction in equilibrium moisture content of acetylated rubberwood compared to the unmodified samples.

#### 3.2 Effect of weathering on equilibrium moisture content of unmodified and acetylated rubberwood

## 3.2. Utjecaj izlaganja vremenskim utjecajima na ravnotežni sadržaj vode nemodificiranoga i acetiliranog drva kaučukovca

Unmodified and modified wood used in outdoor application are subjected to weathering, which involves the exposure of wood to ultraviolet rays. The effect of UV on the wood surface leads to degradation of lignin, which is thereafter washed out with water either in form of rain or snow. In the present study, unmodified rubberwood weathered under accelerated conditions showed continuous decrease in moisture content as the weathering period progressed from two to four weeks (Figure 1a). The equilibrium moisture content of unmodified, weathered rubberwood at the observed relative humidity is 4.1 %, 7.6 % and 14 %, respectiely at the end of the four-week period of weathering. These moisture content values of unmodified, weathered rubberwood decreased from the initial moisture content of unmodified and unweathered rubberwood of 5.3 %, 10.3 % and 17.5 %. The decrease in *EMC* of the unmodified rubberwood after weathering can be attributed to washing out of the degraded lignin alongside hemicelluloses, which is closely associated with lignin in the cell wall. These findings were previously observed by Feist et al. (1991), who found out that the exposure of unmodified aspen to weathering for 700 hours led to the degradation of lignin and hemicelluloses, leaving the surface with the inaccessible and moisture resistant cellulose. The attraction of moisture to wood is enhanced by wood polymers (cellulose, hemicelluloses and lignin) due to their ability to form hydrogen bonds with water molecules. Of these wood polymers, hemicelluloses were reported to have the highest proportion of sorption sites. For rubberwood acetylated for 8-hours, moisture content of acetylated rubberwood gradually decreased to 2.9 %, 6.1 %, and 11.3 % at the observed relative humidity after four weeks of exposure to accelerated weathering. These values are higher, compared to rubberwood acetylated for 48 hours with moisture content values of 2.6 %, 5.6 % and 9.9 % at the observed relative humidity. These results indicate that the interaction between moisture and acetylated rubberwood decreased as the acetyl groups blocked the free hydroxyl groups, which should be available to aid weathering of rubberwood surface. However, there seems to be a slight increase in moisture content for weathered acetylated wood compared to the unweathered acetylated wood.

This was clearly observed in rubberwood acetylated for 8-hours, and slightly in samples acetylated for 48-hours, with a higher WPG when compared to the equilibrium moisture content of the unweathered samples. Increase in moisture content observed in weathered acetylated wood may occur because a part of the acetylated products is washed out with the UV-degraded lignin, which is closely related to hemicelluloses in the modified cell wall. Previous studies on Fourier Transform Infrared Spectroscopy (FT-IR) of weathered modified and unmodified rubberwood showed decreasing intensities at spectra bands of 1505 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> (stretching vibration of aromatic C=C of lignin); and 1740 cm<sup>-1</sup> corresponding to vibration of unconjugated C=O in xylan (Pandey and Pitman, 2002; Olaniran et al., 2019). It can be inferred from these studies that removal of lignin during weathering is often accompanied by a significant loss in hemicelluloses content in the unmodified wood and only slight in the modified samples.

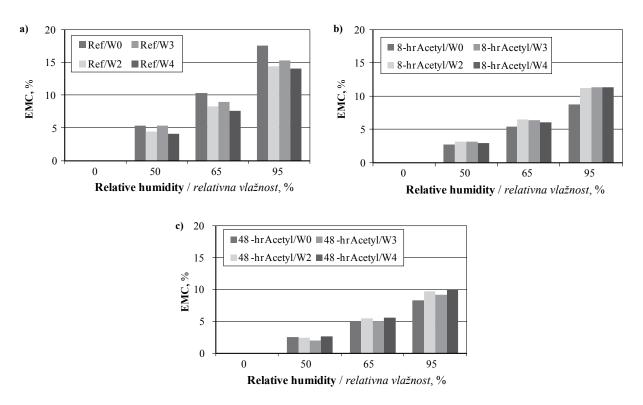


Figure 1 Equilibrium moisture content of (a) unmodified samples, (b) acetylated rubberwood at 8 hours of acetylation, (c) acetylated rubberwood at 48 hours of acetylation after exposure to accelerated weathering (W0 – samples not exposed to weathering, W2 – samples exposed for two weeks, W3 – samples exposed for three weeks, W4 – samples exposed for four weeks)

**Slika 1.** Ravnotežni sadržaj vode (a) nemodificiranih uzoraka, (b) acetiliranog drva kaučukovca pri 8-satnoj acetilaciji i (c) acetiliranog drva kaučukovca pri 48-satnoj acetilaciji nakon ubrzanog izlaganja vremenskim utjecajima (W0 – neizloženi uzorci, W2 – uzorci izloženi dva tjedna, W3 – uzorci izloženi tri tjedna, W4 – uzorci izloženi četiri tjedna)

#### 3.3 Colour change in unmodified and acetylated rubberwood

## 3.3. Promjena boje nemodificiranoga i acetiliranog drva kaučukovca

Base on the above discussion, there are varying degrees of accessibility of moisture in unmodified wood and acetylated wood. Moisture in form of liquid water is a major factor that aids weathering of wood surfaces. The ultraviolet rays react with and break down the lignin polymer resulting in a colour change of wood surfaces. With the presence of water, the degraded lignin is washed out of the wood surface, leading to a total colour change. As shown in Figure 2 (a, b and c), the lightness index,  $L^*$  of the unmodified (Ref) and acetylated samples increased through the fourweek exposure to weathering, whereas, acetylated samples recorded higher values of lightness compared to the unmodified samples (Figure 2d). The lightness index was found to decrease in all the exposed samples after the third week of exposure to weathering. Increase in lightness index was reported to be characteristic of acetylated wood in previous studies (Salla et al. 2012). Increase in lightness of the unmodified rubberwood observed in this study is contrary to the report of Salla et al. (2012), while persistent and higher lightness in acetylated wood is attributed to the photobleaching of the modified surface.

Contrary to the previous observation on the lightness index, no yellowing was found in the reference samples or in the acetylated samples as shown by negative values in Figure 2d. The negative values obtained for yellowing index further confirm that photobleaching occurred in the weathered samples including the reference, contrary to the outcome of previous studies where increased yellowing was observed in the weathered samples all throughout the period of exposure to weathering (Salla et al., 2012; Guo et al., 2017). However, the reason for non-yellowing of the reference samples observed in this study is not yet clear. On the other hand, it is clear as previously reported by Olaniran et al. (2019) that surface degradation of rubberwood under accelerated weathering was prevented by acetylation as no crack, twisting or cupping were observed throughout the exposure period when compared to the reference samples. Therefore, this suggests that, though it is possible to limit moisture interaction and consequently surface degradation in weathered rubberwood through acetylation, resistance to photo-bleaching of acetylated wood surface needs to be improved. This may be achieved by adding another protective layer to

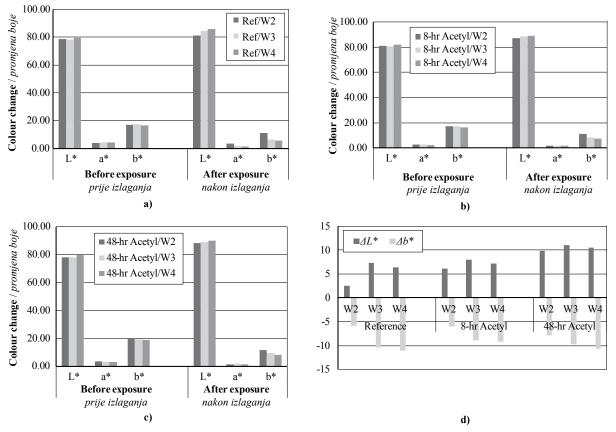


Figure 2 Colour change in rubberwood showing lightness ( $L^*$ ), redness ( $a^*$ ), yellowness ( $b^*$ ) indices for the (a) unmodified samples, (b) samples acetylated for 8 hours, (c) samples acetylated for 48 hours, and (d) shows the change in lightness ( $\Delta L^*$ ) and yellowness ( $\Delta b^*$ )

Slika 2. Promjena boje drva kaučukovca prikazana na temelju parametara svijetljenja ( $L^*$ ), crvenjenja ( $a^*$ ) i žućenja ( $b^*$ ) za (a) nemodificirane uzorke, (b) uzorke acetilirane 8 sati i (c) uzorke acetilirane 48 sati te (d) prikaz promjene svjetline ( $\Delta L^*$ ) i žućenja ( $\Delta b^*$ )

minimize the observed colour change. This additional protection can be achieved by deposition of protective layer on the acetylated wood. Previous researches have experimented on possible layers such as titanium diox-ide/cerium (TiO<sub>2</sub>/Ce) xerogel and zinc oxide (ZnO) nanostructures (Guo *et al.*, 2016; Guo *et al.*, 2017), which can be deposited on wood surface to preserve its aesthetic value especially when the wood is intended for outdoor use.

# 4 CONCLUSIONS

#### 4. ZAKLJUČAK

This study has shown the effectiveness of acetylation on the equilibrium moisture content and colour change in rubberwood exposed to accelerated weathering. The moisture content ratio of the acetylated wood has revealed that even at low *WPG*s of acetylated rubberwood, the modification is still effective in minimizing moisture ingress. In the process of weathering, however, the increasing lightness of weathered acetylated rubberwood gives an indication that its natural aesthetics may not be completely preserved only by acetylation. Hence, it is necessary to apply additional layers of nano-coating with compounds such as ZnO, as demonstrated for other wood species in previous studies, to preserve the natural beauty of rubberwood surface.

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## **5 REFERENCES**

#### 5. LITERATURA

- Balsiger, J.; Bahdon, J.; Whiteman, A., 2000: Asia-pacific forestry sector outlook study: the utilization, processing and demand for rubberwood as a source of wood supply. FAO, Bangkok.
- Chang, S. T.; Chang, H. T., 2001: Comparisons of the photostability of esterified wood. Polymer Degradation and Stability, 71: 261-266.

- de Junior, J. E.; Ohto, H.; da Silva, J. M.; Palma, L. L.; Ballarin, H. A. L., 2015: Potential of rubberwood (*Hevea brasiliensis*) for structural use after the period of latex extraction: a case study in Brazil. Journal of Wood Science, 61: 384-390. https://doi.org/10.1007/s10086-015-1478-7
- Feist, W. C.; Rowell, R. M.; Youngquist, J. A., 1991: Weathering and finish performance of acetylated aspen fiberboard. Wood and Fiber Science, 23: 260-272.
- Gerardin, P., 2016: New alternatives for wood preservation based on thermal and chemical modification of wood – a review. Annals of Forest Science 73: 559-570. https:// doi.org/10.1007/s13595-015-0531-4
- Guo, H.; Fuchs, P.; Cabane, E.; Michen, B.; Hagendorfer, H.; Romanyuk, Y. E.; Burgert, I., 2016: UV-protection of wood surfaces by controlled morphology fine-tuning of ZnO nanostructures. Holzforschung, 70 (8): 699-708. https://doi.org/10.1515/hf-2015-0185
- Guo, H.; Klose, D.; Hou, Y.; Jeschke, G.; Burgert, I., 2017: Highly efficient UV protection of the biomaterial wood by a transparent TiO2/Ce xerogel. ACS Applied Materials & Interfaces, 9 (44): 39040-39047. https://doi. org/10.1021/acsami.7b12574
- Killmann, W.; Hong, L. T., 2000: Rubberwood: the success of an agricultural by-product. Unasylva, 51: 66-72.
- Larsson-Brelid, P.; Simonson, R.; Bergman, O.; Nilsson, T., 2000: Resistance of acetylated wood to biological degradation. Holz als Roh- und Werkstoff, 58 (5): 331-337. https://doi.org/10.1007/s001070050439
- Lim, S.; Ten Choo, K.; Gan, K., 2002: The characteristics, properties and uses of plantation timbers-rubberwood and acacia mangium. Timber Technology Centre, FRIM, 2002.
- Mohebby, B.; Militz, H., 2010: Microbial attack of acetylated wood in field soil trials. International Biodeterioration and Biodegradation, 64: 41-50. https://doi. org/10.1016/j.ibiod.2009.10.005
- Olaniran, S. O.; Etienne, C.; Keplinger, T.; Olufemi, B.; Rüggeberg, M., 2019: Mechanical behaviour of acetylated rubber wood subjected to artificial weathering. Holzforschung, 73: 1005-1016. https://doi.org/10.1515/ hf-2018-0274

- Pandey, K. K.; Pitman, A. J., 2002: Weathering characteristics of modified rubberwood (*Hevea brasiliensis*). Journal of Applied Polymer Science, 85: 622-635. https://doi.org/10.1002/app.10667
- Pu, Y.; Ragauskas, A. J., 2005: Structural analysis of acetylated hardwood lignins and their photoyellowing properties. Canadian Journal of Chemistry, 83: 2132-2139. https://doi.org/10.1139/v05-231
- Rowell, R. M., 1983: Chemical modification of wood: A review. Commonwealth Forestry Bureau, Oxford, England, 6: 363-382.
- Rowell, R. M., 2014: Acetylation of wood A review. International Journal of Lignocellulosic Products, 1 (1): 1-27.
- Salla, J.; Pandey, K. K.; Prakash, G. K.; Mahadevan, K. M., 2012: Photobleaching and Dimensional Stability of Rubber Wood Esterified by Fatty Acid Chlorides. Journal of Wood Chemistry and Technology, 32 (2): 121-136 https://doi.org/10.1080/02773813.2011.62466
- Sandberg, D.; Kutnar, A.; Mantanis, G., 2017: Wood modification technologies – a review. iForest, 10: 895-908. https://doi.org/10.3832/ifor2380-010
- Shigematsu, A.; Mizoue, N.; Kajisa, T.; Yoshida, S., 2011: Importance of rubberwood in wood export of Malaysia and Thailand. New Forest, 41: 179-189.
- Shigematsu, A.; Mizoue, N.; Kakada, K.; Muthavy, P.; Kajisa, T.; Yoshida, S., 2013: Financial potential of rubber plantations considering rubberwood production: wood and crop production nexus. Biomass Bioenergy, 49: 131-142.
- Teoh, Y. P.; Don, M. M.; Ujang, S., 2011: Assessment of the properties, utilization, and preservation of rubberwood (*Hevea brasiliensis*): a case study in Malaysia. Journal Wood Science, 57: 255-266. https://doi. org/10.1007/s10086-011-1173-2
- 22. Thygesen, L. G.; Engelund, E. T.; Hoffmeyer, P., 2010: Water sorption in wood and modified wood at high values of relative humidity, Part I: results for untreated, acetylated, and furfurylated Norway spruce. Holzforschung, 64 (3): 315-323. https://doi.org/10.1515/ hf.2010.044

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