PHOTOSTABILIZATION OF RUBBERWOOD USING CERIUM OXIDE NANOPARTICLES PART 1: CHARACTERIZATION AND COLOUR CHANGES

FOTOSTABILIZACIJA LESA KAVČUKOVCA Z NANODELCI CERIJEVEGA DIOKSIDA 1. DEL: KARAKTERIZACIJA IN SPREMEMBE BARVE

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Abstract / Izvleček

Abstract: *Light induced darkening and deterioration of wood used outdoors is undesirable. Photoprotection of wood could be achieved by using additives that reflect or absorb harmful radiation responsible for degradation. Nano metal oxides have strong absorption in the UV range of solar radiation and good transparency in the visible region. They offer unique benefits in protecting coatings and coated substrates from being degraded by UV radiation. However, to exploit the properties of nanoparticles, homogenous dispersion without agglomeration is necessary. In the present work, the photostabilization of rubberwood surfaces coated with cerium oxide (CeO_2) was studied. The nanoparticles were surface functionalized with an organic alkoxy silane (3-glycidyloxypropyltrimethoxy silane) to improve the homogenous distribution in coatings, and the modified nanoparticles were dispersed in isopropanol and polyurethane (PU) coating. Rubberwood surfaces coated with dispersed nanoparticles (concentration 0.5 % to 6 % w/v) were exposed to a fluorescent UVA light source (λ=340 nm) at 60 °C in an accelerated weathering tester for 500 h and 1000 h. Colour changes due to UV light exposure were monitored using a spectrocolourimeter. Dispersion of CeO_2 nanoparticles in PU coatings (concentration >2 %) restricted the photoyellowing of wood polymers.*

Keywords: *Rubberwood, PU coating, Nanoparticles, Cerium oxide, Photostability, Colour stability*

Izvleček: Degradacija in potemnitev lesa, ki je v uporabi na prostem, je nezaželena. Les je pred učinki svetlobe možno zaščititi z dodatki, ki odbijajo ali absorbirajo škodljivo sevanje, ki povzroča njegovo razgradnjo. Nano kovinski oksidi izkazujejo močno absorpcijo svetlobe v UV območju sončnega sevanja in dobro transparentnost v vidnem območju. Zato ponujajo edinstvene prednosti pri zaščiti premazov in površinsko obdelanih substratov, ki so občutljivi na UV sevanje. Vendar pa je za izkoriščanje zaščitnih lastnosti nanodelcev potrebna njihova homogena disperzija, tako da se ne tvorijo aglomerati. V tem prispevku poročamo o raziskavah fotostabilizacije površin lesa kavčukovca z nanodelci cerijevega dioksida (CeO_2). Nanodelci so bili površinsko funkcionalizirani z organskim alkoksi silanom (3-glicidiloksi propiltrimetoksi silan) za izboljšanje homogene porazdelitve v premazih. Modificirane nanodelce smo dispergirali v izopropanolu in v poliuretanskem (PU) premazu. Površine lesa kavčukovca, na katere smo nanesli dispergirane nanodelce (koncentracija od 0,5 % do 6 % m/v), smo v napravi za umetno pospešeno staranje za 500 ur in 1000 ur in pri 60 °C izpostavili UVA svetlobi (λ = 340 nm). Barvne spremembe zaradi izpostavitve UV svetlobi smo spremljali s kolorimetrom. Disperzija nanodelcev CeO_2 v PU premazih (koncentracija >2 %) je zmanjšala foto-rumenenje lesnih polimerov.

Ključne besede: kavčukovec, PU premaz, nanodelci, cerijev dioksid, fotostabilnost, stabilnost barve

1 INTRODUCTION
1 UVOD

Wood is a versatile raw material that is widely used for indoor and outdoor applications. Consumption of wood and wood products has increased due to concern about the environment (Rowell, 2005; Hill, 2006). Wood has gained lot of attention because of its low embodied energy, which also acts as carbon sink and contributes to climate change mitigation. Being a biological material, unprotected wood is susceptible to degradation due to a combination of environmental factors (sunlight, moisture, heat, atmospheric pollution, chemicals and biological agents) (Feist & Hon, 1984; Williams, 2005; Evans, 2013). Some of the limitations associated when wood is used

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outdoors are the low durability of many species, dimensional instability with change in moisture content, low resistance against fungi and insect attack and photodegradation of wood (Rowell, 2005).

The colour stability of natural wood against light exposure is an important issue from aesthetic point of view. Reducing or eliminating the damaging effects of solar and artificial UV radiation is a major challenge for material scientists. One of the most widely used methods of UV protection is the dispersion of UV-absorbing molecules into a material (George et al., 2005). Photoprotection of wood can be achieved by additives that reflect or harmlessly absorb the light responsible for photodegradation or terminate the free radicals that degrade wood constituents. Inorganic particles can block light from reaching wood substrates and protect wood from photodegradation. Small particles below a certain size are thus able to scatter UV light while having little effect on the visible component of the spectrum. These properties of nanoparticles and their ability to absorb UV light underpins the use of metal oxides (titanium dioxide, iron and zinc oxides) as transparent photoprotective agents for coatings applied onto wood.

Recently, many studies have focused on improving the UV absorption characteristics of wood coatings by incorporation of nanoparticles (Aloui et al., 2007; Clausen et al., 2010; Auclair et al., 2011; Nikolic et al., 2015). Moreover, some studies use nanoparticles along with or in contrast to organic UV absorbers to protect wood from photodegradation (Forsthuber et al., 2013). But the majority of such studies report the use of zinc oxide or titanium dioxide as the nano additives in coatings for UV protection (Allen et al., 2002; Cristea et al., 2010; Fufa et al., 2012; Wang et al., 2014; Miklečić et al., 2015), and very few use cerium oxide as a UV stabilizer (Liu et al., 2010; Blanchard & Blanchet, 2011; Schaller et al., 2011; Saha et al., 2013).

The photostability of yellow cedar veneers pre-treated with micronized iron oxide and cerium oxide nanoparticles was examined by Liu et al. (2010). The results revealed that, in comparison to iron oxide, the cerium oxide nanoparticles were not as effective at restricting the weight loss, tensile strength losses, and preventing the photodiscolouration of exposed veneers. Blanchard and Blanchet (2011) studied the colour stability of ZnO and CeO_2 nanoparticles in comparison with UV absorbers dispersed in a waterborne UV curable polyurethane / polyacrylate resin. The inorganic absorbers performed better in comparison with the organic UV absorbers, while zinc and cerium oxides efficiently reduced yellowing. A similar comparison study was carried out by Schaller et al. (2011) for a longer exposure time. The poor performance of CeO_2 nanoparticles that was found was attributed to the presence of aggregates and lower concentration. The acrylic polyurethane coatings modified with CeO_2 nanoparticles alone or in combination with lignin stabilizer and/or bark extracts showed better protection of thermally treated jack pine compared to coatings containing organic UV absorbers (Saha et al., 2013).

In the present study, the photostability of rubberwood coated with different concentrations of CeO_2 nanoparticles exposed to UV-A light under accelerated weathering conditions is discussed. Colour changes occurring due to UV light irradiation were regularly monitored and analysed. Rubberwood (*Hevea brasiliensis*) is a low durable, light yellowish-brown plantation grown, easy to work, hard wood species. It finds applications in furniture, toys, kitchen accessories, pulp and paper products, and fibreboards.

2 MATERIALS AND METHODS
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2.1 MATERIALS
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Specimens of rubberwood (*Hevea brasiliensis*) of size (150 mm × 75 mm × 5 mm) (length × width × thickness) were prepared from defect-free wood for the evaluation of photostability. Wood specimens were air dried followed by drying in a hot air oven at 65 °C and stored at room temperature. Cerium oxide nanoparticles (~25 nm) were purchased from Sigma Aldrich, 3-glycidyloxypropyltrimethoxy silane (GPTMS) from Gelest Inc., and polyurethane (PU) coating material (without any additives) was procured from Asian Paints, Mumbai. Other chemicals used in the study were of AR grade.

2.2 SURFACE MODIFICATION AND DISPERSION OF NANOPARTICLES

2.2 POVRŠINSKA MODIFIKACIJA IN DISPERGIRANJE NANODELCEV

In order to obtain a homogenous distribution of nanoparticles in solution, alkoxy silane 3-glycidyloxypropyltrimethoxy silane (GPTMS) was used as a surface modifier. The process used for dispersion of CeO_2 nanoparticles was carried out as per the procedure discussed elsewhere in detail (Srinivas & Pandey, 2017).

2.3 CHARACTERIZATION OF SILANE MODIFIED NANOPARTICLES

2.3 KARAKTERIZACIJA NANODELCEV, MODIFICIRANIH S SILANOM

Surface modified nanoparticles were characterized using UV-visible absorption spectroscopy, X-ray diffraction (XRD) and the dispersion of nanoparticles by Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM).

The UV-Vis spectra of surface modified nanoparticles in powder form were measured using an Ocean Optics HR 4000 UV-Vis spectrophotometer (UV-Vis-NIR light source, DT-MINI-2-GS, Jaz detector) at Kuvempu University, Shimoga, Karnataka. The baseline of UV spectra was set by using standard $BaSO_4$. The dried nanoparticle samples were packed tightly in a circular opening (diameter 0.4 cm) with a thickness of 0.5 mm on a glass plate. The UV spectra of samples were recorded using the optical fibre held exactly at 90° to the sample. XRD analysis was carried out to know the phase and size of surface modified nanoparticles. XRD patterns were recorded from 10° to 90° with a PANalytical X'pert pro diffractometer using Cu Kα (λ=1.5418 Å) with a nickel filter. Data were collected from modified nanopowder with a counting rate of 5° per min.

Dynamic light scattering was used to determine the size distribution profile of particles in PU suspension using BIC Zeta PALS. DLS analysis was done at concentration levels of 0.01 % of nanoparticles in liquid suspension (PU base material). PU alone was also analysed to assess any interference in DLS analysis when nanoparticles are used, and the findings showed that it did not have any significant monomer/oligomeric structure which could interfere in the results.

The distribution of nanoparticles in polyurethane was also examined using a high resolution scanning electron microscope (Gemini Ultra 55, with ESB detector at 5.0 kV). Thin films of nanoparticle dispersed in PU were prepared by pouring dispersed solution on a clean plastic sheet. After drying at room temperature, the thin films were pulled from the plastic sheets and kept in a vacuum desiccator for 72 hours before analysis. A thin layer of gold (9 nm) was sputtered onto the thin films mounted on a metal grid using carbon tape to make the sample conductive. XRD, DLS and SEM analysis were carried out at CeNSE, Indian Institute of Science, Bengaluru.

2.4 COATING OF WOOD WITH NANOPARTICLES DISPERSED IN ISOPROPANOL/PU

2.4 POVRŠINSKA OBDELAVA LESA Z NANODELCI, DISPERGIRANIMI V IZOPROPANOLU/PU

In order to know the effects of nanoparticles alone, one set of wood samples were coated with modified nanoparticles dispersed in isopropanol and another set with nanoparticles dispersed in PU coating. Different concentrations (0.5 %, 1.0 %, 2.0 %, 4.0 % and 6.0 %) of silane modified CeO_2 nanoparticles were added to isopropanol or PU, subjected to homogenisation in a homogeniser (IKA T25 digital ULTRA-TURRAX) for 20 minutes at 10 krpm. Wood surfaces were coated with two coats of homogenized solution of nanoparticles using sprayer with an intermittent drying time of one hour and dried overnight at room temperature. A coating thickness of ~50 μm was achieved. All the measurements made on wood samples coated with nanoparticles dispersed in isopropanol were done carefully to avoid loss of the nanoparticle layer from the wood surface.

2.5 PHOTOSTABILITY OF WOOD SURFACES COATED WITH CEO_2 NANOPARTICLE DISPERSED IN ISOPROPANOL/PU

2.5 FOTOSTABILNOST POVRŠIN LESA, OBDELANIH Z NANODELCI, DISPERGIRANIMI V IZOPROPANOLU/PU

The photostability of wood was assessed using a weatherometer (Qlab QUV accelerated weathering tester, UVA-340 lamp) at an irradiance of 0.68 W/m^2, chamber temperature of 60 °C. Initially samples coated with different concentrations of nanoparticle were exposed to UV light. Four replicas of wood samples per treatment were used in

the study. Forty-eight samples were kept in a single run of 500 h. The samples were removed from the weathering tester after exposure of 50 h, 100 h, 150 h, 200 h, 250 h, and 500 h and were analysed for colour changes. Based on the results, only wood samples coated with higher nanoparticle concentrations (2 %, 4 % and 6 %) were exposed to UV light for another 500 h along with control wood samples.

2.6 COLOUR CHANGES
2.6 SPREMEMBE BARVE

Changes in the colour of wood surfaces due to irradiation were measured using a Hunter lab - Lab scan XE model spectrocolourimeter (10° standard observer, D65 standard illuminant, xenon flash lamp source and CIELAB system). The CIELAB system is characterized by three parameters L^*, a^*, b^*. L^* axis represents the lightness, a^* and b^* are the chromaticity coordinates, a^* varies from red (+) to green (-) and b^* varies from yellow (+) to blue (-). Coordinates L^*, a^* and b^* were measured on each sample before and after accelerated weathering exposure. Measurements were taken at six different locations for each sample; the mean value and standard deviation were calculated. Changes in colour coordinates after UV exposure were measured and changes in colour due to exposure were calculated as the ΔL^*, Δa^* and Δb^* values. These values were used to calculate the total colour change ΔE^* as a function of the weathering time, according to the following equation 1 (CIE 1986),

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

The ΔL^*, Δa^* and Δb^* values given in eqn. 1, are the changes in L^*, a^* and b^* parameters due to irradiation with respect to unirradiated and irradiated wood specimens.

3 RESULTS AND DISCUSSION
3 REZULTATI IN RAZPRAVA
3.1 SURFACE FUNCTIONALIZATION OF CEO$_2$ NANOPARTICLE
3.1 POVRŠINSKA FUNKCIONALIZACIJA NANODELCEV CEO$_2$

Most of the widely used organosilanes (R-(CH$_2$)$_n$-Si-X$_3$) have one organic substituent (R) and three hydrolyzable substituents (X). In most surface treatment applications, the alkoxy groups of the trialkoxy silanes are hydrolyzed to form silanol-containing species. The reaction of silane with nanoparticles involves hydrolysis of the three labile groups followed by their condensation to oligomers, the formation of hydrogen bond by oligomers with -OH groups of the substrate and finally a covalent linkage is formed with the substrate with loss of water during drying or curing. The R group (glycidyloxypropyl) remains available for covalent reaction or physical interaction with other phases (PU coating). Among alkoxy silanes, only methoxy silanes are effective without catalysis. In order to minimize agglomeration, nanoparticles were chemically modified with 3-glycidyloxypropyltrimethoxy silane (GPTMS) using ultrasonication. The chemical structure of GPTMS is shown in Fig. 1, as given by the provider. The basic principle of using ultrasonication for dispersion is the cavitation in liquids created by ultrasonication, which accelerates chemical reactions by facilitating the mixing of reactants. It also enables the uniform dispersion of micron-size or nano-size materials (Suslick & Price, 1999).
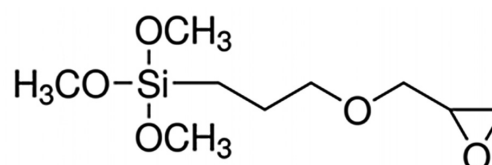

Figure 1. Chemical structure of 3-glycidyloxypropyl-trimethoxy silane (GPTMS).
Slika 1. Kemijska struktura spojine 3-glicidiloksipropiltrimetoksi silan (GPTMS).

3.1.1 Ultraviolet- Visible Absorption spectra
3.1.1 UV-vidni absorpcijski spektri

Nanoparticles modified with GPTMS were characterized using UV visible absorption spectroscopy. The spectra of unmodified and modified nanoparticles are as shown in Fig. 2A. Absorption spectra showed a broad absorption in the region between (200-350) nm, which exhibit the strong tendency of nanoparticles to absorb UV radiation (Arul et al., 2011). The spectra also suggest that surface modification with silane has not altered or posed any interference in the UV absorption region of the nanoparticles, but was also observed to increase absorption in the visible region which affected the transparency of the coating.

3.1.2 X-ray diffraction (XRD) analysis of nanoparticles

3.1.2 Rentgenska praškovna difrakcija (XRD) nanodelcev

X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material, and it can provide information on unit cell dimensions. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample**.** Various factors affect the broadening of diffraction peaks, such as crystalline size, domain size distribution, crystalline facets (external defects) and micro-strain (deformation of the lattice). As the size of the nanocrystals decreases, the line width is broadened. The XRD pattern for CeO_2 nanoparticles is shown in Fig. 2B. The 'hkl' values were compared with the standard JCPDS file (PCPDF 34-0394)20 (Arul et al., 2011). The exhibited XRD peaks correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) of the cubic fluorite structure of CeO_2. There is no spurious diffraction peak found in the above samples. This confirmed that all the compounds were single phase. Further, the intensity of the XRD peaks of the sample reflects that the nanoparticles are crystalline and the broad diffraction peaks indicate very small size crystallites. The average crystallite size was estimated from the full width at half maximum (FWHM) of the diffraction peak of

the powder samples, using Scherrer's formula the average crystallite size of CeO_2, and was found to be 84.08 nm.

3.1.3 Dynamic light scattering (DLS) of nanoparticle dispersions

3.1.3 Dinamično sipanje svetlobe (DLS) disperzij nanodelcev

Silane modified nanoparticles were dispersed in PU using ultrasonication and a homogenizer. The correlation functions of the intensity fluctuations were converted into intensity size distributions and are plotted in Fig. 3. A high proportion of the particle sizes were found between (105-120) nm having a poly dispersity index of 0.144.

3.1.4 Scanning Electron Microscopy of nanoparticles dispersed in PU

3.1.4 Vrstična elektronska mikroskopija nanodelcev, dispergiranih v PU

A scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals derived from electron-sample interactions reveal information about the sample including the external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In order to know the homogenous distribution of surface modified CeO_2 nanoparticles incorporated in PU coating, scanning
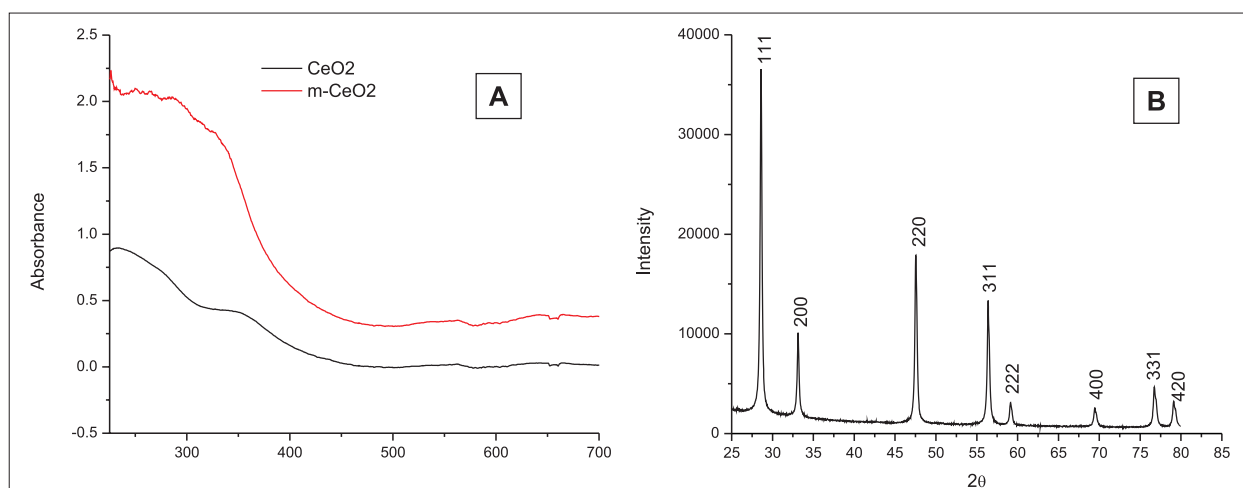

Figure 2. A) UV visible absorption spectra (m-CeO$_2$ means functionalized CeO$_2$) and B) XRD pattern of GPTMS modified CeO$_2$ nanoparticles.

Slika 2. A) UV-vis absorpcijska spektra (m-CeO$_2$ pomeni funkcionaliziran CeO$_2$) in B) rentgenski praškovni difraktogram z GPTMS modificiranih nanodelcev CeO$_2$.

electron micrographs (SEM) were recorded. SEM images of unmodified CeO_2 nanoparticles are shown in Fig. 4A. Severe agglomeration was observed in the case of unmodified CeO_2 particles with an average particle size >500 nm. The surface modified CeO_2 nanoparticles showed a size distribution of around 100-150 nm and a uniform dispersion (Fig. 4B). SEM analysis showed that the surface modification with GPTMS silane has a significant effect in minimizing the formation of agglomerates. All the characterization techniques show that the average size of the nanoparticles in the dispersing medium varies from
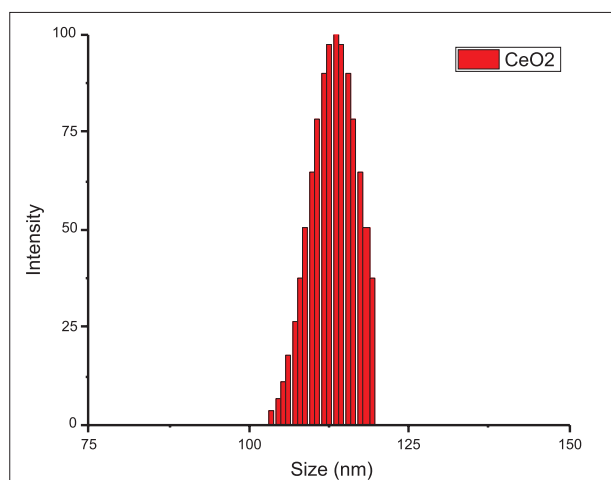
(90-130) nm. But the performance of nanoparticles mainly depends on the particle size, morphology and uniform size distribution. Though the surface modification with silane helped in avoiding the formation of agglomerates and encouraged an even distribution of nanoparticles in the PU coating, it was not effective to maintaining the particle size below 50 nm. Freeman and McIntyre (2008) reported that nanoparticles having a size smaller than wood pores (100 μm) and intercellular pores ((400-600) nm) could penetrate the porous structure of wood and thereby influence wood protection against damaging agents. Hence the size specific properties of nanoparticles can be efficiently utilized in the coating formulations reported in this study.

3.2 PHOTOSTABILITY OF WOOD COATED WITH NANOPARTICLES
3.2 FOTOSTABILNOST LESA, POVRŠINSKO OBDELANEGA Z NANODELCI

Wood specimens coated with modified nanoparticles dispersed in isopropanol and another set with dispersed nanoparticles in PU coating were exposed to accelerated weathering. Analysis of wood coated with nanoparticles dispersed in isopropanol revealed the effects of nanoparticles alone on the wood surfaces, since isopropanol evaporated at room temperature. In contrast, the analysis of nanoparticles dispersed in PU coating revealed the effects of light on PU coating containing the inorganic absorbers as well as the wood surface.
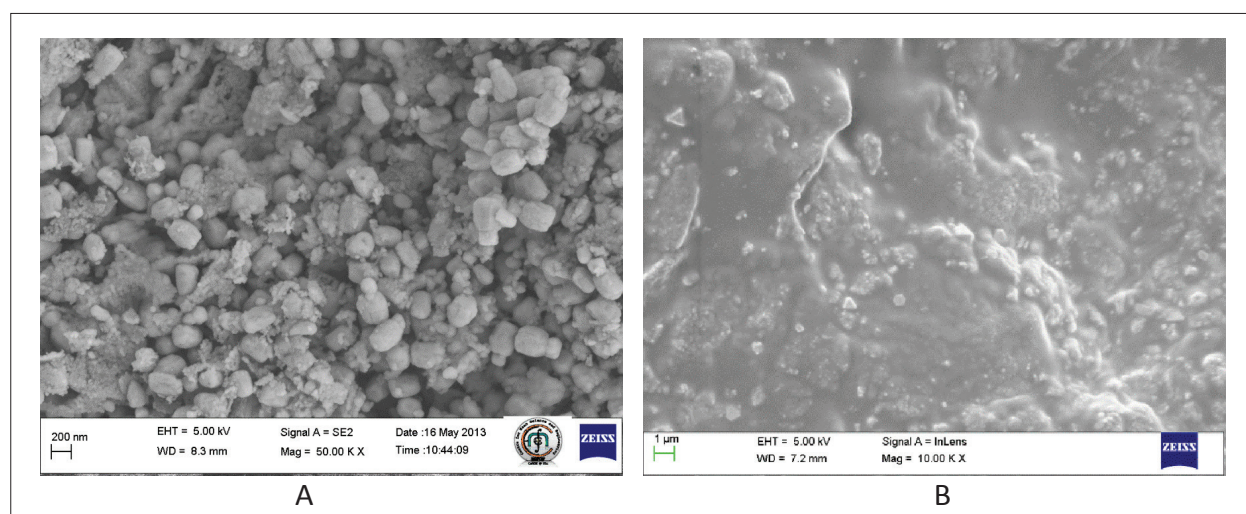

Figure 3. DLS analysis of the particle size distribution of modified CeO_2 nanoparticles in PU coating
Slika 3. Analiza DLS za določitev porazdelitve velikosti modificiranih nanodelcev CeO_2 v PU premazu

Figure 4. SEM images of A) unmodified and B) GPTMS modified CeO_2 nanoparticles dispersed in PU coating.
Slika 4. SEM mikrografi A) nemodificiranih in B) nanodelcev CeO_2 dispergiranih v PU premazu.

3.2.1 Effects of UV irradiation on colour parameters (*L**, *a** and *b**) of nano CeO₂ coated wood

3.2.1 Vpliv UV obsevanja na parametre barve (*L**, *a** and *b**) lesa, površinsko obdelanega z nanodelci CeO₂

Wood when exposed to light initially changes colour, showing the degradation of wood components by light absorption. By measuring the colour change of the clear coated wood with inorganic ab-

sorbers during artificial weathering, it is possible to obtain information on the performance of photostabilization. Changes in colour parameters of wood surfaces coated with nanoparticles of CeO₂ and exposed to UV radiation are shown in Fig. 5. Uncoated wood changes its colour within a few hours of irradiation due to photodegradation of chemical components mainly lignin present in wood (Tolvaj & Faix, 2009; Rosu et al., 2010; Müller et al., 2013). The control wood becomes darker and yellower with an

a   b   c   d

Figure 5. Colour *changes after 1000 h of UV exposure of (a) uncoated, and coated with (b) 2 %, (c) 4 % and (d) 6 % CeO₂ (Top: without PU; Bottom: in PU coating).*
Slika 5. Spremembe barve po 1000 urah izpostavitve UV svetlobi (a) površinsko neobdelanega lesa in lesa, obdelanega z (b) 2 %, (c) 4 % in (d) 6 % CeO₂ (zgoraj: brez PU; spodaj v PU premazu).

increase in the irradiation time. Wood coated with a lower concentration of CeO_2 nanoparticles also showed colour changes with time. Wood coated with concentrations of (2 %, 4 % and 6 %) of nanoparticle loadings showed very less colour change when compared to that seen with lower loadings.

Similarly, wood samples coated with different concentrations of nanoparticles dispersed in PU were subjected to UV light irradiation in a QUV tester. The performance of the nanoparticles dispersed in PU coating on wood surfaces was compared with that of PU coating without nanoparticle. Wood coated with PU alone (without nanoparticles) exhibited severe colour changes, which increased with irradiation time. This indicates that PU coating without any UV stabilizer gets degraded rapidly upon UV light irradiation. Incorporation of nanoparticles in PU limited the colour changes. Figure 5 illustrates the colour changes in wood coated with different concentrations of CeO_2 nanoparticles embedded in PU coatings after 1000 h of UV irradiation. Colour changes in wood coated with CeO_2 dispersed PU were significantly reduced. The presence of CeO_2 gave a lighter colour to the coating, which was retained even after 1000 h of UV exposure. These visual observations were supported with spectroscopic analysis. Coating of wood surfaces with CeO_2 nanoparticles makes wood surfaces lighter in colour, which is indicated by the successive increase in $L*$ values and decrease in the values of $a*$ and $b*$. Higher concentrations of nanoparticles dispersions showed stability against photoyellowing.

The variations in colour coordinates of uncoated and CeO_2 dispersed coatings before UV exposure are given in Table 1. It is seen that the $L*$ value increases while the $a*$ and $b*$ values decrease with an increase in the nanoparticle concentration, which is due to the increase in opacity of the coating. It was also observed that coating of wood with PU has effects on the colour parameters. Wood samples coated with PU had a darker appearance. $L*$ values were observed to be decreased and $a*$ and $b*$ increased in the PU coated wood compared to the corresponding coatings with isopropanol. This may be attributed to the coating material, as it was obtained without any additives. Upon light exposure, colour changes in the uncoated wood surface is indicated by a decrease in the value of lightness ($L*$) and increase in the yellowness $b*$ (Fig. 6). The decrease in the $L*$ parameter

indicates severe darkening of the control wood sample. The $b*$ values of uncoated wood increased. The increase in value can be attributed to the formation of a quinone-like structure from lignin degradation (Feist & Hon 1984). The lightness index ($L*$) of uncoated wood decreased with an increase in irradiation time from 74.23 ± 1.68 (0h) to 69.18 ± 1.13 (500 h) and in wood coated with 0.5 % and 1% CeO_2 the $L*$ values were 72.96 ± 1.98 and 73.73 ± 0.50 after 500 h of exposure. In the case of wood treated with 2 % CeO_2 nanoparticles the $L*$ value varied from 78.33 ± 1.87 to 77.06 ± 1.60, similarly for wood treated with 4 % and 6 % of CeO_2 the values varied from 78.12 ± 1.86 to 76.37 ± 0.58 and 79.70 ± 0.59 to 79.63 ± 0.43, respectively, after 500 h of UV exposure. This shows there was no appreciable decrease in $L*$ values in comparison with uncoated wood and wood coated with lower nanoparticle concentrations. This indicates that the wood coated with a concentration of 2 % and more nano CeO_2 reduces the darkening of the wood surface due to light irradiation.

The chromaticity coordinates $a*$ and $b*$ in the case of uncoated wood increased with an increase in exposure time. This can be attributed to the photoyellowing of the wood surfaces upon light irradiation. The $a*$ value of uncoated wood increased from 6.63 ± 0.66 to 10.65 ± 0.30 after 500 h of UV exposure, in the case of wood coated with lower concentrations of CeO_2., 0.5 % and 1.0 %, the $a*$ values increased as in the control wood. However, in wood samples coated with 2 %, 4 %, and 6 % nanoparticles, the $a*$ value varied from 5.39 ± 1.21 to 5.25 ± 0.70, 4.64 ± 0.85 to 6.63 ± 0.55 and, 4.15 ± 0.66 to 5.25 ± 0.69 for the respective nanoparticle concentrations after 500 h of UV exposure. Yellowness induced in wood due to UV light exposure can be evaluated from $b*$ values. The chromaticity coordinate $b*$ values in the case of uncoated wood increased along with the exposure time. Uncoated wood became darker and yellower as the exposure time increased. In uncoated wood, the $b*$ values increased from 21.31 ± 0.99 to 29.38 ± 1.52 after 500 h of UV exposure. Even in wood coated with 0.5 % and 1.0 % CeO_2, $b*$ values increased with the time of exposure, but in the case of wood coated with 2 % and 4 % CeO_2, the increase in $b*$ values was much lower in comparison to those seen with the control wood. In wood coated with 6.0 % CeO_2, $b*$ values were found to decrease initially from

Table 1. Colour *parameters of wood coated with nanoparticles dispersed in isopropanol and PU coating before UV exposure.*
Preglednica 1. Barvni parametri lesa, obdelanega z disperzijo nanodelcev v izopropanolu in s PU prema-zom z nanodelci pred izpostavljenostjo UV.

Coating	CeO$_2$ in Isopropanol			CeO$_2$ in PU		
	L*	a*	b*	L*	a*	b*
Control	74.23 ± 1.68	7.63 ± 0.66	21.31 ± 0.99	63.26 ± 0.60	14.10 ± 0.08	33.25 ± 1.37
0.5 % CeO$_2$	75.92 ± 2.36	6.35 ± 1.54	20.45 ± 0.87	66.47 ± 0.68	10.53 ± 0.56	31.38 ± 1.30
1 % CeO$_2$	77.00 ± 1.06	6.02 ± 0.56	20.01 ± 0.69	67.01 ± 0.18	10.26 ± 0.90	30.96 ± 1.31
2 % CeO$_2$	78.33 ± 1.87	5.39 ± 1.21	17.30 ± 0.89	67.08 ± 0.41	10.03 ± 0.20	28.30 ± 1.74
4 % CeO$_2$	78.12 ± 1.86	4.64 ± 0.84	16.26 ± 0.67	69.15 ± 1.87	9.58 ± 0.59	23.46 ± 0.79
6 % CeO$_2$	79.70 ± 0.59	4.15 ± 0.65	14.15 ± 0.44	70.76 ± 1.73	9.17 ± 0.22	21.41 ± 0.15

14.15 ± 0.44 to 11.93 ± 1.39 (50 h) but increased to 13.51 ± 1.34 after 500 h of exposure.

Similarly, for wood coated with PU coatings, the lightness index *L** of wood coated with PU alone was found to darken with time, and the *L** values decreased from 63.26 ± 0.60 to 55.23 ± 1.60 after 500 h of UV exposure. The yellowness index *b** was observed to increase from 33.25 ± 1.37 to 49.13 ± 1.62 after 500 h of exposure. In the case of wood coated with nano CeO$_2$ in PU, the *L** values varied from 67.08 ± 0.41, 69.15 ± 1.87 and 70.76 ± 1.73 to 62.79 ± 0.28, 66.10 ± 1.15 and 67.77 ± 0.31 for 2 %, 4 % and 6 % nanoparticle loadings respectively after 500 h of exposure. The *a** values in PU control and wood coated with <1 % nanoparticle loadings showed an increase with time, whereas wood coated with >2 % loadings, *a** values slightly decreased or remained constant. The yellowness index *b** also increased with irradiation time in samples coated with (0.5 - 1.0) % CeO$_2$ and PU alone (33.25 ± 1.38 to 49.13 ± 1.62 after 500 h). The samples coated with 2 % nano CeO$_2$ showed an increase in *b** value (40.44 ± 1.23), and in wood coated with 4 % (30.94 ± 1.53) and 6 % CeO$_2$ (25.89 ± 2.03) samples the *b** values showed minor increase after 500 h of light exposure. Similar colour change results were observed for wood protected by depositing CeO$_2$ coating on surface (Lu et al., 2013; Nair et al. 2018). The changes in lightness (Δ*L**) and yellowness (Δ*b**)

for uncoated and nano coated wood are shown in Fig. 6. Δ*a** values are not discussed, and only the lightness and yellowness indexes are discussed to explain the UV stabilization of wood. The maximum changes were observed in the case of uncoated control wood, which increased with the length of exposure. The negative Δ*L** values indicated the darkening of wood due to degradation from UV light. The Δ*L** values were negligible in wood coated with 6 % of CeO$_2$ even after 500h of UV exposure. The control wood showed an increase in Δ*b** values with time. In contrast, negative Δ*b** values were observed in wood coated with 4 % and 6 % CeO$_2$. This shows the effectiveness of CeO$_2$ nanoparticles at concentrations >2 % to stabilize wood surfaces against UV light induced photo-yellowing.

The Δ*L** and Δ*b** values of PU coating with / without CeO$_2$ nanoparticles after 500 h of UV exposure are presented in Fig. 6. It was observed that changes in Δ*L** values were negative for wood coated with PU alone. Δ*L** values in wood coated with 2 %, 4 % and 6 % CeO$_2$ in PU remained constant. The Δ*b** values in control wood increased with exposure time, and wood coated with 4 % and 6 % CeO$_2$ showed significantly less changes in yellowness (Blanchard & Blanchet, 2011; Saha et al., 2013). These results indicate that the UV resistance of wood coatings increases with the increase in concentration of nanoparticles.
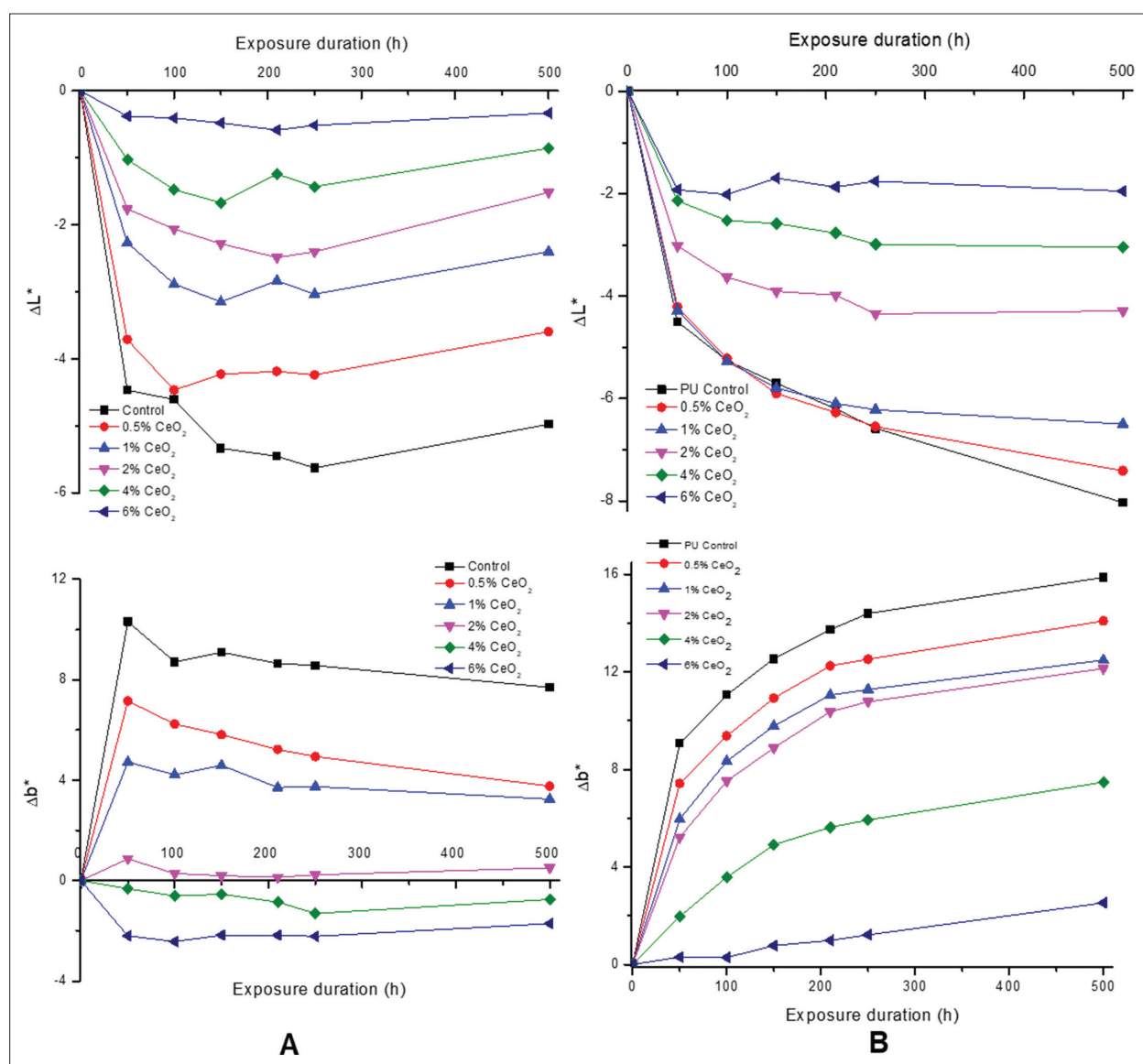
*Figure 6. Changes in the **ΔL*** and Δb* values of control and wood surfaces coated with CeO₂ plotted against time of UV exposure. A) Without PU coating, B) with PU coating.*
*Slika 6. Vrednosti **ΔL*** in Δb* kontrolnih vzorcev in površin lesa z nanodelci CeO₂, ki so bili izpostavljeni UV svetlobi.*

In order to verify the stability of these nano coatings, wood samples which showed good UV resistance were exposed to another 500 h along with control samples. The changes in colour parameters after 1000 h of UV exposure are shown in Fig. 7. With an increase in concentration, nanoparticles may form aggregates and thereby decrease the photostabilization efficacy of coatings (Blanchard & Blanchet, 2011). However, the results revealed that the photostability of wood coated with more nanoparticles was not altered even after longer exposure durations. It was observed that the changes in colour parameters after 1000 h exposure remained constant or only a slight variation was seen compared to the corresponding values after 500 h of exposure. It can be concluded that colour changes are more drastic in the initial hours and after a certain time they become less pronounced.
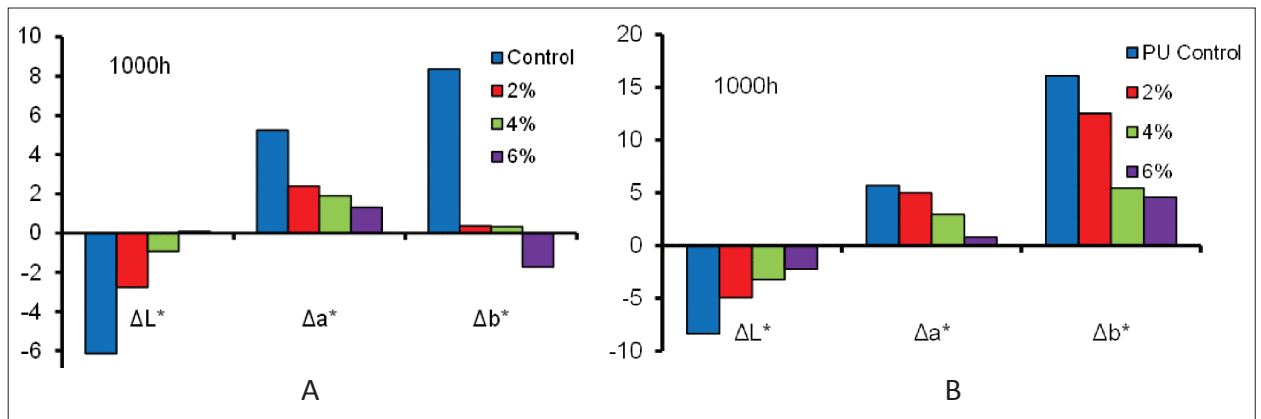
*Figure 7. Changes in the **ΔL*** and Δb* values of control and wood surfaces coated with CeO$_2$ after 1000 h of UV exposure. A) Without PU coating, B) with PU coating.*

*Slika 7. Vrednosti **ΔL*** in Δb* kontrolnih vzorcev in površin lesa z nanodelci CeO$_2$, po 1000 urah izpostavitve UV svetlobi.*

The total colour change (ΔE*) of control and nano coated wood at different time intervals is shown in Fig. 8. The ΔE* in the uncoated control wood and wood with 0.5 % CeO$_2$ increased rapidly with irradiation time. The rate of change was higher during the initial exposure but later was found to decline. The ΔE* values were maximal for uncoated wood (ΔE* = 10), which however were found to reduce with the addition of different nanoparticle concentrations. Wood coated with >2 % nanoparticles showed a much lower increase in ΔE* values

(less than 6), which shows the better colour stabilization than at their respective lower concentrations. Wood samples coated with PU and CeO$_2$ dispersed in PU also showed an increase in ΔE* values with an increase in time. However, the extent of this increase was lower in the case of wood coated with 4 % and 6 % CeO$_2$ loadings (ΔE*<6) in contrast to lower loadings (ΔE* = 18 in PU control wood). The total colour change in uncoated and wood coated with higher nanoparticle concentrations exposed for 1000 h of UV light did not vary much
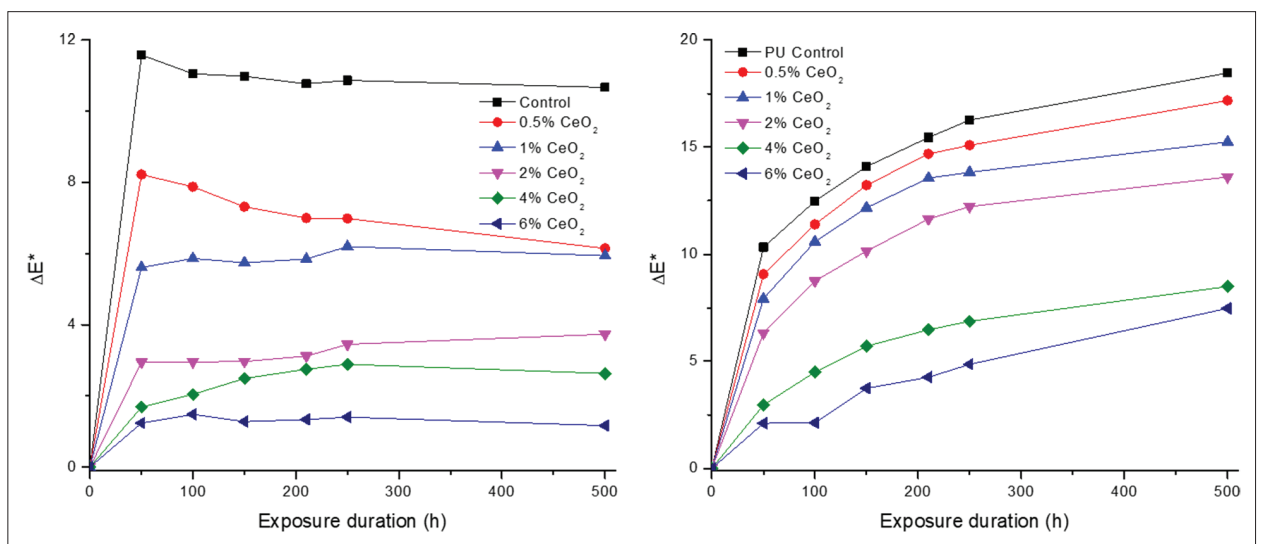

Figure 8. Effects of UV irradiation on the ΔE* values of control and wood surfaces coated with different concentration of CeO$_2$.

Slika 8. Vpliv UV obsevanja na ΔE *vrednosti kontrolnih in površin lesa, prevlečenih z nanodelci z različnimi koncentracijami CeO$_2$.

in comparison with 500 h of exposure. On visual observation, it can be noted that the yellowing of wood surfaces due to light exposure could not be controlled completely in wood coated with nanoparticles dispersed in PU. This may be attributed to the particle size of CeO$_2$ that was >100 nm, and also due to the degradation of the PU coating on light exposure.

In general, it was observed that in comparison to uncoated wood, wood with nanoparticles exhibits improved resistance to photodegradation, which increases along with the nanoparticle concentration. However, higher concentrations of nanoparticles greatly affect the transparency of the coating material.

4 CONCLUSIONS
4 SKLEPI

The efficacy of cerium oxide (CeO$_2$) nanoparticle-based coatings for photostabilization of rubberwood (*Hevea brasiliensis*) surfaces was studied. Nanoparticles were surface functionalized with an organic alkoxy silane (3-glycidyloxypropyltrimethoxy silane) to achieve uniform dispersion of nano metal oxide in isopropanol and polyurethane coatings. Isopropanol or polyurethane coating with a dispersed surface of functionalized nanoparticles of different concentrations (concentration (0.5–6) %) were applied to rubberwood. The coated samples were exposed to a UVA-340 nm light source in an accelerated weathering tester. Colour changes occurring due to UV light exposure were analysed at regular time intervals. Uncoated wood showed severe darkening and yellowing with the increase in exposure time, while the wood coated with nano-dispersions showed less darkening and yellowing. The results revealed that formulations with ≥2 % of nanoparticles can stabilize wood surfaces against UV degradation. It was thus shown that dispersion of nanoparticles in PU coatings can significantly restrict the colour changes and photodegradation of wood polymers.

5 SUMMARY

Surface functionalization of nanoparticles using 3-glycidyloxypropyltrimethoxy silane (GPTMS) was carried out. Modified nanoparticles were dispersed in isopropanol and/or polyurethane (PU) coating. The modified nanoparticles and their dispersion were characterized using UV-Visible absorption spectroscopy, X-ray diffraction, dynamic light scattering (DLS) and scanning electron microscopy (SEM). UV-Visible absorption spectra showed a broad and wide absorbance range for nanoparticles in the UV region. The results from SEM showed that modification with GPTMS was effective in reducing agglomeration and obtaining a homogenous distribution of nano metal oxides in the polymer matrix. The efficacy of CeO$_2$ nanoparticles for photostabilization of rubberwood (*Hevea brasiliensis*) surface was studied. Different concentrations of surface functionalized nanoparticles (concentration (0.5–6) %) were dispersed in isopropanol and polyurethane clear finish, and the obtained formulations were applied on wood. The coated and uncoated samples were exposed to a UVA-340 nm light source in an accelerated weathering tester for up to 500 h and 1000 hours. Colour changes occurring due to UV light exposure were analysed at regular time intervals. The dispersion of nanoparticles in coatings effectively restricted the colour changes and photodegradation of wood polymers, particularly at ≥2 % nanoparticle concentration.

5 POVZETEK

Izvedli smo površinsko funkcionalizacijo nanodelcev s 3-glicidiloksipropiltrimetoksi silanom (GPTMS). Modificirane nanodelce smo dispergirali v izopropanolu in poliuretanskem (PU) premazu. Obdelane nanodelce in njihovi disperziji smo okarakterizirali z UV vidno spektroskopijo, rentgensko difrakcijo, metodo dinamičnega sipanja svetlobe (DLS) in z vrstično elektronsko mikroskopijo (SEM). UV-vidni absorpcijski spektri so za nanodelce pokazali široko območje absorpcije UV svetlobe. Rezultati raziskav s SEM so pokazali, da je bila modifikacija nanodelcev z GPTMS učinkovita pri zmanjševanju aglomeracije in je omogočila homogeno porazdelitev nano kovinskih oksidov v polimerni osnovi. Nato smo proučili učinkovitost nanodelcev CeO$_2$ nanodelcev za foto-stabilizacijo površin lesa kavčukovca (*Hevea brasiliensis*). Pripravili smo disperzijo površinsko funkcionaliziranih nanodelcev v izopropanolu ali brezbarvni transparentni poliuretanski premaz z nanodelci (koncentracija od (0,5 – 6) %).

Pripravka smo nanesli na les. Površinsko obdelane in neobdelane preskušance smo v komori za umetno pospešeno staranje za 500 ur in 1000 ur izpostavili svetlobi tipa UV A (340 nm). Zaradi izpostavljenosti UV sevanju se je spremenila barva in spremembe le-te smo analizirali v rednih časovnih presledkih. Disperziji nanodelcev sta učinkovito omejili barvne spremembe in foto-degradacijo lesnih polimerov, zlasti pri koncentraciji nanodelcev, višjih od 2 %.

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REFERENCES
VIRI

Allen, N. S., Edge, M., Ortega, A., Liauw, C. M., Stratton, J., & McIntyre, R. B. (2002). Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings. Polymer Degradation and Stability, 78, 467–478.

Aloui, F., Ahajji, A., Irmouli, Y., George, B., Charrier, B., & Merlin, A. (2007). Inorganic UV absorbers for the photostabilisation of wood-clearcoating systems: Comparison with organic UV absorbers. Applied Surface Science, 253, 3737–3745.

Arul, N. S., Mangalaraj, D., Chen, P. C., Ponpandian, N., & Viswanathan, C. (2011). Strong quantum confinement effect in nanocrystalline cerium oxide. Material Letters, 652, 635–2638.

Auclair, N. R., Riedl, B., Blanchard, V., & Blanchet, P. (2011). Improvement of Photoprotection of Wood Coatings by Using Inorganic Nanoparticles as Ultraviolet Absorbers. Forest Products Journal, 61, 20-27.

Blanchard, V., & Blanchet, P. (2011). Color stability for wood products during use: Effects of inorganic nanoparticles. BioResources, 6(2), 1219-1229.

CIE (1986). Colorimetry. 2nd Edition, CIE Publication No. 15.2, section 4.2. Commission Internationale del'Eclairage, Vienna, 74 pp.

Clausen, C. A., Green, F., & Kartal, S. N. (2010). Weatherability and Leach Resistance of Wood Impregnated with Nano-Zinc Oxide. Nanoscale Research Letters, 5(9), 1464–1467.

Cristea, M. V., Bernard, R., & Blanchet, P. (2010). Enhancing the performance of exterior waterborne coatings for wood by inorganic nanosized UV absorbers. Progress in Organic Coatings, 69, 432–441.

Evans, P. D. (2013). Weathering of wood and wood composites, 151-213: In Handboook of wood chemistry and wood composite, Second edition. Rowell, R. M. (ed.), Taylor and Francis, CRC Press.

Feist, W. C., & Hon, D. N. S. (1984). Chemistry of weathering and protection, 401- 451: In: The Chemistry of Solid Wood, Rowell, R. M. (ed.), American Chemical Society, Washington DC.

Forsthuber, B., Schaller, C., & Grüll, G. (2013). Evaluation of the photo stabilising efficiency of clear coatings comprising organic UV absorbers and mineral UV screeners on wood surfaces. Wood Science and Technology, 47, 281–297.

Freeman, M. H. and McIntyre, C. R. (2008). A comprehensive review of copper-based wood preservatives with a focused on new micronized or dispersed copper systems. Forest Products Journal, 58(11), 6–27.

Fufa, S. M., Jelle, B. P., & Hovde, P. J. (2012). Effects of TiO_2 and clay nanoparticles loading on weathering performance of coated wood. Progress in Organic Coatings, 76, 1425–1429.

George, B., Suttie, E., Merlin, A., & Deglise, X. (2005). Photodegradation and photostabilisation of wood-The state of art. Polymer Degradation and Stability, 88(2), 268-274.

Hill, C. A. S. (2006). In: Wood modification- chemical, thermal and other processes, C. A. S. Hill (ed.), John Wiley & Sons Press, England.

Liu, C., Ahniyaz, A., & Evans, P. D. (2010). Preliminary observations of the photostabilization of wood surfaces with cerium oxide nanoparticles. In International Research Group on Wood Protection, Stockholm, Sweden, IRG/WP/10-40504.

Lu, Y., Xiao, S., Gao, R., Li, J., & Sun, Q. (2014). Improved weathering performance and wettability of wood protected by CeO2 coating deposited onto the surface. Holzforschung, 68(3), 345-351.

Miklečić, J., Blagojević, S. L., Petrič, M., & Rajković, M. J. (2015). Influence of TiO2 and ZnO nanoparticles on properties of waterborne polyacrylate coating exposed to outdoor conditions. Progress in Organic Coatings 89, 67-74.

Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., & Zöbl, H. (2013). Yellowing and IR-changes of spruce wood as result of UV-irradiation. Journal of Photochemistry and Photobiology B: Biology, 69, 97-105.

Nair, S., Nagarajappa, B. G., & Pandey, K. K. (2018). UV stabilization of wood by nano metal oxides dispersed in propylene glycol. Journal of Photochemistry & Photobiology, B: Biology, 183, 1-10.

Nikolic, M., Lawther, J. M., & Sanadi, A. R. (2015). Use of nanofillers in wood coatings: A scientific review. Journal of Coating Technology Research, 12, 445–461.

Rosu, D., Teaca, C. A., Bodirlau, R., & Rosu, L. (2010). FTIR and color change of the modified wood as a result of artificial light irradiation. Journal of Photochemistry and Photobiology B: Biology, 99, 144-149.

Rowell, R. M. (2005). In: Handboook of Wood Chemistry and Wood Composite, Rowell, R. M. (ed.), Taylor and Francis, CRC Press, Florida.

Saha, S., Kocaefe, D., Boluk, Y., & Pichette, A. (2013). Surface Degradation of CeO2 Stabilized Acrylic Polyurethane Coated Thermally Treated Jack Pine During Accelerated Weathering. Applied Surface Sciences, 276, 86–94.

Schaller, C., Rogez, D., & Braig, A. (2011). Organic vs Inorganic Light Stabilizers for Waterborne Clear Coats: A Fair Comparison. Journal of Coating Technology Research, 9(4), 433–441

Srinivasa, K., & Pandey, K. K. (2017). Enhancing Photostability of Wood Coatings Using Titanium Dioxide Nanoparticles. In: Wood is Good. Pandey, K., Ramakantha, V., Chauhan, S., Arun Kumar A. (eds) Springer, Singapore pp 251-259.

Suslick, K. S., & Price, G. J. (1999). Applications of ultrasound to materials chemistry, Annual Review of Materials Science, 29, 295-326.

Tolvaj, L., & Faix, O. (2009). Artificial Ageing of Wood Monitored by DRIFT Spectroscopy and CIE *L*a*b** Color Measurements. 1. Effect of UV Light. Holzforschung, 49, 397-404.

Wang, X., Liu, S., Chang, H., & Liu, J. (2014). Sol-Gel Deposition of TiO_2 nanocoatings on wood surfaces with enhanced hydrophobicity and photostability. Wood and Fiber Science, 46(1), 109-117.

Williams, R. S. (2005). Weathering of wood, 139-185: In Handbook of Wood Chemistry and Wood Composites, Rowell, R. M. (eds.). CRC press, Florida, USA.