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

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 metallic 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 (CeO₂) 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 spectrophotometer. Dispersion of CeO₂ nanoparticles in PU coatings (concentration >2 %) restricted the photoyellowing of wood polymers.

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

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
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; Miklečič 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).

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
2 MATERIALI IN METODE

2.1 MATERIALS
2.1 MATERIALI

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-glycidoxypropyltrimethoxy 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 NANOĐELC, 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.

2.4 COATING OF WOOD WITH NANOPARTICLES DISPERSING IN ISOPROPANOL/PU

2.4 POVRŠINSKA OBDELAVA LESA Z NANOĐELCI, 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 DISPERSING IN ISOPROPANOL/PU

2.5 FOTOSTABILNOST POVRŠIN LESA, OBDelanih Z NanoĐelci, 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 ºC. 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 analyzed 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 spectrophotometer (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 $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ values. These values were used to calculate the total colour change $\Delta E^*$ as a function of the weathering time, according to the following equation 1 (CIE 1986),

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

The $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ 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

#### 3.1 SURFACE FUNCTIONALIZATION OF CEO$_2$ NANOPARTICLE

##### 3.1.1 Ultraviolet-Visible Absorption spectra

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
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 LEŠA, 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 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 CeO$_2$ coated wood

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 absorbers 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 CeO$_2$ 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
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 76.63 ± 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
Srinivasa, K., Pandey, K. K., & Petrič, M.: Photostabilization of rubberwood using cerium oxide nanoparticles. Part 1: Characterization and colour changes

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 (\( \Delta L^* \)) and yellowness (\( \Delta b^* \)) for uncoated and nano coated wood are shown in Fig. 6. \( \Delta a^* \) 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 \( \Delta L^* \) values indicated the darkening of wood due to degradation from UV light. The \( \Delta L^* \) values were negligible in wood coated with 6% of CeO\(_2\) even after 500h of UV exposure. The control wood showed an increase in \( \Delta b^* \) values with time. In contrast, negative \( \Delta b^* \) 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 \( \Delta L^* \) and \( \Delta b^* \) 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 \( \Delta L^* \) values were negative for wood coated with PU alone. \( \Delta L^* \) values in wood coated with 2%, 4% and 6% CeO\(_2\) in PU remained constant. The \( \Delta b^* \) 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.
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 6. Changes in the $\Delta L^*$ and $\Delta b^*$ values of control and wood surfaces coated with CeO$_2$ plotted against time of UV exposure. A) Without PU coating, B) with PU coating.

Slika 6. Vrednosti $\Delta L^*$ in $\Delta b^*$ kontrolnih vzorcev in površin lesa z nanodelci CeO$_2$ ki so bili izpostavljeni UV svetlobi.
The total colour change ($\Delta E^*$) of control and nano coated wood at different time intervals is shown in Fig. 8. The $\Delta E^*$ 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 $\Delta E^*$ values were maximal for uncoated wood ($\Delta E^* = 10$), which however were found to reduce with the addition of different nanoparticle concentrations. Wood coated with >2 % nanoparticles showed a much lower increase in $\Delta E^*$ 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 $\Delta E^*$ 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 ($\Delta E^*<6$) in contrast to lower loadings ($\Delta E^* = 18$ 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.
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-glycidyloxypropyltrimethoxysilane) 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
5 POVZETEK

Surface functionalization of nanoparticles using 3-glycidyloxypropyltrimethoxysilane (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 homogeneous 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.

Izvedli smo površinsko funkcionalizacijo nanodelcev s 3-glicidiloksipropiltrimetoksi silanom (GPTMS). Modificirane nanodelce smo dispergirali v izopropanol 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 spektro so za nanodelce pokažali 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 polimeri osnovi. Nato smo proučili učinkovitost nanodelcev CeO$_2$ nanodelcev za foto-stabilizacijo površin lesa kavčukovca (Hevea brasiliensis). Pripravili smo disperzijo površinsko funkcionaliziranih nanodelcev v izopropanol ali brezbarvni transparentni poliuretanski premaz z nanodelci (koncentracija od (0.5 – 6) %).
Srinivas, K., Pandey, K. K., & Petrič, M.: Photostabilization of rubberwood using cerium oxide nanoparticles.
Part 1: Characterization and colour changes

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 %.

ACKNOWLEDGEMENTS

The study was supported by the Council of Scientific and Industrial Research (CSIR), New Delhi (Grant No 38 (1198)/08/EMR-II).

REFERENCES

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

Aloui, F., Ahaji, 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, 635-6236.

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 de l’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 Handbook 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., & Grill, 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 TiO2 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., Ahnijay, 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., Petrić, 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., Bodirilau, 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: Handbook 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., Rogetz, 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., & Petrič, M.: Fotostabilizacija lesa kavčukovca z nanodelci cerijevega dioksida.
1. del: Karakterizacija in spremembe barve

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 TiO₂ 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.