Effects of adding TiO₂ nanoparticles to a water-based varnish for wood applied to nine tropical woods of Costa Rica exposed to natural and accelerated weathering

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Abstract The addition of titanium dioxide nanoparticles (TiO₂ nanoparticles) to a water-based varnish used for finishing tropical woods was studied. Three different concentrations of TiO₂ nanoparticles (0%, 1.0%, and 1.5%) were evaluated. The nanoparticles were characterized by means of the transmission electron microscopy and an X-ray diffractometer. The varnish prepared was evaluated for its viscosity, adhesion of the film to the wood, water absorption, and the effects of natural weathering on the color and quality of the varnish. It was found that viscosity decreases as the concentration of TiO₂ nanoparticles increases, while no variation was found in the thickness of the film. Except for *Gmelina arborea* and *Tectona grandis*, the adhesion was not statistically affected. It was found that, in the 9 species tested, incorporation of TiO₂ nanoparticles decreased the values of water absorption. The evaluation of natural weathering showed that the varnish with no added TiO₂ nanoparticles degraded completely after 1 year of weathering

exposure, while the modified varnish film endured. Less color change was observed in lumber treated with the varnish containing TiO₂ nanoparticles. The best performance of the varnish in the nine tropical woods used was observed when TiO₂ nanoparticles were added at 1.5% concentration.

Keywords Coating, Nanotechnology, Tropical species, Additives, XRD spectrum

Introduction

Wooden structures are generally exposed to a number of factors which deter its appearance and performance, such as moisture, UV radiation, and temperature or mechanical stresses.¹ Among the variety of products applied to the surface of lumber, varnishes and coatings are used to protect and enhance the beauty, color, and natural appearance of the wood.² Today, nanotechnology represents a strong alternative for the development of new product formulations that provide greater protection and durability to the wood.³

The development of nanotechnology has helped meet the need for continuous improvement of the industry of adhesives and coatings.^{4–6} Fufa et al.³ mention that less than 10% of nanoparticles in the coatings can help improve the properties of lumber significantly.

Nanofillers can aid the creation of a varnish or coating film that is more resistant to UV radiation, water, fungal growth, stains, and grease.⁷ Numerous studies show how the addition of nanoclays, nanosilica, nanocellulose, TiO₂ and ZnO nanoparticles, and other kinds of nanofillers increase the performance of varnishes and coatings.^{8–11}

The addition of TiO₂ nanoparticles to coatings such as UV-blocking agents is an extensive practice. From the four polymorphs present in TiO₂ nanoparticles (anatase, rutile, brookite, and TiO₂ (B)), rutile offers

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greater effectiveness as a stabilizer of photo-oxidation of polymers, hence its great importance for the coatings industry.^{11,12} In addition to blocking and absorbing large amounts of solar radiation, TiO₂ nanoparticles provide photostabilization as a coating.^{3,11,13}

However, naked TiO₂-filled paint, plastic, and paper commonly undergo pulverization and yellowing discoloration under sunlight, resulting in the decrease of their weathering stability. On the other hand, naked TiO₂ powders with submicrometer size and strong polarity have a tendency to form aggregates, causing a lower dispersion extent in substrates. To overcome the problems, TiO₂ powders need to be coated with inert inorganic films, such as SiO₂, Al₂O₃, or both. Direct coating of SiO₂ or Al₂O₃ on the surfaces of TiO₂ powders has been widely studied.^{14,15}

Likewise, antimicrobial and bactericidal activities of TiO₂ nanoparticles make them an option for the protection of lumber exposed to damage from environmental conditions.⁹ Veronovski et al.¹¹ also mention that one advantage of TiO₂ nanoparticles is that, instead of migrating, these remain in materials, promoting greater effectiveness against UV rays.

Environmental conditions present in the tropical region, such as high temperatures and the presence of rainfall throughout almost all of the year, allow a great variety of tropical species to develop in countries such as Costa Rica.¹⁶ Nonetheless, one limiting factor found in the use and exploitation of many species used in reforestation is the scarce knowledge about the chemical properties, drying, preservation, natural durability of the wood, and resistance or color change of the varnishes applied to these lumber species.¹⁷

In general, studies about color and varnish performance on the surface of lumber with or without nanoparticles are oriented to species from tempered regions, among which *Betula pendula*,¹⁸ *Cryptomeria japonica*,¹⁹ and *Picea abies*^{3,18,20–22} stand out. Because of this orientation, many finishing product factories, including those from Costa Rica, develop their products based on the behavior observed in temperate-climate lumber. However, although limited, there are some studies on the behavior of various varnishes in tropical lumber, such as those on *Cedrela odorata*, *Carapa guianensis*, *Tectona grandis*, and *Acacia mangium*.^{23–25}

Degradation of the surface of the varnish (in color and appearance) on wood in the open air is one of the disadvantages of the varnishes.²⁶ Different studies^{18,21,22} have found that ultraviolet (UV), visible, and infrared light are the ones generating the greater chemical reactions in the components of the wood and the varnish, causing degradation of the latter.

The purpose of this work was to study the effect of the addition of TiO₂ nanoparticles on the UV light tolerance of a water-based wood varnish applied to nine tropical species (*Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyra-*

midale, *Tectona grandis*, and *Vochysia ferruginea*). Also, to show changes that occurred in viscosity, level of adhesion, and water absorption of the varnishes, the durability of nanocomposite coatings was evaluated through accelerated and natural weathering.

Materials and methods

Materials

Titanium dioxide nanoparticles (TiO₂ nanoparticles) of the commercial brand Hombitec RM400[®] (http://www.sachtleben.de/fileadmin/pdf_dateien/brochures/043_HOMBITEC.pdf) were employed, provided by Sachtleben Chemie (Germany). Information supplied by the manufacturer indicates that it is a long-term UV-absorbing TiO₂ nanoparticle for use in wood varnishes, with an approximate primary particle size of 10 nm and a specific surface area of 110 m² g⁻¹, yellowish, in powder form, and with a TiO₂ percentage of 78%; doped with an organic and inorganic surface treatment (Al₂SO₃).

The TiO₂ nanoparticles were tested in a wood varnish of the commercial brand Barnizol[®], supplied by the company Xilo Química (Costa Rica). This varnish is water based and contains 3–10% acrylic dispersant, 1–5% Natrosol, 1–8% Texanol, 1–5% propylene glycol, 0.1–3% Triton X-100, 1–5% triethanolamine, 1–5% sodium polyacrylate, Mergal K-10, and Mergal-89. (http://www.grupoxilo.com/app/files/chemicalproducts/files/26_securityfile_barnizuv3en1msds.pdf).

The species used to test the varnish with the added nanoparticles were *Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyramidale*, *Tectona grandis*, and *Vochysia ferruginea*, which are species traditionally employed in Costa Rica for fabrication of wooden doors and other products, as well as engineering products which demand intensive use of varnishes.^{27–29} These lumbars were obtained from different markets of sawn wood.

Preparation of the coating with TiO₂ nanoparticles

TiO₂ nanoparticles were added to the varnish in two concentrations as a function of its weight: 1% and 1.5%. Evaluations were done with respect to varnish with no added TiO₂ nanoparticles. In this way, 3 varnish types were prepared: 2 with TiO₂ nanoparticles (1.0% and 1.5%) and 1 without TiO₂ nanoparticles. Incorporation of TiO₂ nanoparticles into the resin was carried out in two stages. In the first stage, the weight of the nanoparticles necessary to prepare 4 L of the varnish with the concentrations of 1% and 1.5% was calculated; this amount of nanoparticles was then diluted in 100 mL of water (dispersion A) by means

of mechanical stirring. In the second stage, the aqueous nanoparticle mixture was added to the paint, after previous calculation of the amounts of different components of the varnish (resin, diluting water, and additives). The resin was slowly added to the diluent until total suspension was achieved, then the additives were slowly added in parallel to the addition of nanoparticles until their dispersion was guaranteed.

Characterization of the varnish

First, the structure and presence of TiO₂ nanoparticles in the coating were observed by means of the Transmission Electron Microscopy (TEM) and the X-ray diffractometer (XRD), and the viscosity of the coating was evaluated. The equipment model Hitachi-7700 was employed for the TEM. A 1.1 mg sample of TiO₂ nanoparticles was taken and 1 mL of ethanol at 95% was added to it. This was then ultrasonified for 20 min. Afterwards, a 2 µL sample was taken and placed on a Cu 600-mesh grid covered with a collodion film. For XRD spectra were determined for TiO₂ nanoparticles, two different varnishes with TiO₂ nanoparticles and for four main components of varnish (Natrosol, acrylic dispersant, Mergal K-10, and Mergal-89).

X-ray diffraction patterns of the cured varnishes were obtained with the PANalytical Empyrean Series 2 diffractometer (Cu-Kα, 6°–40° 2θ), together with the PANalytical High Score Plus software. Analysis of the samples was done within the range of the characteristic bands of TiO₂ nanoparticles, with 2θ ranging from 20° to 80°. A 1-mm-thick, 26-mm-long, and 76-mm-wide film was prepared in order to obtain the samples for the study of the XRD patterns. The coating was poured on a 1.5 mm neoprene rectangle placed on a glass plate. The sample was left to dry at room temperature for 2 days.

Last, the characterization of viscosity was performed employing a 600 mL Low Form Griffin Beaker with a 500 mL working volume of adhesives in a Brookfield-11+ Pro LV.2.4.4, according to the ASTM D2256-11 standard.³⁰ A spindle number of 3 was used for all three types of varnishes. Viscosities were evaluated at the speeds of 2, 5, 8, 11, 14, 17, 20, 26, 29, and 35 rpm.

Wood species, surface preparation, and application of coating

The behavior of the three types of varnishes (2 with nanoparticles and 1 without them) was evaluated in 9 tropical species (*Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyramidale*, *Tectona grandis*, and *Vochysia ferruginea*). For each species, 945 samples with the dimensions of 150 mm length, 65 mm width, and 4.3 mm thickness were prepared.

Prior to application of the coating, all sample surfaces were polished using 100 grit sandpaper and

two layers of coating were applied using a Laboratory Lacquer Roller Coating machine (BKL Bürkel). An average 32-µm-thick film per layer was applied, after which the samples were left to dry for 4 h. All samples were climatized to 12% moisture content for 1 week.

Dry film thickness, adhesion test, and water absorption

Dry film thickness of the coating and its adhesion and moisture absorption were assessed for the three types of varnishes (2 with nanoparticles and 1 without them) in the 9 tropical species. First, the dry film thickness was measured according to the ASTM D6132-13 standard,³¹ for which a PosiTector® 200 series ultrasonic coating thickness gage (DeFelsko, USA) was employed. This test was carried out on 81 samples prepared with the varnish, and each sample was measured in 2 different places (9 species × 3 varnishes × 3 samples × 2 different places = 162 measurements).

The samples were then divided into two halves. The first half was used to measure adhesion by means of a tape test, according to the ASTM D3359-09 standard.³² The measurement consisted of slicing the coating film with a crosshatch cutter along two directions (one perpendicular to the other), then placing an adhesive tape at the crossing point and proceeding to remove the tape by pulling in a single smooth action. Damage caused to the varnish film was classified into 6 categories depending on the area removed, as detailed in the ASTM D3359-09 standard.³²

The other half was used to measure water absorption, following the methodology proposed by Kowalczyk³³ and Ekstedt and Östberg.³⁴ Samples with the varnish at the edges and the back side were coated with paraffin wax in order to prevent water penetration through the unvarnished areas. Once those sides were dry (24 h later), the samples were weighed and their varnished surface was placed in contact with distilled water. The samples were weighed again after 24 and 72 h. The period of water absorption concluded after 7 days, and the samples were weighed once again. Water absorption (WP) was determined through the increase in weight of the test samples, according to the following equation:

$$WP\left(\frac{g}{m^2}\right) = \frac{m_2 - m_1}{A}, \quad (1)$$

where m_1 is the mass of the sample (before testing), m_2 is the mass of the water-treated sample, and A is the area of the tested varnished surface.

UV protection determination

For the samples in this determination, it was necessary to prepare a 200-µm-thick (approx.), 26-mm-long, and

76-mm-wide film. The coating was poured onto a glass sample plate. The sample was dried at room temperature for 2 days. Then the UV-Vis spectra of the film coating were recorded with a Perkin Elmer UV/Vis spectrophotometer (Lambda 2S) in transmittance mode at a resolution of 2 nm^{-1} . The scanning range was 150–800 nm. For each film, three measurements were carried out on different spots per cycle.

Wood color evaluation

Color was assessed through weathering exposure of the 9 wood species with the 3 types of varnishes with different contents of TiO_2 nanoparticles (0.0%, 1.0%, and 1.5%). Two kinds of weathering exposure were tested: natural and accelerated. A total of 432 samples were tested (9 species $\times$ 3 varnishes $\times$ 16 samples) for each condition of exposure. In natural weathering (NW), wood samples were exposed for 365 days (1 year) with an inclination of 15° South in an area free of shade where the samples were directly impacted by rain, sun, and wind. The test began in November 2013 and ended in November 2014. Wood samples were exposed in the province of Cartago in Costa Rica ($9^\circ 50' 59''\text{N}$; $83^\circ 54' 37''\text{W}$). The climatic conditions were widely detailed by Valverde and Moya²³ and Salas et al.²⁵ For accelerated weathering (AW), UV exposure was administered by means of a weathering Q-Lab chamber (QUV/spray model). The ASTM G154-12a standard was used for this test.³⁵ The exposure consisted of a 4-h cycle in two phases: first, 4 h of UV radiation at 50°C and 0.71 W/m^2 (with a mercury bulb of type UVB 313L and a wavelength of 310 nm), followed by a second phase of condensation which lasted 2 h and consisted of using evaporated water at 50°C . The UVB 313 bulbs are known to distort the chemical components compared to natural weathering. This is due to the action of light with a wavelength shorter than that found on the surface of the earth. Thus, results from UVB 313 weathering are often found to not correlate directly with natural weathering. The total exposure amounted to 500 h for each species. For AW, the color was measured at the end of the 500 h of exposure but, for NW, color was assessed in different time points. Wood samples in this condition were evaluated between the 10th and 12th hour in the morning and without any event of rainfall before the measurement. The color of the surface was measured every 15 days during the first 3 months, after which the color was measured monthly until exposure time was terminated.

Color measurement was done with a Hunter Lab MiniScan XE Plus spectrophotometer. The CIE Lab standardized chromatologic system was used. The range of this measurement is from 400 to 700 nm with an 11-mm opening at the point of measurement. For the observation of reflection, the specular component (SCI mode) was included at a 10° angle, which is normal for the specimen surface (D65/10), a field of

vision of 2° (Standard observer, CIE 1931), and an illumination standard of D65 (corresponding to daylight in 6500 K). The MiniScan XE Plus generated three parameters for each measurement, namely L^* (luminosity), a^* (variation of color from red to green), and b^* (variation of color from yellow to blue).

Color change (ΔE^*): It was determined as the net color variation for each varnish in a period of time. This difference was determined according to the ASTM D 2244 standard formula, detailed in equation (2).^{36,37} The color difference was determined for each type of varnish in each species in the different types of exposure.

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

where ΔE^* denotes the wood color difference; $\Delta L = L^*$ value before weathering $- L^*$ value in different types of exposure; $\Delta a = a^*$ value before weathering $- a^*$ value in different types of exposure; and $\Delta b = b^*$ value before weathering $- b^*$ value in different types of exposure.

Statistical analysis

Per species, a one-factor (one-way ANOVA) analysis of variance was applied to film thickness, water absorption, color change, and coating surface quality index. The model included these parameters as dependent variables and the TiO_2 nanoparticle concentration as the independent source. The difference among the averages was assessed through Tukey's test with a level of significance of $P < 0.05$.

Results and discussion

Characterization of the coating

TEM observations and XRD patterns

TEM observations of TiO_2 nanoparticles showed that the TiO_2 powder in rutile phase consists of both spherical and rod shapes (Figs. 1a and 1b). Furthermore, it can be estimated that the particle size of the samples is in microscale with the grain size of about 30–70 nm. The XRD patterns of the TiO_2 nanoparticles and varnish without nanoparticles, as well as their presence in the varnish, are shown in Fig. 1a. The TiO_2 nanoparticles showed strong diffraction peaks at 27, 36, 41, 43, 54, 56, 62, 68, and 69, which correspond to (110), (101), (200), (111), (210), (211), (220), (002), (310), (301), and (112) planes of rutile TiO_2 nanoparticles (JCPDS number 98-003-3842). In the rutile phase, the powder appeared randomly containing crystals and both spherical and rod shapes.^{38,39} The varnish without TiO_2 nanoparticles presented strong diffraction peaks

Fig. 1: (a) and (b) TEM image showing the shape of TiO₂ nanoparticles; (c) XRD patterns of TiO₂ and coatings with TiO₂ nanoparticles at 1.0% and 1.5%; (d), (e), and (f) comparison of diffraction intensity between rutile TiO₂ and coatings with TiO₂ nanoparticles at 1.0% and 1.5%, and (g) XRD patterns of four main components or varnish. Comparison between coatings with and without TiO₂ nanoparticles is not present because no coincidence was found

at 10.34, 12.03, and 24.56 (Fig. 1a), which correspond to Mergal-89 component of varnish (Fig. 1g). For three varnishes, a dispersion peak at 19.5° appeared (Fig. 1c), which is attributed to hydroxypropyl methylcellulose content in the Natrosol component of varnish (Fig. 1g).

Regarding TiO₂ nanoparticles in the varnish, a different XRD pattern was observed: a strong diffraction peak was observed at 27° (Fig. 1c), while weak signals of the varnishes with TiO₂ nanoparticles (Figs. 1e and 1f) appeared at 36°, 41°, and 43°. Meanwhile, in the varnish with 1.5% concentration of

TiO₂ nanoparticles, signals appeared weak at 54° and 56° (Fig. 1f). Then TiO₂ nanoparticles in the varnish are presented in rutile plane. This weakening of TiO₂ nanoparticles signals in the varnishes is attributed to the loss of crystallinity of nanoparticles.³⁸ According to Vatanpour et al.⁴⁰ and Li et al.,⁴¹ the TiO₂ nanoparticles were distributed in the matrix of the varnish resin or there is a possibility of interaction between the nanoparticles and the resin and new composites are thus produced.

Viscosity

Viscosity decreased as the rotational speed increased in the three different coatings (Fig. 2), a behavior known as ‘shear thinning’ that is characteristic of pseudoplastic fluids.⁴² Coatings to which TiO₂ nanoparticles were added did not show any significant variation in viscosity at speeds below 5 rpm. The behavior observed below this speed (5 rpm) is expected when added to any parent nanofillers because of low energy. Viscosity was lower in the coating with 1% TiO₂ nanoparticles than that of the coating with 1.5% concentration (Fig. 2). Above 5 rpm, nevertheless, a slight decrease could be observed in the viscosity of the modified coating in relation to the coating with no TiO₂ nanoparticles.

This decrease of viscosity in relation to coating without TiO₂ nanoparticles may be attributed to the preparation of the varnish with TiO₂. The nanoparticles were suspended in water (300 mL), which was then added to the coating, thus causing dispersion of the solids and a consequent reduction in viscosity.⁴³

Fig. 2: Absolute viscosity of the tested coatings with different concentrations of TiO₂ nanoparticles

Film thickness and adhesion test measurements

The thickness of the varnish films was not significantly affected in most of the species for both concentrations of TiO₂ nanoparticles, with the exception of *G. arborea* and *T. grandis*, where statistical differences appeared only between the varnish with 1.5% of TiO₂ nanoparticles and the varnish without nanoparticles (Table 1). One important aspect to highlight from the results of the film thickness measurement for *O. pyramidale* is that the values varied from 58.0 to 60.5 μm, far superior than those of the rest of the species, which ranged from 30.5 to 35.1 μm.

The assessment of the adhesion test showed differences in *G. arborea* and *T. grandis*. For both species, the film of the varnish showed greater adhesion when treated with TiO₂ nanoparticles (Table 1). No differences were observed for the rest of the species between the varnish with TiO₂ nanoparticles and the one with no added nanoparticles.

The adhesion test assessed the resistance of the varnish coating on the surface of the wood; the adhesion force between the varnish and the wood surface was measured, as were the internal forces of the varnish (cohesion).² Then, according to the results of the adhesion test (in every case greater than 4B), the varnish with added TiO₂ nanoparticles showed adequate adhesion properties similar to those of the varnish with no added nanoparticles, indicating that the forces intervening in adhesion between the film of the varnish and the surface of the wood were not influenced by the nanoparticles. In *C. odorata*, however, adhesion of the film was weak, as indicated by the lowest values of the adhesion test, probably influenced by the large amount of nonpolar extractives present in this type of wood.^{44,45} As a result, forces intervening in the adhesion between the varnish and the surface of the wood were weaker.²

Water absorption

Results of the water absorption test in the different time lapses evaluated (24, 72, and 168 h) showed that the value of this variable increased with the time immersed in water spent by the lumber with the films of varnish of all three surface coatings (Fig. 3). Moreover, it was observed that for each period of absorption the value for water absorption was similar among the different species, with the exception of *C. odorata* and *G. arborea* (Figs. 3b and 3e), which showed values slightly lower than those of the other species for the longer periods. Among the results for the different species, no significant differences were found in *E. cyclocarpum* and *T. grandis* regarding water absorption values for the three varnishes in the three time lapses (Figs. 3d and 3h). Meanwhile, no significant differences were observed in the water absorption values of *C. odorata* and *C. alliodora* in the periods of 24 and 72 h, although lower water

Table 1: Film thickness and percent of area removed during coating test, using different concentrations of TiO₂ nanoparticles

Species	TiO ₂ nanoparticle concentration (%)	Film thickness (μm)	Area removed (%)
<i>Acacia mangium</i>	0.00	33.9 a	2 (4B)
	1.00	33.0 a	9 (4B)
	1.50	35.1 a	2 (4B)
<i>Cedrela odorata</i>	0.00	34.7 a	0 (3B)
	1.00	34.7 a	0 (3B)
	1.50	34.3 a	0 (3B)
<i>Cordia alliodora</i>	0.00	33.4 a	2 (4B)
	1.00	34.3 a	2 (4B)
	1.50	30.5 a	1 (4B)
<i>Enterolobium cyclocarpum</i>	0.00	34.7 a	0 (5B)
	1.00	35.1 a	0 (5B)
	1.50	34.3 a	1 (5B)
<i>Gmelina arborea</i>	0.00	36.4 a	1 (4B)
	1.00	33.9 ab	1 (5B)
	1.50	31.3 b	1 (5B)
<i>Goethalsia meiantha</i>	0.00	33.4 a	2 (5B)
	1.00	33.0 a	1 (5B)
	1.50	33.4 a	1 (5B)
<i>Ochroma pyramidale</i>	0.00	58.0 b	9 (4B)
	1.00	58.8 b	5 (4B)
	1.50	60.5 b	5 (4B)
<i>Tectona grandis</i>	0.00	33.0 b	2 (4B)
	1.00	34.3 ab	17 (5B)
	1.50	35.1 a	3 (5B)
<i>Vochysia ferruginea</i>	0.00	33.4 a	1 (4B)
	1.00	34.3 a	2 (4B)
	1.50	32.2 a	2 (4B)

Different letters indicate statistical differences at 95% in coating with three different TiO₂ nanoparticle concentrations

absorption was observed in the 168-h period at the surface of the lumber with the TiO₂ nanoparticle varnish (Figs. 3b and 3c). In the rest of the species (*A. mangium*, *G. arborea*, *G. meiantha*, *O. pyramidale*, and *V. ferruginea*), immersion in water of the surface of the wood with the nanoparticles in either concentration did not affect water absorption after 24 h; however, when this period was increased to 72 or 168 h, water absorption values in both varnishes with TiO₂ nanoparticles decreased relative to the varnish with no added nanoparticles (Figs. 3a, 3e–3g and 3i).

Moisture absorption in the finished lumber is determined by the absorption of the varnish and, to a lesser extent, by the properties of the substrate or the wood.³⁴ This could be the explanation for the similarity between the values of water absorption found among the species. Regarding the lower values of moisture absorption in *C. odorata* and *G. arborea*, these can be explained by the lower water absorption value of these two wood species,^{47,48} which causes the scarce amount of water absorbed by these species.

Absorption of the varnish is influenced, in the first place, by the type of solvent used to dissolve the resin, waterborne coatings generally tending to be more permeable than solventborne coatings.⁴⁶ This factor

constitutes the principal cause for the high water absorption values found in this study (Fig. 3), since the varnish employed is a solventborne coating. In the same way, water absorption of the varnish is influenced by the addition of different binder and solvent types, as well as the pigment volume concentration, and, above all, by constituents containing hydroxyl and etheric groups.³³ However, by adding TiO₂ nanoparticles these groups become less available to water, which reduces water absorption in the varnishes modified with these nanoparticles regarding the different species analyzed in this study.

UV protection determination

The UV–Vis absorbance and transmittance spectra of three varnishes (with and without TiO₂ nanoparticles) are shown in Fig. 4. It can be seen that the absorbance and transmittance spectra of varnishes with and without TiO₂ nanoparticles have similar shapes. Besides, it was observed that the three varnishes absorbed strongly in the UV region (275–400 nm), which indicates that the highest absorbance or transparency of varnish films is limited. In fact, the commercial sheet

Fig. 3: Water absorption for varnish with TiO_2 nanoparticles tested in nine tropical species. Different letters indicate statistical differences at 95% in coating with three different TiO_2 nanoparticle concentrations

Fig. 4: UV-Vis absorbance and transmittance spectra of clear varnish with and without TiO_2 nanoparticles

indicated that the varnish is cataloged as opaque. There are some differences between varnishes with and without TiO_2 nanoparticles. The film prepared with TiO_2 nanoparticles at 1.5% presented the highest absorbance (Fig. 4a) and therefore the lowest trans-

mittance (Fig. 4b) in the UV and visible zone. The varnish prepared with 1.0% of TiO_2 nanoparticles presented higher absorbance than that without TiO_2 nanoparticles before 300 nm, but the absorbance between 300 nm and the visible area was higher in

Fig. 5: Color change (ΔE^*) values of three types of varnishes with different concentrations of TiO_2 nanoparticles exposed to both natural and accelerated weathering in nine tropical woods. Different letters indicate statistical differences at 95% in coating with three different TiO_2 nanoparticle concentrations

varnish with 1.0% of TiO_2 nanoparticles than that in varnish without nanoparticles (Fig. 4a). Then, the varnishes prepared with TiO_2 nanoparticles presented higher absorbance and lower transmittance than that without TiO_2 nanoparticles, while the varnish prepared with 1.5% TiO_2 nanoparticles presented higher absorbance and lower transmittance than the varnish prepared with 1.0% TiO_2 nanoparticles in the UV and visible area.

Color change

In all species, a greater ΔE^* was found in the samples exposed naturally in relation to those exposed to accelerated conditions (Fig. 5). For *E. cyclocarpum*, color change in the varnish with no added TiO_2 nanoparticles was statistically higher than that in both varnishes with TiO_2 nanoparticles in AW (Fig. 5d), whereas for *A. mangium* and *C. odorata*, a difference in ΔE^* appeared only in the varnish with 1.5% of TiO_2 nanoparticles (Figs. 4a and 4b). Meanwhile, for *C. alliodora*, *G. arborea*, *G. meiantha*, *O. pyramidale*, and *V. guatemalensis* in AW, the varnish without TiO_2 nanoparticles had a statistically lower ΔE^* value than

the varnishes with TiO_2 nanoparticles (Figs. 5c, 5e–5g, and 5i). *T. grandis* was the only species in which no statistical differences were observed among the different types of varnishes (Fig. 5h).

Regarding the two types of varnishes under AW condition, a statistically lower value of ΔE^* was observed in the varnish with 1.5% of TiO_2 nanoparticles in *A. mangium*, *C. odorata*, and *V. ferruginea* (Figs. 5a, 5b, and 5i). No statistical differences were observed between both varnishes with TiO_2 nanoparticles in *C. alliodora*, *E. cyclocarpum*, and *T. grandis*. *G. arborea* and *G. meiantha* were the only species in which the varnish with 1.0% concentration had a higher value than with 1.5% concentration (Figs. 5e and 5f).

For NW conditions, it was observed that the varnish with no added TiO_2 nanoparticles was no longer present by the time of assessment after 365 days; nevertheless, color was still measured. In most of the species, color change (ΔE^*) was statistically higher in the varnish with no added TiO_2 nanoparticles than in the modified varnishes, with the exception of *E. cyclocarpum* and *T. grandis*, which did not show differences among the three types of varnishes (Figs. 6d and 6h). By observing the behavior in time of ΔE^* in

Fig. 6: Variations in time of ΔE^* for three types of varnishes with different TiO_2 nanoparticle concentrations in nine tropical woods exposed to natural weathering

these conditions, it was confirmed once again that color change at the surface of wood is lower in varnishes with TiO_2 nanoparticles (Fig. 6), with the exception of *E. cyclocarpum* (Fig. 6d). Another aspect observed was that, after 300 days of exposure, an increase in color change tends to take place in many of the species (Fig. 6).

Regarding varnishes with the two concentrations (1.0% and 1.5%), a statistically lower ΔE^* value was only observed for the varnish with 1.5% concentration in the lumber from *V. ferruginea* (Fig. 5i). For the rest of the species (*A. mangium*, *C. odorata*, *C. alliodora*, *G. arborea*, *G. meiantha*, and *O. pyramidale*), the values were statistically equal for both varnishes with TiO_2 nanoparticles (Fig. 5). Regarding behavior in time, however, it is observed that *C. odorata*, *C. alliodora*, and *T. grandis* show the lowest value of ΔE^* in the varnish with 1.0% TiO_2 nanoparticles (Figs. 6b, 6c, and 6h), while the rest of the species show little difference between both concentrations (Fig. 6).

Variation of the ΔE^* value between NW and AW, as well as the higher ΔE^* values for the different species or the different concentrations of TiO_2 nanoparticles (Figs. 4 and 5), is due to the fact that during NW there is a constant variation of solar radiation, moisture, amount of water, contamination, and biotic agents, which accelerate color degradation processes in comparison to AW, in which these biotic

agents do not intervene.¹⁸ In this respect, Creemers et al.⁴⁹ point out the difficulty of reproducing the many natural conditions intervening in NW in an accelerated test under laboratory conditions.

Degradation of the varnishes under the exposure conditions (NW or AW) is produced because ultraviolet light causes the breakage of bonds of organic compounds present in the varnish as well as in the coatings,^{10,13} resulting in the degradation of the wood and the coating. If the varnish does not contain the adequate elements against UV rays, deterioration may occur as fast as it would on a wood surface with no varnish.¹⁸

Addition of the TiO_2 nanoparticles to the varnish favors the absorption of a great amount of UV rays (Fig. 4), thus increasing durability.¹¹ This behavior was evident in most of the samples to which a modified coating was added (Figs. 5 and 6), where stabilization and delayed color degradation could be observed. However, the decrease observed in degradation after 300 days of exposure, as ΔE^* tends to increase, is probably due to the fact that some components of the wood or even the TiO_2 nanoparticles have already begun to be removed because of the effects of solar radiation and rain, allowing the degradation of lignin to begin with the resulting color loss.^{3,9,10}

Furthermore, variation in the concentration of TiO_2 nanoparticles (1.0% and 1.5%) does not reflect statis-

tical differences in the protective action provided by the varnish to many of the species (Fig. 2). This behavior can be correlated to the distribution of nanoparticles, which may not have been homogenous throughout the matrix. The TiO₂ nanoparticles show a tendency toward agglomeration,¹¹ a phenomenon which may have occurred during preparation of the coating with 1.5% TiO₂ nanoparticles, contributing to the lack of differences between the concentrations.

Finally, variations of the ΔE^* value in the durability behavior of the varnish across different species (Fig. 6) are due to variations in the chemical compounds—mainly in the extractives—present in each type of wood⁵⁰ and their ability to interact with the varnish.¹⁹ For example, acetylation of OH groups, which may vary among species, is a commonly used strategy in the chemical formulation of varnishes in order to avoid photodegradation.⁵¹

Conclusions

TEM observations of TiO₂ nanoparticles showed that the TiO₂ powders in rutile phase exhibit both spherical and rod shapes. When these are added to the varnish, a significant variation can be observed in the viscosity of the varnish with TiO₂ nanoparticles in relation to the one with no added nanoparticles. Viscosity is lower in the varnish with 1.0% TiO₂ in relation to the one with 1.5%.

The film thickness, adhesion test, and water absorption in the varnishes with both concentrations of TiO₂ were not significantly affected, although in some species these parameters were indeed affected: the adhesion test was affected in *G. arborea* and *T. grandis* and a difference appeared between varnishes in *C. odorata* and *G. arborea*.

In all species, color change (ΔE^*) was higher in those samples under natural exposure than in those under accelerated conditions. The varnish with no added nanoparticles showed a statistically higher color change of the wood than both varnishes with TiO₂ nanoparticles, but the 1.5% concentration of nanoparticles was the one showing the least color change for many of the species and different weathering conditions.

The factors determining the penetration of the coating with TiO₂ nanoparticles and the UV dispersion associated with the various constituents of the varnish sufficed to protect the different surfaces of the tropical lumbers used. Photodegradation was thus delayed, and suitable performance against damages caused by moisture and UV radiation was attained.

Acknowledgments The authors wish to thank the Vicerrectoría de Investigación y Extensión at the Instituto Tecnológico de Costa Rica (ITCR) for the financial support provided for this study.

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