THE EFFECT OF TITANIUM DIOXIDE NANOPARTICLES OBTAINED BY MICROWAVE-ASSISTED HYDROTHERMAL METHOD ON THE COLOR AND DECAY RESISTANCE OF PINEWOOD

Paula Zanatta[1], Marília Lazarotto[2], Pedro Henrique Gonzalez de Cademartori[3], Sérgio da Silva Cava[1], Mário Lúcio Moreira[1,4], Darci Alberto Gatto[1,♣]

ABSTRACT

This study aimed to synthesize titanium dioxide nanoparticles by microwave-assisted hydrothermal method to incorporate them to the structure of *Pinus elliottii* wood. The color changes and the decay resistance of impregnated wood was investigated. The titanium dioxide nanoparticles were impregnated into *Pinus elliottii* wood by vacuum-pressure and simple immersion methods. Furthermore, *Pinus elliottii* wood was treated with chromated copper borate solution tocompare their effectiveness to the titanium dioxide treated wood. The titanium dioxide nanoparticles impregnated by vacuum-pressure were presented especially on the wood surface, forming a homogeneous coating. The titanium dioxide nanoparticles did not change the natural color of wood and, at the same time, decreased the degree of the white rot fungus (*Ganoderma applanatum*) colonization in the wood structure and the wood decay, compared to the untreated one. The titanium dioxide treated wood samples provided similar protection against decay in comparison to wood treated with chromated copper borate. The impegnation with titanium dioxide nanoparticles can be a good alternative to decrease/avoid the fungi proliferation, providing to *Pinus elliottii* wood a self-cleaning mechanism.

Keywords: *Ganoderma applanatum*, hydrothermal microwave, *Pinus elliottii*, vacuum-pressure method, wood preservation.

INTRODUCTION

Wood is widely used for different purposes (Rowell 2012, Lu *et al.* 2014) with good performance. However, wood is highly susceptible to deteriation by xylophagous organisms due to its chemical composition. This susceptibility limits the use of wood, especially for exposure in high humidity conditions.

[1]Programa de Pós-Graduação em Ciência e Engenharia de Materiaias, Centro de Desenvolvimento Tecnológico, Universidade Federal de Pelotas, Pelotas, RS, Brasil.

[2]Departmento de Agronomia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brasil.

[3]Universidade Federal do Paraná, Curitiba, PR, Brasil.

[4]Instituto de Física e Matemática, Departamento de Fisica, Universidade Federal de Pelotas, Pelotas, RS, Brasil.

♣Corresponding author: darcigatto@pq.cnpq.br

Among these xylophagous organisms, fungi are the most aggressive organisms, leading wood to irreversible damages. Kelley *et al.* (2002) affirmed that deterioration and discoloration caused by fungi result in 10-15% of wood devaluation. Another consequence of fungal deterioration is the appearance of defects, such as cracks, and the wood shrinkage (De Filpo *et al.* 2013).

Many type of treatments have been used to protect wood against fungal attack. Among these treatments, heating, chemical modification and impregnation (Humar *et al.* 2004, Lande *et al.* 2004, Tripathi *et al.* 2014, Rassam *et al.* 2012) should be highlighted. Part of these technologies can modify the wood structure, improving more than one property. For example: heat treatment can increase the biological durability of wood and can provide higher dimensional stability (Esteves and Pereira 2008). However, the use some technologies have restrictions to the health and to the environment, as well as about their effectiveness and feasibility (Lu *et al.* 2014).

New technologies with low environmental impact and economically feasible are being developed, improving the wood life cycle. In this context, nanotechnology may provide interesting alternatives to develop new and efficient wood treatments. Once the materials are in the nanometric scale, they have different properties, such as higher surface area and higher reactivity (De Filpo *et al.* 2013). When applied onto wood, they have potential to improve physical and mechanical properties (Taghiyari and Schmidt 2014, Rassam *et al.* 2012).

In the last years, the wood modification based on surface coating and incorporation of oxides or polymers have been attracted attention to the formation of new functional composite materials (Devi and Magi 2013). Recent studies have proposed new alternatives for the development of these functional composites, especially using tetraethyl orthosilicate (TEOS) (Donath *et al.* 2006), amino silicones (Ghosh *et al.* 2013), alkoxysilanes (Cappelletto *et al.* 2013), zinc oxide (ZnO) nanostructures (Salla *et al.* 2012) and titanium dioxide (TiO_2) nanoparticles (Sun *et al.* 2010).

TiO_2 nanoparticles play an interesting role to modify the materials because their photocatalytic activity, low toxicity, action as fungicidal and bactericidal agent and action as a semiconductor with band gap at 3.2 eV. They are economically feasible and can provide hydrophobic or hydrophilic characteristics to the materials. Furthermore, the TiO_2 is characterized by the crystallization in three strucures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) (Huang *et al.* 2000, Kazuhito *et al.* 2005, Sun *et al.* 2010, Gupta and Tripathi 2011, Pelaez *et al.* 2012, De Filpo *et al.* 2013, Gao *et al.* 2015, Gharagozlou and Bayati 2015). TiO_2 can be synthesized by different methods, of which microwave-assisted hydrothermal is very promising because its advantages, such as few steps during the process, low waste production, low energy consumption, relative low cost, direct and uniform heating of the precursor, low temperature and low time to modify the materials, ability to obtain product with high purity (Murugan 2006, Bilecka *et al.* 2010, Moreira 2010, Silva 2013).

The effect of TiO_2 in the properties of wood and wood-based products has been investigated by other research groups. TiO_2 can reduce the anisotropy and the volumetric swelling of the wood (Sun *et al.* 2010). In addition, TiO_2 can provide to wood different degrees of wettability, enabling its application in different conditions (Gao *et al.* 2015). It also protects wood against UV degradation (Tuong and Chu 2015). Wang *et al.* (2012) observed that TiO_2 gels can increase the stiffness of the wood cell wall and then improves the wood mechanical strength. De Filpo *et al.* (2013) showed the efficiency of TiO_2 nanoparticles to protect the wood against the deterioration by both brown-rot and white-rot fungi.

The study wood impregnation by TiO_2 is an interesting alternative to improve the wood performance under different exposure conditions. Therefore, TiO_2 nanoparticles were produced by microwave-assisted hydrothermal method and then incorporated into the structure of *Pinus elliottii* wood, with the following objectives: a) to determine the best method of impregnation of these nanoparticles, simple immersion or vacuum-pressure; b) to investigate the color changes of *Pinus elliottii* wood after the TiO_2 impregnation; c) to investigate the effect of TiO_2 nanoparticles in the wood decay resistance against *Ganoderma applanatum* fungus.

MATERIALS AND METHODS

Raw Material

Pinus elliottii Engelm. wood boards were obtained from a sawmill located in the city of Pelotas, Brazil. The boards were cut into wood small samples with dimensions of 2,5 x 2,5 x 0,9 cm for the fungal tests and with 2,5 x 2,5 x 10 cm for the color tests. The wood moisture content was set at around 12% before the impregnation of TiO_2 nanoparticles. The nanoparticles were synthesized from titanium oxysulfate ($TiOSO_4$) and sodium hydroxide (NaOH) precursors, all of them supplied by Sigma-Aldrich.

Production and characterization of TiO_2 nanoparticles

The method used to produce the TiO_2 nanoparticles was the microwave-assisted hydrothermal. Two solutions containing 0,01 mol of $TiOSO_4$ (precursor solution) and 0,6 mol of NaOH (mineralizer solution) in distilled water were prepared with constant stirring. After the homogenization, the solutions were mixed, remaining under constant stirring until to reach 50°C and pH 14. This solution was transferred to a Teflon reactor and heated using microwave radiation for 20 minutes at 160°C with heating rate of 160°C/min.

At the end of the synthesis, the white powder formed in the reaction was washed by centrifugation at room temperature until neutral pH (~7). Then, it was dried at 60°C for 8 hours.

For the determination of the crystallization and the identification of different TiO_2 phases, a Bruker diffractogram (D8 Advance model) with CuK (1,5406 A) and scan rate of 0,02°/s in a range of 20° to 80° was used. The morphology of TiO_2 nanoparticles was investigated by Scanning Electron Microscopy (SEM, JSM - 6610LV), operating at high vacuum and 15 kV.

Wood impregnation with TiO_2 nanoparticles

TiO_2 nanoparticles were dispersed in distilled water (7,5 mg/ml). This dispersion remained on a magnetic stirrer for homogenization. The wood modification was performed by vacuum-pressure and simple immersion methods. In the first method, the nanocomposites were produced in an autoclave under vacuum-pressure. The wood samples were subjected to an initial vacuum of 600-700 mmHg for 30 minutes. Then, TiO_2 dispersion was placed inside the autoclave, remaining at constant pressure of 8 bar for 1,5 hours. Subsequently, a final vacuum of 600-700 mmHg was performed for 15 minutes to remove waste material (not impregnated). In the second method, the samples were immersed for 7 days into the TiO_2 dispersion without vacuum and pressure. After both procedures, the wood samples were kept in a climatic chamber (20°C and 65% RH) to reach 12 % equilibrium moisture content.

The untreated and treated samples were characterized by SEM coupled with Energy Dispersive Spectrometry (EDS) to investigate the degree of TiO_2 impregnation. SEM images were taken at high vacuum and under lower power energy to prevent wood degradation by the ion beam. EDS analysis was performed to determine the chemical composition of the samples.

Wood impregnation with CCB

CCB (chromated copper borate) solution with 2,5% of active ingredients was used as positive treatment. The CCB solution was prepared by dissolving 63,5% sodium dichromate, 26% copper sulfate and 10,5% boric acid in distilled water (Galvão *et al.* 2004). The conditions of treatment were the same used in TiO_2 impregnation by vacuum-pressure and simple immersion.

Color evaluation

Color changes of the wood samples were measured using a colorimeter Konica Minolta (model CR 400). The equipment was set for use a light source D25 and illumination angle of 10°, according to the *Commission International de L'Eclairage* (CIE-L*a*b*) standard. Two measurements in the tangential direction of each wood sample were performed to obtain the parameters L* (lightness), a* (red-green chromatic coordinate) and b* (blue-yellow chromatic coordinate). Chroma (C*), hue angle (h) and color difference (ΔE) were determined by Equation 1, Equation 2 and Equation 3, respectively.

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

$$h = \tan g^{-1}\left(\frac{b*}{a*}\right) \qquad\qquad (2)$$

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad\qquad (3)$$

$C*$ = chroma; h = hue angle; $a*$ = red-green chromatic coordinate; $b*$ = blue-yellow chromatic coordinate; ΔE = color difference; $\Delta L*$, $\Delta a*$ e $\Delta b*$ = variation of lightness, red-green chromatic coordinate and blue-yellow chromatic coordinate of untreated and impregnated wood samples.

Decay resistance

The accelerated laboratory tests of natural decay resistance of untreated and impregnated wood were performed according to the ASTM D2017 standard (ASTM 2005). The decay resistance was analyzed using a colony of white-rot fungus *Ganoderma applanatum* (Persoon ex Wallroth) Patouillard, provided by the Setor de Biodegradação e Preservação da Madeira, Laboratório de Produtos Florestais (LPF) from the Serviço Florestal Brasileiro (SFB) located in the city of Brasília (Brazil). The mycelium was cultivated in malt-agar extract for 21 days under an incubation temperature of 25 ± 3 °C and 12 h in the presence of day light. The malt-agar extract was prepared by dissolving 20g of malt and 20g of agar in one liter of distilled water.

Glass containers of approximately 600mL were filled with 100g of commercial soil with capacity of 40% water retention and pH 6. The moisture of the soils was checked and adjusted to 130% of retention capacity. Six replicates for each treatment were used.

In each container, a support plate of *Pinus elliottii* sapwood (0,3 x 2,9 x 3,5 cm) were placed, serving as substrate for the initial establishment of the fungal colony. All containers containing moistened soil and the support plate were autoclaved at 120°C and 1,9 atm for 40 minutes. Then, a disc of 5 mm in diameter of fungal mycelium was aseptically transferred on each support plate, and the flasks were incubated for 30 days in a climatic chamber (20°C and 65% RH) without light.

The untreated and the impregnated wood samples were dried at 50°C to reach constant mass and they were sterilized in the autoclave at 120°C for 1 hour. Then, each sample was put in contact with the support plate in each bottle, where the fungus had already established itself for 30 days. The fungus remained in contact with wood for 16 weeks under the same incubation conditions mentioned above. The ASTM D2017 standard was adapted for exposure of the TiO_2-treated wood samples to 12h of light, as previously stated by Foster *et al.* 2011, Markowska *et al.* 2011 and Harandi *et al.* 2016. These authors affirmed that TiO_2 absorbs UV radiation and can form reactive oxygen species through the recombination electron/hole, which can degrade the fungi wall, inhibiting their respiration and, consequently, resulting in their death.

After 16 weeks, the mycelia were removed and all the wood samples were dried at 50°C to measure the mass loss by fungal attack. The decay resistance was determined according to the rating established by ASTM D2017 standard (Table 1). SEM images were captured from the cell wall of the wood samples after the exposure to the fungus.

Table 1. Decay resistance as a function of the mass loss or residual mass established by the ASTM D2017 standard.

| Class of resistance	Mass loss (%)	Residual mass (%)
Highly resistant	0 - 10	90 – 100
Resistant	11 - 24	76 – 89
Moderately resistant	24 - 44	56 – 75
No resistant	≥ 45	≤ 55

Statistical analysis

The average values of the colorimetric parameters, and mass loss after the accelerated decay tests were evaluated by analysis of variance (ANOVA) at 95% of confidence level. When the null hypothesis was rejected, the mean values were compared with Tukey test at 5% probability of error.

RESULTS AND DISCUSSION

Structural characterization of TiO_2

The analysis of X-Ray Diffraction (XRD) showed the formation of anatase (PDF 21-1272) and rutile (PDF 21-1276) TiO_2 phases (Figure 1). The nanoparticles presented diffraction patterns of broad peaks and low crystallinity. This enlargement is common in particles with small size (Mendes *et al.* 2012). The diffractogram shows the crystalline planes of TiO_2 nanoparticles and they confirmed that the presence of anatase phase was predominant. The microwave-assisted hydrothermal method and the presence of $SO4^{-2}$ ions resulting from the precursor $TiOSO_4$ can inhibit the formation of rutile phase, stabilizing the anatase (Sun *et al.* 2014). An enlargement of the peaks can be observed, in which there is the presence of both phases due to the overlapping of the diffraction peaks of the individual phases. Therefore, besides the instrumental broadening and the size of the TiO_2 nanoparticles, the overlay contributes to this enlargement. This overlap occurred at 25,31° and 27,43° of anatase and rutile phases, respectively. A baseline was drawn to correct the background generated in the diffractogram due to amorphous fraction of TiO_2 phase. The intensity of the peak (200) did not correspond to a preferred orientation of the anatase phase due to this baseline.
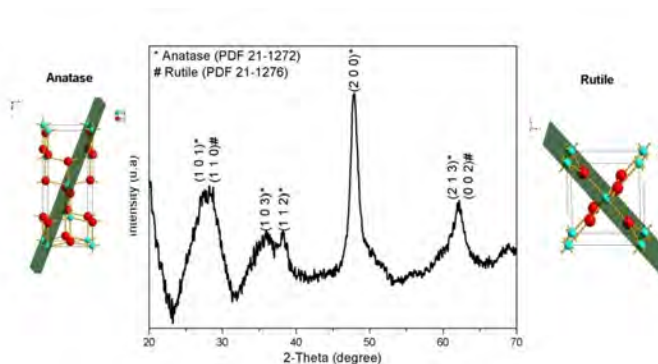
Figure 1. XRD patterns of TiO_2 powders synthesized by microwave-assisted hydrothermal method.

The TiO_2 powders formed a roughly spherical morphology with grains measuring around 50 nm. The enlargement of the diffraction peaks corroborated with the small size of the TiO_2 nanoparticles. Such nanoparticles formed agglomerates with approximately 500 nm (Figure 2), which are typically formed by van der Waals forces. The agglomeration of these nanoparticles came from induced dipoles in the synthesis method, which carry out short-range interactions and can be easily broken by the action of pressure during the impregnation.
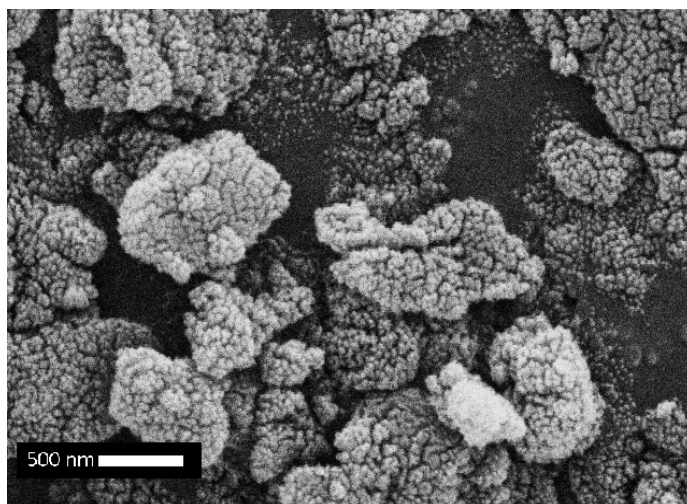

Figure 2. SEM images of TiO_2 nanoparticles synthesized by the microwave-assisted hydrothermal method.

Characterization of TiO_2 impregnated wood

The appearance of the surface and of the microstructures of coniferous wood is well described in previous studies (Wimmer 2002, Siegloch and Marchiori 2015). The surface is rough (Figure 3a) and the softwood is basically represented by tracheids with diameter bigger than 10 micrometers (Figure 3a(iii)), which characterizes its high porosity. These SEM images illustrated the efficiency of the impregnation of TiO_2 nanoparticles into the pinewood structure due to the size of the tracheids and the nanoparticles. The nanoparticles impregnated by vacuum-pressure were allocated preferably into the surface, forming a homogeneous coating (Figure 3b(i)), and they are deposited into the tracheids (Figure 3b(ii)). The interaction of these nanoparticles may be due to physical interactions or hydrogen bonds occurring between the OH present in the polymers of the cell wall and the hydrolyzed TiO_2 (Wang *et al.* 2014, Pori *et al.* 2016). On ther other hand, the simple immersion method was not able to unlock the access to the inner part of the tracheids (Figure 3c(ii)). Thus, only a superficial coating with low amount of TiO_2 was obtained, since no vacuum-pressure was applied, allowing the nanoparticles decantation. The absence of surfactants contributed to the decantation of the TiO_2 nanoparticles.
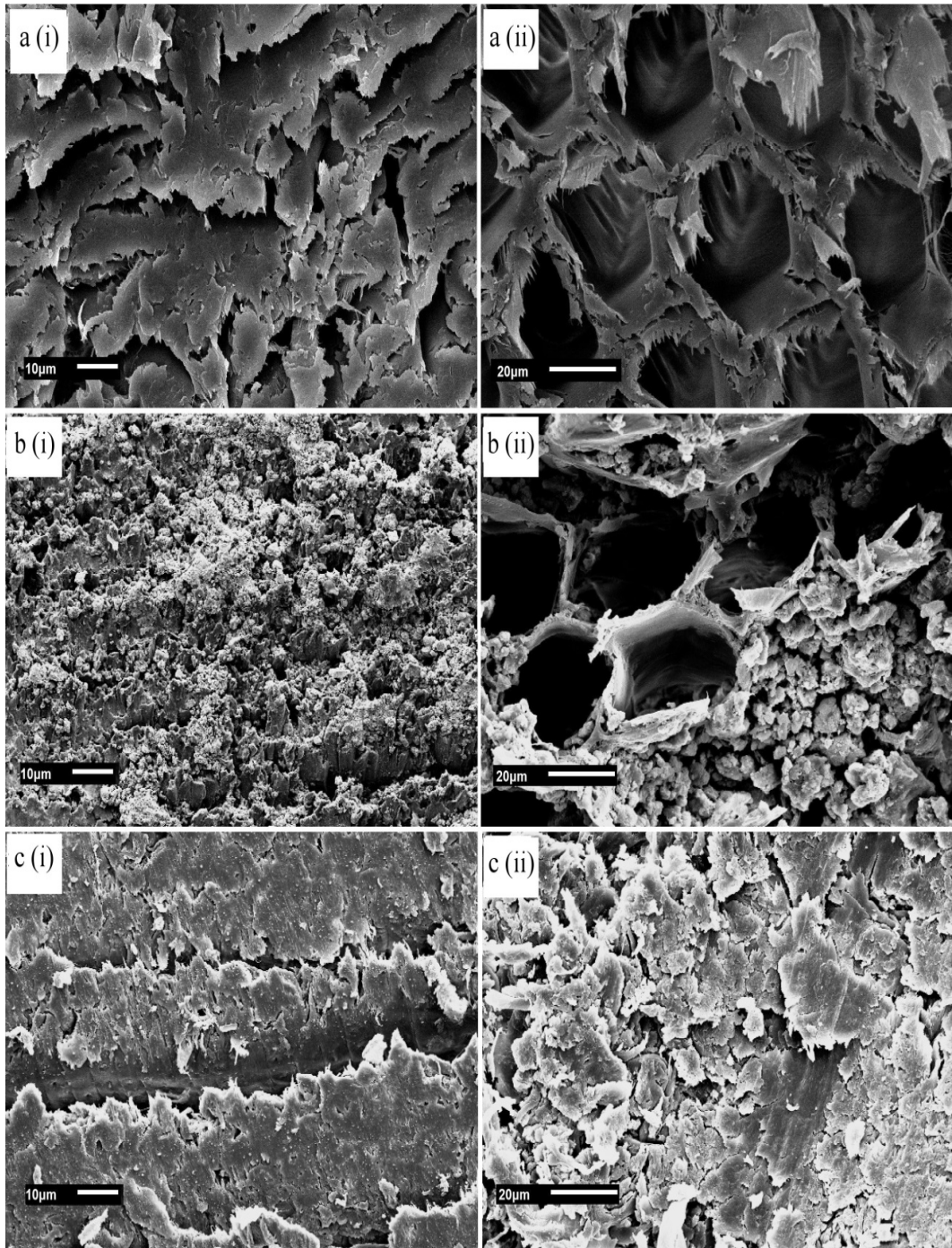
Figure 3. SEM images of untreated *Pinus elliottii* wood (a), wood impregnated with TiO_2 by vacuum-pressure (b) and wood impregnated with TiO_2 bysimple immersion (c). Where: (i) wood surface; (ii) wood tracheids.

The chemical mapping by EDS (Figure 4) confirmed the effectiveness of the vacuum-pressure method. The application of vacuum and pressure during the wood impregnation with TiO_2 nanoparticles resulted in a higher intensity of the Ti peak compared to the simple immersion method, which the last
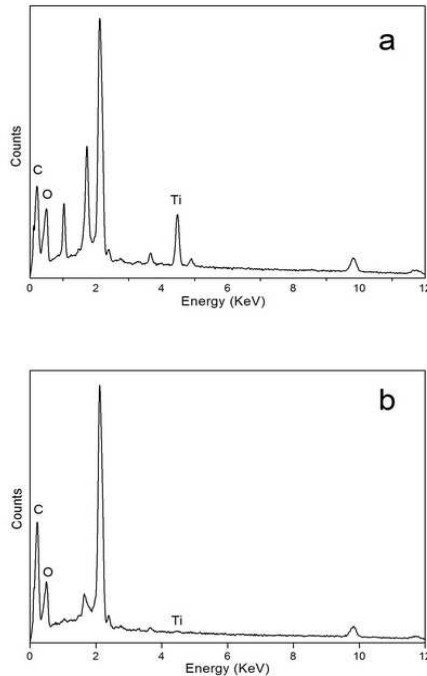
did not present a significant peak.

Figure 4. Energy dispersive X-ray spectroscopy of *Pinus elliottii* wood impregnated with TiO$_2$ nanoparticles using vacuum-pressure (a) and simple immersion (b) methods.

Color evaluation

TiO$_2$ impregnation did not change the natural color of *Pinus elliottii* wood. On the other hand, the wood impregnated with CCB became greenish, limiting their use for esthetic purposes, especially for decoration and furnitures. The TiO$_2$ nanoparticles did not change significantly the lightness (L*), red-green chromatic coordinate (a*) and hue angle (h) (Table 2). The parameter L* remained stable after the TiO$_2$ impregnation, while the impregnation with CCB resulted in wood darkening, reducing a* due to the oxidation of copper adsorbed and fixed onto the wood cell wall. The saturation (C*) decreased significantly in the wood treated with CCB, where as its remained constant for wood impregnated with TiO$_2$.

Table 2. Average values of lightness (L*), chromatic coordinates (a* and b*), chroma (C*) and hue angle (h*) of untreated and TiO$_2$-impregnated wood.

Treatments	Colorimetric parameters				
	L*	**a***	**b***	**C***	**h°**
TiO$_2$ by pressure-vacum	75,28 a*	6,96 ab	26,84 a	27,74 a	75,45 b
TiO$_2$ by immersion	74,73 a	7,21 a	26,41 a	27,56 a	73,51 b
CCB by vacuum-pressure	49,33 b	3,95 c	19,05 c	19,47 c	78,25 a
CCB by immersion	46,31 b	3,50 c	16,90 c	17,29 c	78,27 a
Untreated wood	77,42 a	6,16 b	23,20 b	24,02 b	75,27 b
F-ratio	**251,89****	**37,74****	**39,74****	**41,77****	**12,69****

*Average values followed by the same letter do not differ statistically from each other by the Tukey's test at 5% of probability of error. **Significant at 5% of probability of error by the F test of the analysis of variance.

Decay resistance

Table 3 shows the mass loss of untreated and TiO_2-impregnated wood. The untreated wood showed high deterioration in its structure. The mass loss reachs 23-32%, and the untreated wood was classified as moderately resistant. The wood impregnated with TiO_2 by vacuum-pressure did not exceed 13% of mass loss, which means a resistant wood. The use of vacuum and pressure for TiO_2 impregnation increased the effectiveness, as well as, the adhesion and the interaction of the nanoparticles with the wood cell wall. The small deterioration of wood impregnated with TiO_2 by vacuum-pressure is due to the physical barrier formed by the adhesion of TiO_2 into the cell wall, avoiding the wood deterioration through the digestive enzymes released by the fungus. The ability of the TiO_2 to assign a hydrophobic character to the surfaces (Sun *et al.* 2010) should be considered. TiO_2 nanoparticles may have decreased the capacity of water absorption of wood, difficulting the fungal colonization, since these organisms need moisture for their development.

Table 3. Mean values for the apparent specific gravity at 12% of moisture content before and after the fungal attack, and mass loss of untreated and treated *Pinus elliottii* wood.

Treatments	ρ (g/cm³) before fungal attack	ρ (g/cm³) after fungal attack	Mass loss (%)
TiO_2 by vacuum-pressure (dark room)	0,6812	0,6305	12,06 a
TiO_2 by vacuum-pressure (12h of light exposure)	0,6058	0,5344	6,604 a
TiO_2 by simple immersion	0,6033	0,4647	23,824 b
CCB by vacuum-pressure	0,7018	0,6634	5,474 a
CCB by simple immersion	0,6638	0,6264	5,636 a
Untreated wood	0,6257	0,4604	26,532 b
F-ratio			**15,86****

*Average values followed by the same letter do not differ statistically from each other by the Tukey's test at 5% of probability of error. **Significant at 5% of probability of error by the F test of the analysis of variance.

The decay resistance of wood impregnated with TiO_2 by simple immersion was similar to the resistance of untreated wood. The variation of mass loss was from 5 to 32%, remaining in the same class of resistance of untreated wood. However, this variation may be due to the low impregnation efficiency during the immersion step. The absence of vacuum and pressure may difficult the penetration of the nanoparticles inside the wood cell wall, as previously observed in Figure 3. The simple immersion resulted just in a slight surface coating, which helps the easy proliferation of the fungus into the wood cell wall.

The wood samples treated with CCB presented the same degree of deterioration for both vacuum-pressure and simple immersion methods. The mass loss was lower than 6% and the wood was classified as highly resistant. The mass loss of wood impregnated with TiO_2 by vacuum-pressure method did not differ statistically from the wood treated with CCB, proving the efficiency of the TiO_2 nanoparticles to protect wood against white-rot fungus. Nevertheless, from an environmental point of view, the CCB is more toxic than the TiO_2 nanoparticles, which makes the last a good alternative for wood preservation with low environmental impact.

Figure 5a shows the mycelial growth in the untreated wood. The penetration of the hyphae inside the wood cell wall resulted in an increase of the wood roughness. This high deterioration causes greater disintegration of the microfibrils. The mycelial growth and the presence of hyphae in the TiO_2-impregnated wood (Figure 5b and Figure 5c) was lower than in the untreated wood, since no significant changes in the roughness were observed in both cases. These results confirm the effectiveness of TiO_2

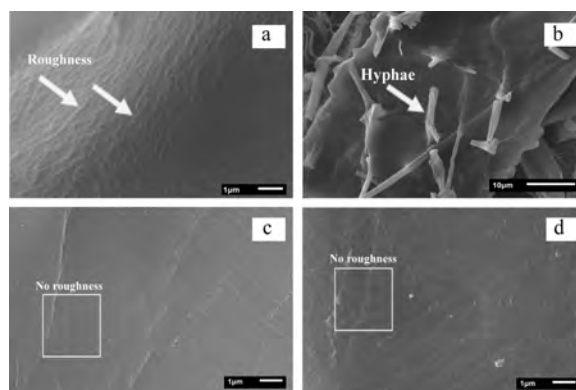nanoparticles to increase the wood decay resistance.

Figure 5. SEM images of untreated wood (a), hyphae penetrating into the untreated wood (b), CCB-treated wood treated no roughness (c) and wood impregnated with TiO_2 by vacuum-pressure no roughness (d) after *Ganoderma applanatum* attack.

The TiO_2 impregnation by the vacuum-pressure method was efficient to protect wood against the white-rot fungus under different environments, either in the presence or absence of light. In such cases that wood is deteriorated by fungi, this treatment with TiO_2 nanoparticles can be a good alternative to decrease/avoid fungal proliferation, providing to wood a self-cleaning mechanism. These observations are in accordance with the statements presented by De Filpo *et al.* (2013) and Harandi *et al.* (2016). Both studies identified significant increase of TiO_2 effectiveness in the presence of light.

CONCLUSIONS

The vacuum-pressure method presented the best conditions to impregnate *Pinus elliottii* wood with TiO_2 nanoparticles. This method did not change the natural color of *Pinus elliottii* wood, providing an attractive visual aspect for aesthetic purposes. The impregnation with TiO_2 nanoparticles makes *Pinus elliottii* wood more resistant to *Ganoderma applanatum* fungus than the untreated wood. TiO_2 impregnation of *Pinus elliottii* wood up on activation by light reached the same resistance of wood treated with CCB, however these nanoparticles have lower environmental impact than a CCB preservative. This methodology has the wood impregnation more environmentally-friendly, increasing and/or preserving the main aspects of wood, which can contribute to improve its practical applications.

ACKNOWLEDGMENTS

REFERENCES

American Society For Testing And Materials. ASTM. 2005. Standard method for accelerated laboratory test of natural decay resistance of woods. ASTM D 2017. Philadelphia.

Bilecka, I.; Niederberger, M. 2010. Microwave chemistry for inorganic nanomaterials synthesis. *Nanoscale* 2: 1358-1374.

Cappelletto, E.; Maggini, S.; Girardi, F.; Bochicchio, G.; Tessadri, B.; DI Maggio, R. 2013. Wood surface protection with different alkoxysilanes: a hydrophobic barrier. *Cellulose* 20: 3131-3141.

The effect of titanium dioxide..: Zanatta *et al.*

Maderas. Ciencia y tecnología 19(4): 495 - 506, 2017

De Filpo, G.; Palermo, A.M.; Rachiele, F.; Nicoletta, F.P. 2013. Preventing fungal growth in wood by titanium dioxide nanoparticles. *International Biodeterioration & Biodegradation* 85: 217-222.

Devi, R.R.; Maji, T.K. 2013. Effect of nanofillers on flame retardancy, chemical resistance, antibacterial properties and biodegradation of wood/styrene acrylonitrile co-polymer composites. *Wood Science and Technology* 47: 1135-1152.

Donath, S.; Militz, H.; Mai, C. 2006. Creating water-repellent effects on wood by treatment with silanes. *Holzforschung* 60: 40-46.

Esteves, B.; Pereira, H. 2008. Wood modification by heat treatment: A review. *BioResources* 4: 370-404.

Foster, H.A.; Ditta, I.B.; Varghese, S.; Steele, A. 2011. Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity. *Applied Microbiology and Biotechnology* 90: 1847-1868.

Galvão, A.P.M.; Magalhães, W.L.E.; Mattos, P. P. De. 2004. Processos práticos para preservar a madeira. Embrapa, Documentos 96. Colombo, PR.

Gao, L.; Zhan, X.; Lu, Y.; Li, J.; Sun, Q. 2015. pH-dependent structure and wettability of TiO_2-based wood surface. *Materials Letters* 142: 217-220.

Gharagozlou, M.; Bayati, R. 2015. Photocatalytic characteristics of single phase Fe-doped anatase TiO_2 nanoparticles sensitized with vitamin B12. *Materials Research Bulletin* 61: 340-347.

Ghosh, S.C.; Militz, H.; Mai, C. 2013. Modification of *Pinus sylvestris* L. wood with quat-and amino-silicones of different chain lengths. *Holzforschung* 67: 421-427.

Gupta, S.M.; Tripathi, M. 2011. A review of TiO_2 nanoparticles. *Chinese Science Bulletin* 56: 1639-1657.

Harandi, D.; Ahmadi, H. ; Achachluei, M.M. 2016. Comparison of TiO_2 and ZnO nanoparticles for the improvement of consolidated wood with polyvinyl butyral against white rot. *International Biodeterioration & Biodegradation* 108: 142-148.

Huang, Z.; Maness, P.C.; Blake, D.M.; Wolfrum, E.J.; Smolinski, S.L.; Jacoby, W.A. 2000. Bactericidal mode of titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry* 130: 163-170.

Humar, M.; Bokan, M.; Amartey, S.A.; Šentjurc, M.; Kalan, P.; Pohleven, F. 2004. Fungal bioremediation of copper, chromium and boron treated wood as studied by electron paramagnetic resonance. *International Biodeterioration & Biodegradation* 53: 25-32.

Kazuhito, H.; Hiroshi, I.; Akira, F. 2005. TiO_2 Photocatalysis: A Historical Overview and Prospects. *Japanese Journal of Applied Physics* 44: 8269.

Kelley, S.S.; Jellison, J.; Goodell, B. 2002. Use of NIR and pyrolysis-MBMS coupled with analysis for detecting the chemical changes associated with brown-rot biodegradation of spruce wood. *FEMS Microbiology Letters* 209: 107-111.

Lande, S.; Westin, M.; Schneider, M. 2004. Properties of furfurylated wood. *Scandinavian Journal of Forest Research* 19: 22-30.

Lu, Y.; Feng, M.; Zhan, H. 2014. Preparation of SiO_2–wood composites by an ultrasonic- sol–gel technique. *Cellulose* 21: 4393-4403.

Markowska-Szczupak, A.; Ulfig, K.; Morawski, A. 2011. The application of titanium dioxide for deactivation of bioparticulates: an overview. *Catalysis Today* 169: 249-257.

Mendes, P.G.; Moreira, M.L.; Tebcherani, S.M.; Orlandi, M.O.; Andrés, J.; Li, M.S.; Diaz-

Mora, N.; Varela, J.A.; Longo, E. 2012. SnO_2 nanocrystals synthesized by -assisted hydrothermal method: towards a relationship between structural optical properties. *Journal of Nanoparticle Research* 14: 1-13.

Moreira, M. 2010. Titanatos de alcalinos terrosos: a ordem associada à desordem. 2010. 113 f, Tese (Doutorado em Química)–Departamento de Química, Universidade Federal de São Carlos, São Carlos.

Murugan, A.V.; Samuel, V.; Ravi, V. 2006. Synthesis of nanocrystallineanatase TiO_2 bymicrowave hydrothermal method. *Materials Letters* 60: 479-480.

Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O'shea, K.; Entezari, M.H.; Dionysiou, D.D. 2012. Areview on the visible light active titanium dioxide photocatalysts for environmentalapplications. *Applied Catalysis B: Environmental* 125: 331-349.

Pori, P.; Vilčnik, A.; Petrič, M.; Sever Škapin, A.; Mihelčič, M.; Šurca-Vuk**, A.; Novak, U.; Orel, B. 2016.** Structural studies of TiO_2/wood coatings prepared by hydrothermal deposition of rutile particles from $TiCl_4$ aqueous solutions on spruce (*Picea abies*) wood. *Applied Surface Science* 372: 125-138.

Rassam, G.; Abdi, Y.; Abdi, A. 2012. Deposition of TiO_2 nano-particles on wood surfaces for UV and moisture protection. *Journal of Experimental Nanoscience* 7: 468-476.

Rowell, R.M. 2012. *Handbook of wood chemistry and wood composites*. CRC press.

Salla, J.; Pandey, K.K.; Srinivas, K. 2012. Improvement of UV resistance of wood surfaces by using ZnO nanoparticles. *Polymer Degradation and Stability* 97: 592-596.

Siegloch, A. M.; Marchiori, J. M. C. 2015. Anatomia da madeira de treze espécies de coníferas. *Revista da Ciência da Madeira* 6: 149-165.

Silva, L. 2013. Síntese e caracterização do composto $SrTiO_3$ e $SrTi1-xFexO_3$ através do método hidrotermal assistido por microondas, 2013. Universidade de São Paulo.

Sun, B.; Zhou, G.; Shao, C.; Jiang, B.; Pang, J.; Zhang, Y. 2014. Spherical mesoporous TiO_2 fabricated by sodium dodecyl sulfate-assisted hydrothermal treatment and its photocatalytic decomposition of papermaking wastewater. *Powder Technology* 256: 118-125.

Sun, Q.; Yu, H.; Liu, Y.; Li, J.; Lu, Y.; Hunt, J.F. 2010. Improvement of water resistance and dimensional stability of wood through titanium dioxide coating. *Holzforschung* 64: 757-761.

Taghiyari, H.R.; Schmidt, O. 2014. Nanotechnology in wood-based composites panels. *International Journal of Bio-Inorganic Hybrid Nanomaterials* 3: 65-73.

Tripathi, S.; Pant, H.; Kashyap, A.K. 2014. Decay resistance against basidiomycetes fungi of heat-treated pinus roxburghii and mangifera indica wood. *Journal of Tropical Forest* 26: 203-207.

Tuong, V.M.; Chu, T.V. 2015. Improvement of Color Stability of Acacia Hybrid Wood by TiO_2 Nano Sol Impregnation. *Bioresources* 10(3): 5417-5425.

Wang, B.; Feng, M.; Zhan, H. 2014. Improvement of wood properties by impregnation with TiO_2 via ultrasonic-assisted sol–gel process. *RSC Advances* 4: 56355-56360

Wang, X.; Liu, J.; Chai, Y. 2012. Thermal, mechanical, and moisture absorption properties of TiO_2 composites prepared by a sol-gel process. *BioResources* 7: 893-901.

Wimmer, R. 2002. Wood anatomical features in tree-rings as indicators of environmental change. *Dendrochronologia* 20: 21-36.