

MICROWAVE-ASSISTED SOLVOTHERMAL: AN EFFICIENT AND NEW METHOD TO OBTAIN HYDROPHOBIC WOOD SURFACES

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ABSTRACT

The objective of this work was to form a hydrophobic surface in a highly porous wood by coating and incorporating TiO₂ micro/nano structures through the microwave-assisted solvothermal method, without need any pre- or post-modification of the wood substrate, using low temperatures and short times. The behavior and morphology of the TiO₂-treated surfaces was characterized using scanning electron microscopy (SEM), while the elemental composition was determined via energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. The results indicated that the crystallization of the TiO₂ anatase phase was efficient and fully coated the wood surface during the solvothermal process. The treated wood contained TiO₂ particles agglomerate with an average diameter of 200 nm that also allowed to coat an abundant fraction of tracheids cell walls. When investigated through X-ray spectroscopy-mapping, the element titanium appeared abundantly throughout the wood. After TiO₂ growth in wood through the microwave-assisted solvothermal method, a roughness at the micro/nano scales structures was created on the wood surface, originating an increase in the contact angle up to 137°, which characterizes the appearance of a hydrophobic surface. The TiO₂-treated wood demonstrated 85% of water absorption after 400 h of immersion, while untreated wood reached 160%, suggesting that the microwave-assisted solvothermal process promotes a delay in the progression of water absorption. This feature can improve the dimensional stability of wood, contributing to the increase of its durability and applications.

Keywords: Nanoparticles, *Pinus elliotti*, wettability, wood modification, wood technology.

INTRODUCTION

The hydrophilic nature of the polymers (cellulose, hemicellulose and lignin) constituting wood cell wall results in a material sensitive to moisture, mainly when exposed to environmental conditions. These polymers contain groups OH and oxygen in their chains that attract water through means of hydrogen bonds (Evans *et al.* 2000, Sedighi-Moghaddam 2015). Another cause for water affinity is the presence of porous structures, as the tracheids in the case of conifers, that provide wide circulation of liquids (Jia *et al.* 2016).

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These conditions lead to volumetric changes in the wood structure and induces tensions in the cell wall, causing deformations such as warping and cracking (Sun *et al.* 2010, Zheng *et al.* 2015). In addition, water absorption favors the proliferation of fungi, since they require moisture to develop. This feature compromises the use and durability of the wood and limits wood samples applications in humid conditions.

Therefore, it is necessary the implementation of protective agents to avoid water absorption in wood cell wall. Currently, many approaches using surface treatment, have been reported and developed to minimize the effects of water wood absorption, for example, with waxes, cold plasma and ceramics (Lesar and Humar 2011, Sun *et al.* 2012, Wang *et al.* 2012, Liu *et al.* 2015, Zheng *et al.* 2015, Cademartori *et al.* 2016, Jia *et al.* 2016).

Inspired on lotus leaves, which have high capacity to repel water, the creation of a hydrophobic surface becomes a promising approach in order to optimize the implementation of wood in several environments with different moisture contents. Artificial hydrophobic surfaces are manufactured by the combination of chemical composition, morphology and roughness of surface coatings (Zhang *et al.* 2008).

Some ceramic nanoparticles such as TiO₂, ZnO and SiO₂, were used for wood modification and have great potential in the development of diverse surfaces with suitable wettability for different conditions. These compounds showed good efficiency in converting hydrophilic OH groups in hydrophobic surfaces (Liu *et al.* 2015, Lu and Hu 2016). Among others, some of the methodologies reported for wood modification and creating hydrophobic surfaces are sol-gel processes (Lu *et al.* 2014) hydrothermal processes (Gao *et al.* 2015), depositions at room temperature (Zheng *et al.* 2015), coating processes (Rassam *et al.* 2012) and of impregnation by pressure (Zanatta *et al.* 2017).

The development of faster and more environment friendly procedures is essential to the current scenario. In this sense, the microwave-assisted solvothermal (MAS) method, widely used for nanoparticles synthesis (Moura *et al.* 2014, Wang *et al.* 2015), rarely reported for wood modification. This method becomes attractive to coat, grow and impregnate inorganic materials on the surface and inside the wood tracheids, as it is simple, with few steps, and present reduced synthesis time and temperature (Diebold 2003). TiO₂ can be easily obtained by MAS and it has been greatly used to prepare rugged and self-cleaning surfaces with high hydrophobicity (Liu *et al.* 2015, Huang *et al.* 2000). TiO₂ is currently one of most widely used multifunctional nano-materials, it is a polymorph with low toxicity which crystalizes under three distinct structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic), being the anatase the most interesting structure due to its photoactivity and typical grain size (Lee *et al.* 2010).

In this context, the objective of this work was to form a hydrophobic surface in a highly porous wood by coating and incorporating TiO₂ particles through the microwave-assisted solvothermal method, without need any pre- or post- modification of the wood substrate. Accordingly, this paper presents studies of (i) preparation of TiO₂ particles through titanium isopropoxide and (ii) wood modification with TiO₂ micro/nano structures and its characterization. Finally, the behavior and morphology of the TiO₂-treated wood was observed. The results of this study reveal the possibility for wood modifications and hydrophobic surface formation able to delay the absorption of water, which contributes to the formation of woods more resistant to moisture and durable.

MATERIALS AND METHODS

Materials

The *Pinus elliottii* wood used in the study was provided by reforestation in southern Brazil, more precisely in the Pelotas city region. The size used for the samples was 10 x 10 x 10 mm, stabilized at 12% of moisture. All the samples were prepared from the first log (3 m in length from the base of the trees), avoiding defects in the samples (Missio *et al.* 2016). For the TiO₂ growth were employed titanium isopropoxide (Ti [OCH(CH₃)₂]₄) at 97% purity and ethyl alcohol (C₂H₆O) 95%, obtained

from Sigma-Aldrich and Synth, respectively.

Synthesis of TiO₂ and wood modification

The MAS method was used for wood modification. To crystallize the TiO₂ on and inside the wood, an alcoholic solution of 30 mL was stirred with 0,07 mol⁻¹ of titanium isopropoxide and ethyl alcohol. Subsequently the *P. elliotii* samples were added to the solution, which remained under constant stirring and nitrogen flow for 10 minutes. The solution with wood samples was transferred to teflon reaction cell and then coupled to the microwave system. After reaching 140°C at heating rate of 6°C/minute, the surface modification of the wood occurred for 60 minutes at this temperature. Finally, the wood samples were dried at 100°C for 24 h. In order to verify that only TiO₂ was formed, the same procedure was performed without the addition of wood samples.

Characterization

Structural and morphological analysis

By X-ray Diffraction (XRD) was verified the presence of TiO₂ in the wood samples. This characterization was performed by a Rigaku diffractometer with Bruker rotating anode, model D8 Advance, using Cu Kα1 (λ = 1,5406 Å) and Cu Kα2 (λ = 1,5406 Å) radiations, at 40 kV and 150 mA in a range of 10°-90°. By Scanning Electron Microscope (SEM) (JEOL JSM - 6610LV) under high vacuum, at 15,00 kV, the coating and the impregnation of the wood surface and tracheids were evaluated. Energy-dispersive X-ray Spectroscopy (EDX), coupled with SEM, was performed to verify the chemical composition of the samples.

Hydrophobicity and liquid water uptake

The hydrophobicity of the untreated and wood-TiO₂ samples was evaluated by measuring the static contact angle at six different times: 5, 20, 35, 50, 65 and 80 seconds after the contact of the droplet (20 μl of deionized water) on the sample surface. It was used a Drop Shape Analyzer goniometer, model DSA25, configured for the sessile drop method. In order to verify the influence of the MAS process on the surface of the wood, the wettability test was carried out on samples of wood that underwent the solvothermalization, without the titanium precursor.

The water absorption was measured by the immersion of the samples (at 12% of moisture content) in deionized water for a period of 400 h. There were five replicates. Periodically, the weight of each sample was collected with an analytical balance. The percentage of weight change, as per Equation 1, was used to determine the water uptake of wood.

$$\Delta W(\%) = \left[\frac{W_1 - W_0}{W_0} \right] \times 100 \quad (1)$$

Where: ΔW = weight variation; W₀ = weight of the sample before the immersion (12% moisture) (g); W₁ = weight of the sample after the immersion (g).

RESULTS AND DISCUSSION

Structural and morphological analysis

Before the wood modification process, the TiO₂ structure was firstly investigated. After applying for 60 min the MAS process over the precursor solution of titanium isopropoxide and ethyl alcohol, a white precipitated powder was obtained and it was characterized by XRD and SEM. The XRD pattern showed the peaks relate to pure anatase phase (JCPDS File 21-1272), as shown in Figure 1a. This is a very important result because the anatase TiO₂ phase is normally found associated to an amount

of rutile phase. Additionally, SEM images show that the particle agglomerates had roughly spherical shape with an average size of 200 nm.

Being able to produce TiO_2 through the MAS method, a new methodology for wood modification was developed. Unlike the XRD of untreated wood (Figure 1b), the crystalline structure of the treated wood obtained by MAS method indicated that the wood was dominated by TiO_2 anatase phase (Figure 1c), indexed by the peaks at 24° , $37,8^\circ$; $48,3^\circ$; 53° and $74,9^\circ$ while only the peak at 45° corresponds to the rutile phase (JCPDS file 21-1276). The rutile phase can be found in the treated wood because its formation is favored in acidic conditions, as the pH of the reaction medium dropped with the addition of the samples to the solution (Mourão *et al.* 2009). It was noted that the combined action of the solvent, microwave radiations, as well as the acidity of the solution might have modified the crystalline planes of cellulose. The maximum intensity of crystalline cellulose fraction (002) is identified by the peak at $22,5^\circ$, which decrease in the TiO_2 -treated wood. This may be the result of the MAS process, affecting the hydrogen bonds of the crystalline portion of the cellulose (El Oudiani *et al.* 2011, Perrone 2015). This intensity decrease occurred in combination with changes in the cellulose shape. In other words, the changing in cellulose unit cell parameters can explain the increased in intensity of the peak at $34,8^\circ$, representing the crystallographic plane (040) of type I cellulose.

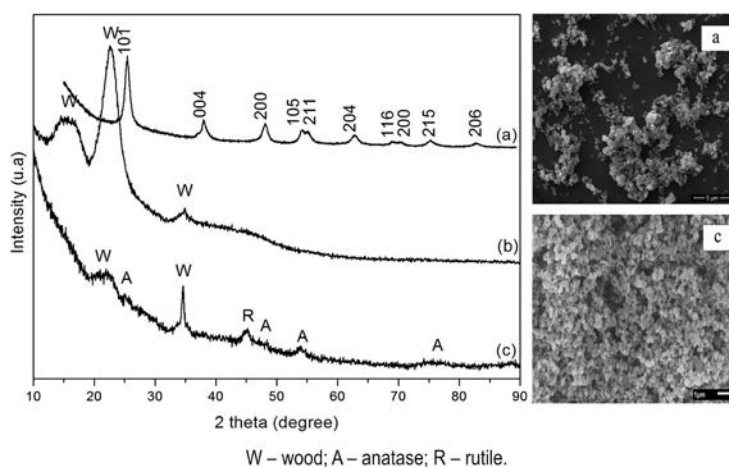


Figure 1: XRD and SEM of the (a) TiO_2 nanoparticles, (b) natural wood and (c) TiO_2 -treated wood surfaces synthesized by the MAS method.

The appearance of the surface and the anatomical structures of coniferous wood is well described in previous studies (Wimmer 2002, Siegloch and Marchiori 2015). It is known that the surface is rough (Figure 2a) and it is characterized by pores (tracheids) in the micrometer order, with a diameter greater than 10 micrometers (Figure 2c), which lead to its high porosity. So, naturally, a drop of water is absorbed quickly by tracheids, entering the interfaces of the cell wall (volume change) and filling the lumen (weight change), attributing its hydrophilic character. This condition limits its use to decks, external structures, openings, garden furniture, frames, as it favors the impregnation or modification by other materials or products.

Due to the micrometric size of tracheids, it is not expected that the treated wood presents totally clogged pores with TiO_2 particles. However, to avoid the liquid absorption, it is necessary to employ the hydrophobic features of TiO_2 anatase phase deposited on the surface (Figure 2b) and inside (Figure 2d) the wood. TiO_2 was crystallized in the cell wall, inside the lumen and on the surface of the wood, and TiO_2 spheres were distributed uniformly on the surface of the wood. In some places, there was a continuous coating on and in the wood, including pits (Figure 2e) and rains (Figure 2f), in the longitudinal section. The roughness obtained from the formation process of the wood modification, both on the surface and in the cell wall of the wood, ranged from micro to nanoscale, resembling the hydrophobic hierarchical surface characteristics found in nature.

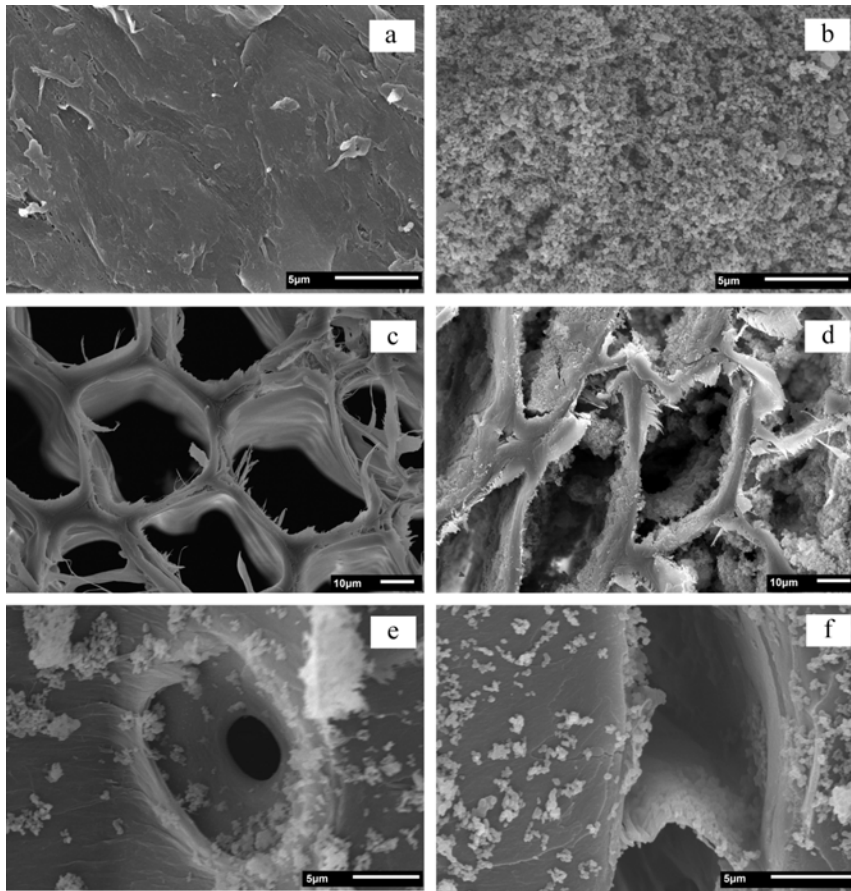


Figure 2: SEM images of the natural wood and the TiO₂-treated wood. (a) natural wood surface; (b) TiO₂-treated wood surface; (c) pores of the natural wood; (d) TiO₂-treated wood pores; (e) and (f) TiO₂ interaction with structures present in the wood (pits and rains).

SEM-EDX cross-section images of the samples demonstrates that the surface was entirely coated by TiO₂ (Figure 3b) as observed in Figure 2b; inside the tracheids, the coating is not so efficient, as demonstrate in Figures 2e and f. In any way this cannot be a limiting factor, once it is flagrant the contribution of TiO₂ on the wood surface compared to the untreated wood, which primarily presents Carbon (C), Oxygen (O) and Nitrogen (N) (Figure 3a). In some areas of the SEM images, it is not possible to verify the presence of TiO₂ nanoparticles inside the cell wall of tracheids. However, when investigating through EDX-mapping, it was noticed that even in the longitudinal section, where there was no direct contact with the precursor solution, the element titanium appeared abundantly throughout the wood (Figure 3 b, i, ii). This may suggest that the titanium, in addition to the coat, fills the micro spaces inside the cell wall. For this reason, it may be expected that the properties of the TiO₂-treated wood are differentiated, when compared with the natural wood.

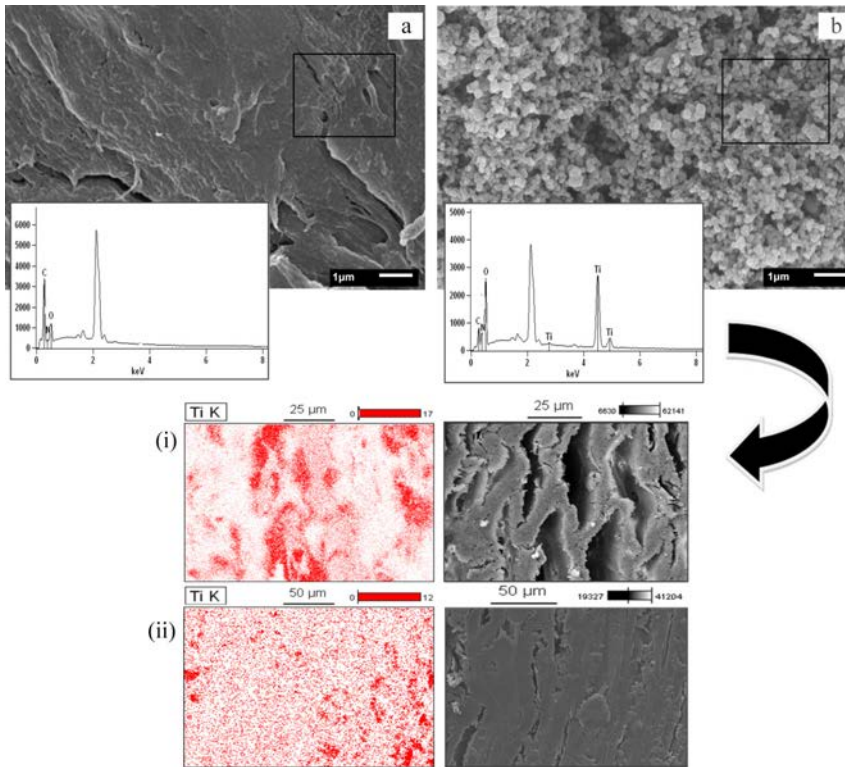


Figure 3: SEM-EDX chemical composition of the (a) natural wood and (b) TiO_2 -treated wood. The titanium X-ray mapping of the (i) cross and (ii) tangential section of the TiO_2 -treated wood.

Hydrophobicity

The polymers (cellulose, hemicellulose and lignin) of the wood contain numerous hydrophilic groups which absorb water and, in the case of pine wood, also there are large cavities that facilitate fluid circulation and storage. Besides, after it penetrates into these cavities, water is quickly absorbed by the cell wall of the tracheids. In order to avoid water penetration into the tracheids, TiO_2 crystallization on the surface of wood can supply a hydrophobic character to treated wood. The wettability analysis to assess the TiO_2 efficiency in this process was made at the cross section, because it is the part that presents greater water absorption in relation to the other sections. Figure 4 shows the evolution of static contact angle of the water droplet on the wood surface (cross section of tracheids) as a function of time.

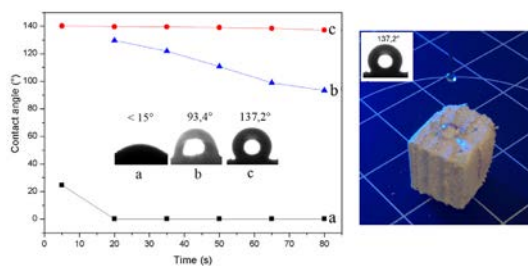


Figure 4: Contact angle evolution against time for the (a) natural wood (b) wood exposed to MAS conditions and (c) TiO_2 -treated wood.

The initial contact angle measured for untreated wood was very low, less than 26° , and water was completely absorbed in 20 s. When the MAS process was employed over wood, without the titanium precursor during the solvothermalization, the initial contact angle increases up to 125° and it was associated to a delayed water absorption (Figure 4) due to obstruction of the cavities. A final contact angle of $93,4^\circ$ was reached 80 s after the addition of the water drop on the wood surface, indicating less water absorption and spreading compared to untreated wood.

After TiO_2 growth in wood through the MAS method, the coating created on the surface of wood changed the topographic characteristics of surface, adding a roughness in nano/micrometric scale and the contact angle increases to 137° , which characterizes the appearance of hydrophobic surface, with the surface area of the wood increases with the addition of these structures. In addition to modifying the surface of the wood, there is the possibility that the TiO_2 particles deposited on the substrate inactivate some OH^- groups present in the polymers of the wood cell wall. Another important aspect associated to the hydrophobicity increase is the high stability of the contact angle through a long time (Figure 4). This stability of the water droplet shows that the decrease of the contact angle in treated wood is not influenced by the evaporation of the droplet, but only by the high hygroscopicity of the wood.

It is important to mention that there are reports of hydrophobic surfaces through wood surface modification with metal oxides (Zheng *et al.* 2015, Liu *et al.* 2015). However, the great advantage of this work is that the method used does not require previous treatment or functionalization of the nanoparticles. Furthermore, the manufacturing of this surface is obtained in a short period of time, with one step and do not use expensive and toxic chemical reactants in the process.

Liquid water uptake

Figure 5 shows the evolution of the wood water absorption during 400 h of immersion, where it is clear the decrease of the water absorption for TiO_2 -treated wood, when compared to the untreated material. Untreated and TiO_2 -treated wood reached a steady state in approximately 160 h. The weight variation in this period is due to the absorption of water in the lumen and/or cell wall of the wood. The weight variation of TiO_2 -treated wood reached 85% after 400 h of immersion, while the untreated samples reached 160%. The treated wood by MAS process delayed the absorption of water, due to the presence of TiO_2 and the Ti element prevented water adsorption in the empty spaces of the cell wall. This allows greater dimensional stability. After 400 h of immersion the samples did not show great color variation or turbidity, which makes believe that there was low leaching of TiO_2 nanoparticles. This indicates a strong and stable attachment of the TiO_2 -coating to the wood surface and may be occurring through hydrogen bonds between the particles and the OH^- groups present in the polymeric groups of the wood (Wang *et al.* 2014).

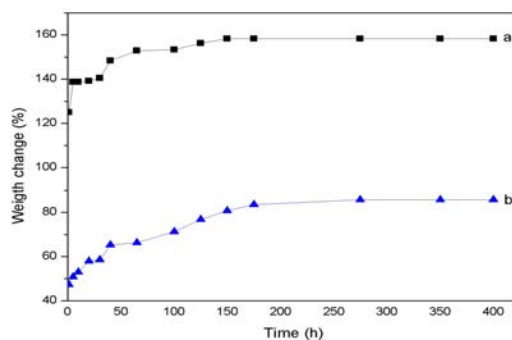


Figure 5: Variation of the weight percentage of the (a) natural wood and of the (b) TiO_2 -treated wood during 400 h of immersion in water.

CONCLUSIONS

In the present study, the MAS new process proved to be efficient in modifying wood with inorganic materials, producing composite based on wood and TiO₂. This treatment was performed at low temperatures and for a short time, without the need for additional treatments. The hierarchical structures of TiO₂ anatase phase were visualized on the surface and on the cell wall of the wood. The chemical element Ti was mapped in the empty spaces of the cell wall, indicating good impregnation and distribution of the precursor solution in the wood matrix. During the process, the structures of TiO₂ created a coating on the wood surface, reducing the free surface energy. This led to the formation of macro, micro and nanometric structures on the surface of the TiO₂-treated wood, changing to hydrophobic the original hydrophilic surface. In addition, the water absorption of the modified wood was lower in compared to the untreated wood. Therefore, the MAS process is promising for wood modification and provides a pathway for the formation of woods more resistant to moisture, expanding its applications.

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REFERENCES

- Cademartori, P. H. G.; Nisgoski, S.; Magalhães, W. L.; De Muniz, G. I. B. 2016.** Surface wettability of Brazilian tropical wood flooring treated with He plasma. *Maderas-Cienc Tecnol* 18 (4): 715-722.
- Diebold, U. 2003.** The surface science of titanium dioxide. *Surface Science Reports* 48 (5): 53-229.
- El Oudiani, A.; Chaabouni, Y.; Msahli, S.; Sakli, F. 2011.** Crystal transition from cellulose I to cellulose II in NaOH treated *Agave americana* L. fibre. *Carbohydrate Polymers* 86 (3): 1221-1229.
- Evans, P. D.; Wallis, A. F. A.; Owen, N. L. 2000.** Weathering of chemically modified wood surfaces. *Wood Science and Technology* 34 (2): 151-165.
- Gao, L.; Zhan, X.; Lu, Y.; Li, J.; Sun, Q. 2015.** pH-dependent structure and wettability of TiO₂-based wood surface. *Materials Letters* 142: 217-220.
- 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 (2): 163-170.
- Jia, S.; Liu, M.; Wu, Y.; Luo, S.; Qing, Y.; Chen, H. 2016.** Facile and scalable preparation of highly wear-resistance superhydrophobic surface on wood substrates using silica nanoparticles modified by VTES. *Applied Surface Science* 386: 115-124.

- Lee, S.; Cho, I.S.; Noh, J.H.; Hong, K.S.; Han, G.S.; Jung, H.S.; Shin, H. 2010.** Correlation of anatase particle size with photocatalytic properties. *Physica Status Solidi (a)* 207 (10): 2288-2291.
- Lesar, B.; Humar, M. 2011.** Use of wax emulsions for improvement of wood durability and sorption properties. *European Journal of Wood and Wood Products* 69 (2): 231-238.
- Liu, M.; Qing, Y.; Wu, Y.; Liang, J.; Luo, S. 2015.** Facile fabrication of superhydrophobic surfaces on wood substrates via a one-step hydrothermal process. *Applied Surface Science* 330: 332-338.
- Lu, X.; Hu, Y. 2016.** Layer-by-layer deposition of TiO₂ nanoparticles in the wood surface and its superhydrophobic performance. *BioResources* 11 (2): 4605-4620.
- Lu, Y.; Feng, M.; Zhan, H. 2014.** Preparation of SiO₂-wood composites by an ultrasonic-assisted sol-gel technique. *Cellulose* 21 (6): 4393-4403.
- Missio, A. L.; de Cademartori, P. H. G.; Mattos, B. D.; Santini, E. J.; Haselein, C. R.; Gatto, D. A. 2016.** Physical and Mechanical Properties of Fast-Growing Wood Subjected to Freeze-Heat Treatments. *BioResources* 11 (4): 10378-10390.
- Moura, K. F.; Maul, J.; Albuquerque, A.R.; Casali, G.P.; Longo, E.; Keyson, D.; Santos, I.M.G. 2014.** TiO₂ synthesized by microwave assisted solvothermal method: Experimental and theoretical evaluation. *Journal of Solid State Chemistry* 210 (1): 171-177.
- Mourão, H. A. J. L.; Mendonça, V.D.; Malagutti, A. R.; Ribeiro, C. 2009.** Nanoestruturas em fotocatalise: uma revisão sobre estratégias de síntese de fotocatalisadores em escala nanométrica. *Química Nova* 32 (8): 2181-2190.
- Perrone, O. M. 2015.** Avaliação térmica e estrutural do bagaço de cana de açúcar pré tratado com ozônio, ultrassom e micro-ondas para produção de etanol celulósico por hidrólise enzimática. [online] available: <<http://repositorio.unesp.br/handle/11449/127894>> [accessed 02.12.2016].
- Rassam, G.; Abdi, Y.; Abdi, A. 2012.** Deposition of TiO₂ nano-particles on wood surfaces for UV and moisture protection. *Journal of Experimental Nanoscience* 7 (4): 468-476.
- Sedighi-Moghaddam, M. 2015.** Wettability of modified wood. Doctoral Dissertation, KTH Royal Institute of Technology.
- Siegloch, A.M.; Marchiori, J.N.C. 2015.** Anatomia da madeira de treze espécies de coníferas. *Revista Ciência da Madeira* 6 (3): 149-165.
- Sun, Q.; Lu, Y.; Zhang, H.; Zhao, H.; Yu, H.; Xu, J.; Liu, Y. 2012.** Hydrothermal fabrication of rutile TiO₂ submicrospheres on wood surface: an efficient method to prepare UV-protective wood. *Materials Chemistry and Physics* 133 (1): 253-258.
- 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 (6): 757-761.
- Wang, B.; Feng, M.; Zhan, H. 2014.** Improvement of wood properties by impregnation with TiO₂ via ultrasonic-assisted sol-gel process. *RSC Advances* 4 (99): 56355-56360.
- Wang, X.; Liu, J.; Chai, Y. 2012.** Thermal, mechanical, and moisture absorption properties of wood-TiO₂ composites prepared by a sol-gel process. *BioResources* 7 (1): 0893-0901.
- Wang, X.; Tian, J.; Fei, C.; LV, L.; Wang, Y.; Cao, G. 2015.** Rapid construction of TiO₂ aggregates using microwave assisted synthesis and its application for dye-sensitized solar cells. *RSC Advances* 5 (12): 8622-8629.
- Wimmer, R. 2002.** Wood anatomical features in tree-rings as indicators of environmental change. *Dendrochronologia* 20 (1-2): 21-36.

Zanatta, P.; Lazarotto, M.; Gonzalez De Cademartori, P. H.; Cava, S. D. S.; Moreira, M. L.; Gatto, D. A. 2017. The effect of titanium dioxide nanoparticles obtained by microwave-assisted hydrothermal method on the color and decay resistance of pinewood. *Maderas-Cienc Tecnol* 19 (4): 495-506.

Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. 2008. Superhydrophobic surfaces: from structural control to functional application. *Journal of Materials Chemistry* 18 (6): 621-633.

Zheng, R.; Tshabalala, M. A.; LI, Q.; Wang, H. 2015. Construction of hydrophobic wood surfaces by room temperature deposition of rutile (TiO₂) nanostructures. *Applied Surface Science* 328: 453-458.