The use of microwave system to deposit TiO$_2$ particles on wood surface to improve water repellency

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Abstract

The objective of the present study is to modify the surface of *Pinus elliottii* wood by means of the deposition and impregnation of TiO$_2$ particles synthesized through the microwave-assisted solvothermal method. Initially, TiO$_2$ nanoparticles were obtained from titanium isopropoxide in alcohol at 140°C, for 60 min, through a reaction cell coupled to an adapted microwave system. *elliottii* samples were added to TiO$_2$ rich solution after the synthesis and, once more, subjected to microwave solvothermalization process at 90°C for 60 minutes and self-generated pressure 3-bar. The X-ray Diffraction evidenced that the nanostructures observed through Scanning Electron Microscopy corresponded to the anatase crystalline phase. Particles in agglomerates formed a homogeneous cover on the surface, it is likely that there was interaction through hydrogen bonds with the OH radicals found in wood cell walls. The microwave action makes molecules prone to align due to electric field influence, fact that makes it possible having an oriented and uniform deposition on the surface and its impregnation into the wood. In addition, the hydrophobicity measured through sessile drop analysis showed that the adopted method was capable of turning the original wood surface from hydrophilic into hydrophobic. The treated samples that were immersed in water for 400 hours showed significant water absorption delay, therefore the method proved effective to modify the surface structure of the wood, fact that gives it special features to increase its durability and stability

Keywords: Surface modification, Hydrophobicity, Coating, Microwave

Introduction

Wood is a material that is distinguished in relation to its natural characteristics and some potentially controllable properties, such as the resistance to biological deterioration and dimensional stability, as opposed to other materials of a different nature. The great flora diversity allows this material to be used in different areas since each species presents peculiar characteristics. However, every wood presents hygroscopicity issues related to dimensional instability and to the attack of xylophagous microorganisms. These factors can lead to defects and to fast deterioration, fact that limits wood applicability.

Surface modification processes based on inorganic materials are of interest to researchers who find in them an alternative to minimize specific issues that limit wood use. These processes aim at improving properties related to resistance to fire (Sun et al., 2012), to the attack of microorganisms (De Filpo et al., 2013), to UV radiation (Salla et al., 2012) and to water (Jia et al., 2016); consequently, they
increase wood durability and broadens its use. These processes are based on the idea of producing multifunctional wood presenting lower toxicity than that of wood in natura, since the most commercially used treated wood represent risk to the environment, fact that goes against the main wood-modification and wood treatment objectives (Lowden and Hull, 2013; Hill, 2006).

The interest in the deposition of titanium dioxide (TiO2) particles on wood has been growing, since this ceramic presents low toxicity and easy obtainment, as well as has great potential to give different characteristics to wood, and to turn it into a functional material (Sun et al., 2012; De Filpo et al., 2013; Gao et al., 2015; Chu et al., 2014). Science has proven that TiO2 deposition on wood through the adoption of different methods, such as sol-gel, conventional hydrothermal, immersion and deposition through layers, slows the water absorption process in wood and improves its dimensional stability and the lotus effect happens as in most plant leaves (Rassam et al., 2012; Liu et al., 2015; Zheng et al., 2015; Lu and Hu, 2016). Murigan et al. (2006) and Moura et al. (2014) reported to have obtained TiO2 ceramics by applying the microwave-assisted thermal system, which consumed little energy and produced particles at low temperatures in shorter periods-of-time. The ceramics produced through this system leads to a product of high purity, as well as minimizes residue production (Murugan et al., 2006; Bilecka and Niederberger, 2010). This method is fast and available for the construction of new wood-based materials; moreover, the new model is an alternative to modify wood surface. The process also reduces processing costs and steps, besides preserving the original porosity, mechanical properties and aesthetic characteristics. The idea is to accelerate the Pinus elliottii wood surface protection process by using TiO2 at low controlled temperatures under very high pressure to cause particle deposition and greater interaction between the two materials through microwave action in order to reach appropriat modification (Cavalcante et al., 2016; Poonia et al., 2016).

Thus, the aim of the present study was to use a microwave system to modify the surface of Pinus elliottii wood by means of the deposition and impregnation of TiO2 particles synthesized through the microwave-assisted solvothermal method, as well as to verify the effect from the connection of these two materials when in contact with water.

**Material and methods**

The microwave-assisted solvothermal method was used to obtain the TiO2 particles (Figure 1). Firstly, 30mL of alcohol suspension was prepared with titanium isopropoxide and ethyl alcohol at pH between 4 and 5 in order to get crystalline TiO2; the suspension remained under constant stirring for 10 minutes and continuous nitrogen flow. The solution was transferred to a teflon reaction cell after the preparation, and it was, then, coupled to the microwave system. The microwave irradiation system was programmed for 60 minute synthesis at 140°C, at heating rate 7°C/min and self-generated pressure 8-bar.

**Fig. 1.** Schematic illustration depicting the microwave-assisted solvothermal method.

The solution was cooled at room temperature after synthesis; six Pinus elliottii wood samples (dimension 1 x 1 x 1 cm) were transferred to the same reaction vessel, which contained the newly formed TiO2 particles. Again, the reaction cell was hermetically sealed and programmed for 60 minutes at 90°C and self-generated pressure 3-bar - time long enough to modify the wood surface. Finally, the wood samples were dried at 100°C for 24 hours.

The X-Ray Diffraction (XRD) technique was used to assess the TiO2 phase formation. The crystalline phase generated through XRD was identified by comparing the diffractogram of samples analyzed according to the Joint Committee on Powder Diffraction Standards (JCPDS). The TiO2 deposition and impregnation into wood, as well as its morphology and the chemical composition of the sample were assessed through Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS) in order to have the
The use of microwave system to deposit TiO$_2$ particles on wood surface to improve water repellency

surface and interior (tracheid) view of the wood. The contact angle of a 20 µl drop with the wood surface was detected through wettability. Hydrophobicity was checked in triplicate on the transverse plane of the samples, it was done through the sessile droplet method at different times (5, 20, 35, 50, 65, 80 seconds) by using a goniometer model DSA25. Water absorption was measured by immersing the samples in water for 400 hours. The samples were periodically weighed; thus, the weight-change percentage was calculated according to Equation 1

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

Wherein: $\Delta W =$ weight variation; $W_0 =$ sample weight before immersion (0% moisture) (g); $W_1 =$ sample weight after immersion (0% moisture) (g).

**Results and discussion**

Figure 2 shows the X-ray Diffractogram of the white powder formed directly from the microwave-assisted solvothermal synthesis at 140°C and self-generated pressure 8-bar for 60 minutes, prior to the particle deposition process applied to the wood surface. It is possible observing the unique and crystalline formation of the anatase phase, which is represented by peaks at 25.6°, 38.6°, 48.1°, 54.2°, 55.1° 62.7°, 68.8°, 70.3°, 75.3° and 82.8°. These peaks are the standards set by the indexed crystallographic data sheet JCPDS File 21-1272. According to Moura et al. (2014), the solution at pH between 4 and 5 favors anatase crystallization, and it corroborates the results recorded in the present study. Overall, small-dimension particles pooled as spherical agglomerates (200nm diameter, on average) were observed through micrographs.

The wood surface was completely covered by anatase particles previously formed through the microwave-assisted solvothermal method, their distribution was homogeneous and efficient (Figure 3). Wood micro porosity, known as racheids, favored the impregnation of inorganic structures into the micropores (tracheids), which were adhered to the cell wall. The EDS spectrum showed that the elemental content of the deposited structures was formed by the titanium element (Ti), unlike the control wood, which mostly showed carbon (C) and oxygen (O). Water impregnation in the cellular structure of the molecules happened due to the irradiation of microwaves. Such impregnation enabled wood ions and atoms to move due to the electric field influence, which made the wood prone to align at the dipole-moment (Mcloughlin et al., 2003). Such process allowed the uniform deposition. It is known that wood cell wall is rich in OH free radicals that act as water adsorbents. In addition to the physical interaction resulting from the large particle surface area, it is believed that OH radicals were the means of connection with the TiO$_2$ particles, since the synthesis provides surface charges on the particles, which can bind to the radicals present in the cell wall of the wood. This allow the interaction with the wood through hydrogen bonds. This interaction was also reported by Gao et al. (2015) and Li et al. (2016), who investigated the deposition of these particles on bamboo and wood, respectively, through the adoption of the hydrothermal method, so that these materials could be used for different purposes.

Wood natural roughness is composed by micron structures (Lopes et al., 2014). Figure 4 shows that there is fast water absorption and scattering when a liquid drop is placed on the surface of a wood piece. Tracheids arranged in the axial direction facilitated absorption; OH radicals found in cell walls react with water.

The deposition of TiO$_2$ particles provided three roughness levels: macro, micro and nano structures, which resemble lotus flower and decrease the energy on the surface. According to Zhang et al. (2007) and Zheng et al. (2015), these two factors are essential to achieve superhydrophobicity. Particles, in the current study, generated an interfacial tension that led to a more spherical drop; therefore, they reduced the contact between drop and wood. The contact angle reached approximately 140° ($\pm$6.4) in the modified
wood 80 seconds after the drop; therefore, it was classified as a hydrophobic surface under the luminosity in the room. Pori et al. (2016) got superhydrophobic wood by adopting a hydrothermal process to deposit the rutile TiO$_2$ phase synthesized from the precursor TiCl$_4$. Gao et al. (2015) proved that it is possible reaching super-hydrophobicity when there is no radiation incidence (of any kind) on wood surfaces coated with TiO$_2$. The same applies to the present study, however only one simple deposition and impregnation step was enough to reach hydrophobicity.

Fig. 3. SEM and EDS of the wood after the TiO$_2$ particle deposition and impregnation process (a), and control wood (b).

![Fig. 3](image)

Fig. 4. Wood wettability after the TiO$_2$ particle deposition and impregnation process (a), and control wood (b).

Wood samples immersed in distilled water showed greater resistance to water absorption through mass variation, due to the modified surface (Figure 5). The OH radical availability appeared to be lower, or blocked for H$_2$O adsorption, thus suggesting that the interaction between the two materials is result from radicals in hydrogen bonds.

![Fig. 5](image)

**Fig. 5.** Wood water absorption depending on the time after the TiO$_2$ particle deposition process (a), and control wood (b).

The evidence of increased water resistance proves that the deposition and impregnation of anatase particles improves wood dimensional stability and consequently reduce defects and the attack of xylophagous microorganisms throughout wood lifespan. Water remained transparent after 400 hours, and it is the indication of a stable and lasting bond between wood and TiO$_2$. Such results evidence that the microwave-assisted solvothermal method was efficient for the deposition of TiO$_2$ particles on wood in order to improve its water repellency. Therefore, the method makes wood more suitable for use even under different humidity conditions. Data from inorganic material deposition or impregnation into wood are consistent with data in the literature (Sun et al., 2010; Wang et al., 2012; Lu et al., 2014; Jia et al., 2016).

**Conclusions**

Homogeneous and uniform deposition and impregnation of TiO$_2$ particles was achieved through the solvothermal method using one-step microwave radiation. The deposition, impregnation and interaction between the two materials showed remarkable reduction in water absorption and turned wood surface from hydrophilic into hydrophobic. The water repellency attributed to wood allows to propose a simple and fast new method aimed at modifying wood by using inorganic particles and by generating multifunctional wood for different environments.

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