ABSTRACT

The aim of the present study is to subject Pinus elliottii wood specimens to TiO$_2$-based modification in order to make it resistant to water and UV radiation. The microwave-assisted solvothermal method, which is little reported in the literature, was here in used for this purpose. The adopted methodology led to 1 % mass gain; although it was a low value, it was enough to fully coat the surface of the wood with nanoparticles to the extent of changing its characteristics and turning it into a functional material. The nanoparticle distribution on the surface of the wood changed your natural topography by increasing the surface area and, consequently, increasing the contact angle of the modified wood (approximately 130°). The leaching test showed that the wood remained coated after it was immersed in water, as well as that it did not lose its water-repelling ability. This result demonstrates the stable interaction between the two materials, due to hydroxyl radicals found in them. The coating also protected the wood against UV radiation for 500 hours of intense exposure, besides preserving its initial color. The properties achieved through this simple and fast modification process provide an alternative to help improving the performance of the herein investigated wood species, mainly for applications in environments subjected to high solar incidence and humidity.

Keywords: Hydrophobic surface, microwave system, TiO$_2$-modified wood, wood modification, wood protection.
1. INTRODUCTION

The unique and versatile features of each wood species enable the extensive use of this material and its derivatives, which are adopted as raw material in almost all technology fields. However, since wood is of organic origin and mainly formed by polymers, it is susceptible to weathering events capable of modifying its natural features, thus making it use unfeasible. Wood exposed to external conditions is subject to chemical and physical reactions that strongly contribute to change its properties. The incidence of solar radiation leads to a rapid color change in the wood due to photodegradation on the surface layer of its polymer components: lignin, cellulose and hemicellulose (Salla et al. 2012).

The ultraviolet radiation from the sunlight is the most damaging type because it triggers chemical changes in the wood. It has sufficient energy to cause photochemical degradation in polymers, besides being capable of penetrating the wood to a depth of approximately 75 μm, depending on its original color (Teles and Costa 2014). Light absorption in the specific range from 280 nm to 400 nm (ultraviolet radiation) compromises the mechanical strength and overall appearance of the wood, mainly due to crack formation and color changes, which affect the aesthetics and durability of the wood.

Among the chemical components of the wood, lignin is the main constituent affected by photodegradation, since it absorbs 80 % to 95 % of the total ultraviolet radiation (Teaca et al. 2013). According to (Mitsui and Tsuchikawa 2005), the degradation process resulting from lignin oxidation triggers the production of quinone compounds, which are responsible for the color change in the wood. More specifically, according to (Schaller and Rogez 2007), successive ruptures of hydrogen bonds, and the lignin hydrogen loss, lead to the formation of peroxides with oxygen and, finally, to decomposition into colored by-products.
Another extremely relevant factor for wood integrity refers to its behavior when it gets in contact with water, since it rapidly responds to moisture content changes. The polymers forming the wood are the main responsible for the material’s affinity with water, since they are rich in OH− radicals (Cappelletto et al. 2013). The swelling and contraction resulting from water absorption and desorption induce cell-wall stresses, which generate defects such as warping and cracks (Zheng et al. 2015); cracks are the gateway for wood-degrading organisms.

Nowadays, it is believed that inorganic materials based on metal oxides, such as TiO₂ in particulate or film, have potential to be used as surface protectors with long shelf life TiO₂ effectively enables substrate protection (Rassam et al. 2012) because it is capable of absorbing ultraviolet radiation (Kubacka et al. 2012). In addition, it is able to mimic rough surfaces (in macro, micro and nanoscale) associated with high free surface energies by providing them hydrophobic appearance similar to that of lotus flowers (Ma and Hill 2006, Liu et al. 2015). (Gao et al. 2015) in your study about pH-dependent structure and wettability of TiO₂-based wood surface found chemical changes and thus improvements in the surface contact angle of treated wood. (Rassam et al. 2012) when treating the wood of Fagus orientalis with TiO₂ nano-particles on wood surfaces for UV and moisture protection concluded that the treatment preserved the color of the wood after 200 hours of UV exposure and the contact angle was constant, yet added that this was due to chemical changes in the treatment, especially in OH.

Wood subjected to weathering events can have their performance improved through modification treatments based on ceramics, which can be applied as surface or impregnation coating. Thus, it is worth highlighting some methods adopted for this purpose: immersion (Rassam et al. 2012), dispersion (Cristea et al. 2010), pressure (Zanatta et al. 2017), sol-gel process (Lu et al. 2014), hydrothermal process (Van Chu et
Conifers, such as those belonging to genus *Pinus*, present high lignin content, high porosity and thus a very variable density (0.45 g/cm³ until 0.60 g/cm³) (Acosta *et al.* 2020a, Acosta *et al.* 2020b); thus, they are more susceptible to photodegradation and present greater variation resulting from moisture. Therefore, the aim of the current study was to use TiO₂ particles to modify *Pinus elliottii*. wood through nanocrystal nucleation and growth in order to help improving the modified wood performance when it gets in contact with water or is exposed to extreme ultraviolet radiation conditions.

2. MATERIALS AND METHODS

2.1 Materials

The wood species *Pinus elliottii* Engelm. which is a lignin-rich, porous and low-durability conifer, was herein selected as object of study to allow investigating its photodegradation and its behavior when it gets in contact with water. The wood specimens were obtained in homogeneous stands of adult trees in Pelotas County, Rio Grande do Sul State, Brazil. Subsequently, were cut in a circular saw of the brand BOSCH, model GTS-10J, in the dimensions of: 25 mm x 9 mm x 250 mm, 10 mm x 10 mm x 10 mm and 10 mm x 15 mm x 15 mm (for SEM images) to be subjected to different analyses.

The following reagents were used to produce the TiO₂ particles: titanium isopropoxide (Ti [OCH (CH₃)₂]₄) as Ti precursor, and ethyl alcohol (C₂H₆O) as solvent; at 97 % and 95 % purity, respectively.

2.2 TiO₂-based wood modification
The method used by (Zanatta et al. 2018) was herein adopted to carry out the wood modification using the oxide. An alcohol solution containing 0.07 mol\(^{-1}\) of titanium isopropoxide was prepared under constant stirring and nitrogen flow. Samples were inserted in this medium, which was kept under the aforementioned condition until the precursor solution was fully homogenized. The initial preparation was performed in a Teflon glass, which was transferred to a Teflon reaction cell coupled to a microwave system. This method is known as microwave-assisted solvothermal synthesis; it presents a programming system, which allowed performing the synthesis for 60 minutes at 140 °C, at heating rate 6 °C/minute. The nanocrystal nucleation and growth process took place directly on the cell walls and surface of the wood, which also worked as substrate. At the end of the process, wood samples presenting crystallized TiO\(_2\) on their surface and inside were placed in an oven at 100 °C for 24 hours, for subsequent characterizations.

2.3 Characterization

A field emission gun-scanning electron microscope (FEG-SEM; ZEISS, model Supra 35 VP) was used to generate images at different magnifications. Wood veneers were cut in the tangential direction and subjected to topographic scanning through atomic force microscopy (AFM); they were not subjected to previous preparation to avoid influencing the original roughness of the samples (control and TiO\(_2\)-modified wood). The images and roughness parameters were obtained in a Shimadzu microscope, model SPM-9600 (Japan), which was configured as follows: non-contact mode; scan rate: 0.8 Hz; resolution: 512 pixels x 512 pixels; and scan sizes 10 \(\mu\)m x 10 \(\mu\)m, 5 \(\mu\)m x 5 \(\mu\)m, 3 \(\mu\)m x 3 \(\mu\)m and 1 \(\mu\)m x 1 \(\mu\)m.

2.4 Wettability
Static contact angle measurements were performed, based on the sessile drop method, by using an extended Theta Lite optical tensiometer (TL110), for wettability analysis purposes. A drop of deionized water (volume 5 μL) was deposited on the tangential surface of three control and three TiO₂-modified wood samples; contact angle measurements (5 seconds to 80 seconds) were performed to check the behavior of the drop.

2.5 Immersion-based leaching test

The immersion-based leaching test was used to check the stability of and interaction between crystallized particles in the wood. The modified samples were divided in two groups: group 1, which remained immersed in cold water (room temperature) for 50 hours; and group 2, which remained immersed in hot water (80 °C) for 6 hours. The aforementioned samples were weighed at approximately 0 % moisture content (before) and after they were subjected to the herein adopted leaching conditions. The weight difference was used to analyze the number of particles that leaked out of the material. The wettability analysis was carried out again, based on the previously mentioned parameters, to check the effect of the leaching conditions on the repellency or affinity with water of the surface of the wood. FEG-SEM images of the surface of the samples were taken after the leaching test.

2.6 Photo-stability of the wood samples

The stability of the wood, which is provided by particles exposed to ultraviolet radiation, was achieved through accelerated aging. Eight wood samples (4 control and 4 TiO₂-modified woods) were placed inside a completely black reaction chamber equipped with ultraviolet lamp (OSRAM - UVA – 60 Hz / 9 W / 220 V), which was used as radiation
source at wavelength range 315 nm to 400 nm. Then, they were stored in a conditioned room (20 °C and 65 % relative humidity) for 500 hours. Samples were periodically removed for colorimetric analysis purposes.

2.6.1 Colorimetry

The color change resulting from the exposure to ultraviolet radiation was analyzed based on the system described by the International Commission on Illumination (Commission Internationale de L’éclairage–CIE-L*a*b*). The colorimetric variables (direct exposure to UV rays) of each sample were measured in a Konica Minolta portable colorimeter, model CR-400, with 8 mm sensor aperture, configured for D65 light source and 10° observation angle. Colorimetric parameters such as L*, a* and b* indicated luminosity (black, 0 – white, 100), red (+) – green (-) chromatic coordinate and yellow (+) – blue (-) chromatic coordinate, respectively.

The ∆L *, ∆a * and ∆b * values were calculated based on the difference between the final and initial values of L *, a * and b *, which were used to calculate the overall color variation ∆E * based on aging (Equation 1).

\[
\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\]  

(1)

Where in: ∆E is the wood color change after the exposure to ultraviolet radiation; ∆L *, ∆a * and ∆b are the values obtained through the final (500 hours) and initial (0 hours) L *, a * and b * data.
3. RESULTS AND DISCUSSIONS

The here investigated wood species presents several OH-groups in its cell wall; besides attributing hydrophilic character to the species, these OH-groups are responsible for most of the interactions that happen when the wood is subjected to modification processes or treatments focused on its protection and durability (Lu et al. 2014). Figure 1 describes the modification process and shows the behavior of the TiO2-modified wood surface subjected to the microwave-assisted solvothermal method.

![Image: Experimental scheme of the TiO2-based modification process applied to wood samples based on the microwave-assisted solvothermal method.]

When the wood is added to the precursor solution, there is adsorption on its surface and inside of it (due to capillary tension and gravity). Then, titanium hydroxides (Ti-OH) are formed by taking advantage of the OH- in the wood. According to (Xie et al. 2007), when the precursor arrives on the surface of the wood, it needs to overcome the first energy barrier in order to adsorb to the active sites of the substrate. In addition, when the substrate is rich in OH-, the precursor solution is rapidly adsorbed, as it was observed in the present experiment.

The wood modification process based on microwave radiation, and the thermodynamic conditions leading to crystal nucleation and growth, will be discussed below. Wood was a solid material inserted in the solution; thus, it worked as a...
heterogeneous nucleating agent, which accelerated the crystal solidification (nucleation and growth) process. Based on the FEG-SEM images presented above, it is possible stating that the TiO$_2$ particles were produced at nanometric scale (approximately 10 nm) in submicrometric clusters (approximately 200 nm). The clusters presented uniform surface, i.e., the wood was fully coated - the good distribution of TiO$_2$ particles was favored by the considerable number of active sites in the original wood.

Atomic force microscopy was applied to the tangential section of the samples (usually the most exposed section) to help better understanding the influence of particle distribution on the functional performance of the wood surface. It is worth mentioning that wood represents a challenge to this type of research, since it naturally shows wide topographic pattern variability, which often presents multiple-scale roughness, thus making it difficult to be analyzed (Jim and Kasal 2016).

If one takes into consideration the natural aspect of the wood (without surface preparation for modification purposes), i.e., its rough surface, the scanning applied to smaller areas showed significant increase in the roughness of the wood, unlike the larger areas that presented topography smoothing due to TiO$_2$ particles. It happened because the current study worked at smaller scales with a heterogeneous material such as wood. Its original topography was maskeddue to the exclusion of grooves mainly resulting from anatomical structures such as tracheids, thus suggesting the existence of a previously smooth surface. Micrographic details of the modified wood surface are illustrated in Figure 2.
This assumption is supported by the roughness parameters of the wood with, and without, TiO2. The treated samples tended to present surface smoothing, as shown in Table 1. The scanning of the control wood (100 μm² area size) indicated substantially higher roughness (Sq = 317.3 nm) than that recorded in the TiO2-modified one (Sq = 99.7 nm). This area size (100 μm²) was herein adopted because it was more compatible with the original roughness dimensions of the samples. The aforementioned result due to the fact that the here in adopted area size allows detecting tracheid grooves and irregularities in the cell wall of different anatomical elements, among them: “elevations” and “deep valleys”, in the order of micrometers.
Table 1: Roughness parameters analyzed through AFM in different surface areas of control (W) and TiO2-modified (MW) woods.

<table>
<thead>
<tr>
<th>Area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>MW</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>MW</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>MW</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>MW</td>
</tr>
</tbody>
</table>

| Sa (nm)   | 18,31 | 58,12 | 72,03 | 50,76 | 71,6  | 70,12 | 246,7 | 99,7  |
| Sq (nm)   | 23,20 | 73,39 | 98,05 | 64,63 | 92,91 | 88,61 | 317,3 | 130,2 |
| Sp (nm)   | 71,9  | 340,6 | 577,5 | 272,3 | 645,0 | 403,1 | 1197,0| 746,0 |
| Sv (nm)   | 130,7 | 149,3 | 348,3 | 232,8 | 355,0 | 216,9 | 879,0 | 362,0 |
| As (µm²)  | 1     | 2,1   | 14,54 | 17,93 | 31,49 | 40,38 | 132,3 | 158,4 |

* Sa = arithmetic mean roughness; Sq = quadratic mean roughness; Sp = maximum profile height; Sv = maximum profile valley depth; As = Surface area; W = control wood; MW = TiO2-modified wood.

The here in proposed modification process has significantly contributed to increase the surface area of wood samples subjected to it. Based on Figure 3 (b), it is possible seeing that the surface topography of the modified wood was influenced by the presence of smaller structures (titania nanospheres) in comparison to that of Figure 2 (a). The graph representing the isotropic power spectral function confirms the contribution of smaller scale particles (higher frequency) to topography formation and to area increase; the cross-sectional profile shows shorter distance/proximity between the peaks and valleys in the spectrum of Figure 3 (b).
Figure 3: 3D image and cross-sectional profile of (a) control wood (b) TiO$_2$-modified wood; and (c) graph representing the isotropic power spectral function of the two surfaces, based on the 10 μm x 10 μm profile scanning.

Overall, the here in applied modification process was able to soften the rough surface of the wood, since the TiO$_2$ particles filled the spaces that caused longer peak-valley distance, which increased the roughness values. On the other hand, the typical TiO$_2$ nanosphere structures increased the surface area. (Chang et al. 2015) were able to gradually increase the surface roughness of Cunninghamia lanceolata wood by using dimethylpolysiloxane (PDMS) to increase the controlled silica concentration in the coating. It may have happened due to the addition of this polymer on the wood surface, which led to the formation of a continuous and smooth film. In addition, the increase and the control of inorganic particle concentrations on the wood surface allowed detecting
nanoparticles and their clusters, which expressively increased the mean roughness values. Such result was already expected in the current study, since no polishing or polymer application capable of influencing the initial roughness of the wood was carried out in order to enable the closest reproduction of the original material.

As previously discussed, TiO$_2$ has efficiently coated the wood, increased its surface area, as well as changed and attributed roughness at nanoscale. These parameters directly influence the wettability of materials. Figure 4 shows the change in the contact angles of the drop based on the time it spent on the wood surface.

Figure 4: Contact angle of control (a) and TiO$_2$-modified (b) woods based on time. Bars represent the mean standard deviation.

Polymers comprise several OH$^-$ groups, where as the lumens of cell structures have water storage capacity; together, they naturally provide hydrophilic property to the wood (Liu et al. 2015). Consequently, the control wood initially presented high contact
angle; however, the water was completely absorbed in less than 15 seconds due to capillarity force. This behavior is common when the material in question is wood (Rassam et al. 2012, Kúdela 2014).

On the other hand, the introduction of TiO$_2$ particles made the OH$^-$ in the cell wall less available (view Figure 1) to absorb water. The coating generated a layer between the anatomical structures, which made it difficult for the water to pass, besides changing the wood topography in a way to attribute hydrophobic character to it. The OH$^-$ became less available due to the chemical adsorption of nanoparticles. This phenomenon happens because the nanoparticles, whose surface is rich in OH$^-$ groups, grow through hydrolysis-condensation; thus, a new condensation will enable the interaction between the wood (cell wall) and nanoparticle surfaces.

It is known that there must be synergy between roughness and low surface energy for a surface to become superhydrophobic. In the current case, it was not possible reaching values higher than 150° because agents capable of decreasing the surface energy were not used in the wood modification process.

As the wood presented macro and microscale roughness (Wang et al. 2014; Liu et al. 2015), the incorporation of TiO$_2$ nanoparticles contributed to the formation of a hierarchical surface (nano- and micro-clusters). The wood topography changed, and it allowed the droplets to appear in an almost spherical shape. Thus, the TiO$_2$-modified wood presented high water repellency, also known as hydrophobicity. This behavior is consistent with the model by (Wenzel 1936), wherein the whole surface gets in contact with the drop, with no air trapped between the structures. Thus, the hydrophobic character is attributed to the surface area increase.

Liu et al. 2015, produced superhydrophobic wood by associating the two herein previously mentioned parameters. On the other hand, (Wang et al. 2014) used a
hexadecyltrimethoxysilane (HDTMS) treatment in the wood modification process; they
were able to reduce the surface free energy, but only found contact angles close to 130°.
(Gao et al. 2015) were able to produce wood with different contact angles just by
changing the pH in the modification process; the maximum contact angle was 132.7°.
Therefore, it is possible seeing that the aforementioned results are similar to the ones
recorded in the present experiment. The great advantage of the current study over the
others lies on the possibility of using a homogeneous coating, in a single stage, in the
microwave system. Based on the easiness of the herein adopted process, we believe that
it is possible obtaining superhydrophobic wood through surface energy control
(functionalization), according to the model by (Cassie and Baxter 1944).

The modified woods were immersed in cold (50 h) and hot (6 h) water to allow
investigating the stability of the hydrophobicity effect, as shown in Figure 5.
Figure 5: Graph presenting the mass variation in the TiO₂-modified wood, according to the Leaching test by cold (50 h) (a) and hot (6 h) (b) immersion, as well as its respective FEG-SEM and contact angle images.

Firstly, the current result indicated that the modification process increased by 1%, on average, the initial mass of the samples. The immersion leaching made them lose approximately 0.2% of it after the time they remained immersed in water in different environments. The standard deviation recorded high value. However, it happened due to the heterogeneity (anatomical variation) of the wood. The mass gain rate recorded after the wood was modified was much lower than the one found in the literature; however, it
was sufficient and adequate to enable equivalent properties to the ones found in the studies by (Van Chu et al. 2014, Lu et al. 2014), who recorded mass gain of approximately 7% (TiO2) and 25% (SiO2), respectively.

With respect to the mass loss after leaching, it was evident that, despite reducing the surface particles, both tests were not able to remove the coating, since the wood samples remained hydrophobic, although they presented slightly lower contact angle (approximately 120°). The microscopy image confirmed that TiO2 particles fully coated the wood surface, thus not allowing the modification to become ineffective. Thus, the images allow confirming the interaction between the two materials, as well as that such interaction remained stable even under adverse conditions.

Another important aspect to be taken into consideration is that even the results of treatments that efficiently obtained hydrophobicity can be considered innocuous if the color of the treated material - in the present case, the wood - is significantly changed. Thus, color determination and photoresistance tests were performed to check whether the treatment adopted in the present study affected the natural color of the wood samples.

Woods exposed to ultraviolet radiation are subject to photodegradation, which can be seen through changes in their surface color; the photodegradation process results from chemical changes in the polymers forming the wood. According to (Hon and Shiraishi 2000), the post-irradiation color dues to the emergence of chromophore groups resulting from the break of cellulose and lignin bonds; lignin is the main polymer responsible for such phenomenon due to its ability to absorb light at short wavelengths (between 200 nm and 380 nm).

Colorimetric parameter readings were performed during the wood aging process in order to assess the UV radiation-resistance capacity enabled by the TiO2 coating in the wood modification treatment. Results are shown in Figure 6.
Figure 6: Changes in colorimetric parameters such as luminosity L *, chromatic coordinates a * and b *, and total color change (ΔE) in control and TiO2-modified woods exposed to UV radiation for 500 hours. W = control wood; MW = TiO2-modified wood.

The L *, a * and b * values recorded for the control wood showed that the UV radiation darkened the wood surface and gave it a reddish-yellow color. In addition, the highest luminosity decrease happened mainly in the first exposure hours. On the other hand, the modified wood, which presented lighter color in the first hours, kept its parameters almost unchanged, thus confirming the acquired ability to resist this type of radiation due to the presence of TiO2.

According to (Teaca et al. 2013), lignin is responsible for absorbing 80 % to 95 % of the total UV light absorbed by the wood. Thus, the increase in chromaticity coordinates a * and b * is attributed to the formation of quinones and quinoid-like structures due to lignin depolymerization and oxidation, which involved radicals - possibly phenoxy radicals (Hon 2001). The energy deriving from this region of the...
The electromagnetic spectrum is sufficiently high to break the chemical bonds of organic compounds in the wood. It results in reduced mechanical resistance, color change and in eventual cracks, which reduce the long-term shelf life of the workpiece (Salla et al. 2012).

The modification process helped improving wood durability; moreover, it did not lead to significant changes in any color parameter after the exposure to radiation. This result indicates that the TiO2 coating applied to the wood surface was able to prevent and restrict the photodegradation on the surface of the wood. Such efficiency becomes evident in the color change (ΔE) graph (Figure 5).

The resistance to irradiation and photodegradation was achieved because the oxide chosen to modify the wood presents high capacity to absorb UV radiation. This characteristic due to its electronic structure, which is characterized by one filled valence band and one empty conduction band (Kubacka et al. 2012); its optical gap is in the order of 3.2 eV. According to (Faure et al. 2013), surface modifications focused on protecting the wood against UV rays adopt significantly thicker coating; therefore, dispersion issues should be taken into account. If one takes into consideration the here in previously reported images showing particles on the wood surface, it is possible stating that the applied process provided a suitable protective layer with good particle distribution, which is a relevant factor for the resistance to accelerated aging. These issues were also addressed by (Sun et al. 2012), who produced wood protected from the effects caused by photodegradation.

4. CONCLUSIONS

The current results allow concluding that the TiO2-based wood modification process applied through the microwave-assisted solvothermal method was efficient. The main improvements lie on hydrophobicity and protection against UV radiation, which
were simultaneous obtained and protected the wood in a synergistic way. A highly hydrophobic character, represented by the contact angle 130°, was achieved due to the modification of the original topography of the material, which increased its surface area. Overall, the herein adopted modification process was able to smooth larger wood structures, as well as to increase the wood surface area, due to the contribution of smaller TiO₂ structures, which led to increased contact angle. A uniform coating of UV-radiation absorbing particles was generated in the wood. Despite reducing the surface particles, both tests (leaching to cold and hot water) were not able to remove the coating, since the wood samples remained hydrophobic, although they presented slightly lower contact angle. This coating was suitable to protect the chemical modifications of the surface polymers when they were exposed to the herein adopted radiation range, since it was represented by the minimal change in the total color variation.

ACKNOWLEDGEMENTS

The authors are grateful to CAPES/PROCAD 2013/2998/2014, CNPq and FAPERGS, for the financial support; as well as to Federal University of Rio Grande do Norte, for the FEG-SEM, AFM and wettability analyses.

REFERENCES


Wood Treated by In Situ Polymerization of Methyl Methacrylate (MMA). *Forests* 1–10.

https://doi.org/10.3390/f11070768


https://doi.org/10.1016/j.matlet.2014.12.035


