Accepted Manuscript

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PII: S0169-4332(16)30510-4
DOI: http://dx.doi.org/doi:10.1016/j.apsusc.2016.03.065
Reference: APSUSC 32831

To appear in: APSUSC

Received date: 2-12-2015
Revised date: 6-3-2016
Accepted date: 7-3-2016

Please cite this article as: Pavel Pori, Aljaž Vilčnik, Marko Petrič, Adrijana Sever Škapin, Mohor Milešič, Angela Šurca Vuk, Urban Novak, Boris Orel, Structural studies of TiO₂/wood coatings prepared by hydrothermal deposition of rutile particles from TiCl₄ aqueous solutions on spruce (Picea Abies) wood, Applied Surface Science
http://dx.doi.org/10.1016/j.apsusc.2016.03.065

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Structural studies of TiO$_2$/wood coatings prepared by hydrothermal deposition of rutile particles from TiCl$_4$ aqueous solutions on spruce (Picea Abies) wood

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Graphic abstract

Subtraction IR (left) and Raman (right) spectra of TiO₂ particles deposited on wood
Highlights

- Rutile (TiO$_2$) particles were deposited on wood from aqueous TiCl$_4$/HCl solutions
- Deposition of rutile particles was controlled by changing processing conditions
- Ti-O…wood interactions were studied from subtraction IR and Raman spectra
- Ti-O…hemicellulose and Ti-O…lignin interphase interactions were identified
- Hydrothermal treatment impregnated wood and made wood superhydrophobic
Abstract

A low temperature approach was developed for the deposition of rutile TiO\textsubscript{2} particles on a wood surface by hydrolysis of TiCl\textsubscript{4} in aqueous solutions acidified with HCl, and crystallization at 75 and 90 °C (1 h). Prior to hydrothermal treatment, *Picea Abies* wood was first soaked in a 0.5 mmol/l aqueous solution containing anionic surfactant sodium dodecyl sulphate (SDS, Sigma Aldrich) for 2 h at 80 °C. The crystal structure of the hydrothermally made rutile particles was determined with XRD, while the morphology of the deposited TiO\textsubscript{2} particles and their distribution in the wood were examined with SEM and EDX measurements. The penetration and amount of deposited rutile particles could be modified by changing the deposition conditions. Thicker layers were obtained from more concentrated aqueous TiCl\textsubscript{4} solutions with and without added HCl, and with longer deposition times and higher temperatures of the hydrothermal treatment.

The interaction of TiO\textsubscript{2} particles with hemicellulose and lignin in wood was established from infrared attenuated total reflection (FT-IR ATR) and Raman spectra measurements, from which the spectra of wood were subtracted. Analysis of the subtraction spectra showed the presence of titania particles on the wood surface, revealing also the establishment of TiO\textsubscript{2}-wood coordinative bonds of titanium ions with hemicellulose and lignin. The red frequency shift of the OH stretching modes suggested interaction of the TiO\textsubscript{2} particles with water molecules of wood. TiO\textsubscript{2} deposited on wood treated with SDS became hydrophobic (water contact angles (WCA) of 150°), contrasting the properties of untreated wood with a deposited TiO\textsubscript{2} particle coating, which remained hydrophilic.

**Keywords:** wood, TiO\textsubscript{2} deposition, aqueous TiCl\textsubscript{4} solutions, FT-IR ATR, Raman spectra, TiO\textsubscript{2}/wood interactions

1. Introduction

Wood is one of the most abundant biopolymeric materials, with high application potential because it combines mechanical strength and excellent thermal isolation properties with
aesthetic appeal, enabling its use in building construction, as an insulation material and for furniture [1]. There are a few drawbacks. As a biopolymer, wood is also a source of nutrients for microorganisms and is thus vulnerable to attack by fungi and insects [2]. Because of its hydroxylated nature, wood shows poor dimensional and optical stability. The main cause of the destruction of wood is attributed to lignin. In outdoor applications, the combination of UV light [3] with moisture [4] and temperature [5, 6], leads to complete destruction of the lignocellulosic network and to wood degradation [7-12].

TiO$_2$ (rutile) was chosen here for the protection of wood because, as a high refractive index material (n = 2.7) [13] and wide band gap semiconductor, it strongly scatters solar radiation and absorbs UV light [14], which reduces the yellowing of wood.

Protective treatment of wood is as old as its use [15]. Tar, pitch and natural oils in combination with inorganic fillers [16, 17] have been used since ancient times to inhibit weathering deterioration of wood: acetylation [18], impregnation with preservatives [19, 20], heat treatment [21, 22] and surface treatment with inorganic metal salts [23, 24]. Sol-gel technology has been applied to improve wood properties by the creation of nanoscale SiO$_2$ and TiO$_2$/wood composites [25]. Titania sols have been used for impregnation of wood, with various results. Complete soaking of wood has been achieved by impregnation with TiO$_2$ via an ultrasonic–assisted sol-gel process based on tetrabutyl titanate (TBT) [26]. SEM images showed that titania gels generated a thin and homogeneous nanocrystalline film coating on the cell walls, while EDX mappings revealed that titanium elements existed in the whole wood body. Under milder conditions of vacuum impregnation of wood with Ti(Obu)$_4$ [27] titania was deposited in the lumens and partially also in the wood cells. Vacuum and ultrasonic methods both enhance the dimensional stability of wood, by preventing the formation of cracks, retard combustion of the wood matrix and diminish biological attacks. Even better results with smaller water sorption and swelling of the wood have been obtained by the deposition of various hydrophobic coatings (sodium dodecyl sulphates (SDS)) [28-34], hexadecyltrimethoxysilane [35], perfluorodecytriethoxysilane [34] on top of wood hydrothermally treated (110 °C, 6h) in tetrabutyl orthotitanate ethanol solutions [28], immersed in tetrabutyl titanate ethanol-water solutions [29-33, 35] and in TiCl$_3$/water solutions [34]. The advantage of the treatment of wood in TiCl$_3$ aqueous solution [34] is the formation of titania particles, which form hierarchical structures on the wood surface.
necessary to achieve superhydrophobic properties of wood and water contact angles above 150°.

We aimed here to make wood that was impregnated to a depth of at least a few hundreds of micrometers with titania and was also water repellent. Among various methods, the hydrothermal processing of wood in TiCl₄ aqueous solutions at low temperatures (up to 70 °C) was chosen because the aqueous TiCl₄ solution can easily penetrate the hydrophilic and nanoporous [36] structure of wood, whereby complex hydrated titanium ions can interact with the wood components (lignin, hemicellulose) and impregnate the wood structure. On the other hand, the high oxygen (ether and hydroxyl) content of wood acts as an effective nanoreactor, enabling in situ synthesis of TiO₂ nanoparticles and the formation of particles on the inner surface of the lumens in wooden body. In addition, the TiO₂ particles enable formation of a hierarchical (secondary) structure of the wood surface, which is prerequisite for obtaining superhydrophobic properties of wood. Sodium dodecylsulphate (SDS) was used as a hydrophobic agent applied on the wood before the wood was hydrothermally treated in the TiCl₄ aqueous solution.

We borrowed knowledge of how to make TiO₂ particle coatings on wood from studies devoted to the fabrication of monodispersed titania particles from TiCl₄ aqueous solutions [37]. By using a hydrothermal method and autoclaving conditions, Cheng et al. [38] showed that high acidity and high Cl⁻ concentrations are beneficial to the formation of the rutile phase from HCl solutions of TiCl₄. Thermolysis of TiCl₄ in HCl solutions was used by Pottier et al. [39] for the preparation of brookite and rutile polymorphs. It has been shown [40-42] that rutile predominately forms from high concentration water TiCl₄ solutions and at high HCl concentrations but, under milder conditions, brookite and rutile appear together. Precipitation of titania took place when the hydroxo or chloride ligands were eliminated in the course of thermolytic or hydrothermal processing and a neutral complex (TiO₂·nH₂O) formed, as already stated by Cheng et al. [38]. First, by olation, the octahedra link together through dehydration reactions between hydroxo and hydrato ligands and, in the next step, polymers form consisting of either octahedra sharing equatorial edges or polymers of octahedra sharing equatorial edges and apical edges.
The main aim of this study, in addition to successful deposition of rutile particles on wood, was to obtain a clearer picture of how the titania precursors and the formed particles interacted with the hydrated network of wood components (lignin and hemicellulose).

The FT-IR ATR spectroscopic technique was chosen for this purpose because this technique has been extensively employed for the identification of vibrational modes of cellulose and its derivatives [43-47] with different moisture contents [48-50] in the presence of various (mainly silane-based) coatings [51-53], providing a useful platform for investigations of adsorption [51] and silane/-C-OH interactions between the coatings and cotton fibres [52, 54].

The problem of identification of the interactions of titania precursors and TiO₂ particles grown from TiCl₄ aqueous solutions on wood was thus reduced to finding vibrational bands in the FT-IR ATR and Raman spectra of hydrothermally treated *Picea Abies* wood that could be attributed to the Ti-O vibrational bands with molecular groups of lignin [55, 56] and/or hemicellulose. Interactions of the latter with TiO₂ have not yet been reported. We extended our studies on the Raman spectra of the TiO₂/wood coatings because the vibrational bands appearing in the Raman spectra of wood and its components (cellulose, hemicellulose and lignin) have been assigned in detail by Agarwal [57] and Yamauchi et al. [58] and, in addition, the intensity of the OH stretching and O-H-O deformational bands in the Raman spectra is fairly weak, facilitating more detailed assignment of bands of the coordinative bonds of wood components with titanium ions.

The effect of hydrothermal treatment of *Picea Abies* wood was also determined in this study by measuring the CIELab colour coordinates of treated wood. SEM micrographs were examined for assessment of morphological properties, while the penetration of TiO₂ within wood was determined by EDX elemental analysis. We aimed to confirm from the EDX measurements that the TiO₂ particles were located not only in the lumens but also in the cell walls, as conceived from the FT-IR ATR and Raman spectra analysis done in this study. Finally, water contact angles (WCA) were measured in order to verify whether the hydrothermally grown rutile particles also imparted hydrophobic properties to the wood, which was first pre-treated with sodium dodecylsulphate (SDS), in contrast to what has been done by others [31, 59, 60], who deposited SDS on top of TiO₂ treated wood.
2. Experimental

2.1. Materials

2.1.1. Preparation of TiO2/wood samples

Spruce wood (*Picea Abies* (L.) Karst.) pieces with dimensions 25 mm (radial, R) × 25 mm (tangential, T) × 30 mm (longitudinal, L) were used. All samples were impregnated with distilled water in a vacuum chamber by the Ruping full-cell pressure impregnation method.

First, wood samples were impregnated by dipping into a 0.5 mmol/l aqueous solution containing anionic surfactant sodium dodecyl sulphate (SDS, Sigma Aldrich) for 2 h at 80 °C. It should be noted that SDS has already been used for making a TiO2/wood surface hydrophobic [30-32, 60], but the SDS was applied on top of an already prepared TiO2/wood surface [32] and not on bare wood, as was done here.

After treatment with SDS, the samples were rinsed with distilled water and dried in an oven at 100 °C for 5 min. Samples were put into reactors containing 0.5 mol/l aqueous solutions of TiCl4 (Sigma Aldrich) with different HCl concentrations (Sigma Aldrich). The TiCl4 solutions were previously prepared by drop-wise addition of TiCl4 into ice-cold distilled water, while gently stirring. The added HCl solutions differed in the concentration of HCl: 0 mol/l, 0.01 mol/l, 0.1 mol/l, 0.5 mol/l and 1 mol/l HCl. The mass ratio between the TiCl4 solution and the added HCl solution was 1:1. The samples were dipped in the solutions for up to 1 h at different temperatures, i.e., 25 °C, 50 °C, 75 °C and 90 °C. Wood with deposited TiO2 looked pale white because the applied TiO2 was translucent and the actual particle could not be seen with the naked eye. For measurements of the XRD spectra, TiO2 particles were collected from the opaque solutions by centrifugation, washed with distilled water and subsequently dried at 80 °C. After the reaction, the TiO2/wood samples were rinsed with distilled water, dried in an oven at 100 °C for 5 minutes and then held under room conditions (20 °C and 65 % relative air humidity) until a constant mass was achieved. Slices (few mm thick, RxL section) of wood were cut with a microtome from the conditioned TiO2 modified wood blocks in order to
prepare specimens for Raman, FT-IR ATR spectroscopy and scanning electron microscopy (SEM). TiO$_2$/wood samples prepared within the frame of this study are presented in Table I.

Table I. Reaction conditions for hydrothermal treatment of spruce wood: 0.5 M TiCl$_4$, 0 to 1 M HCl and 1 h time of treatment at various temperatures.

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>HCl M [mol/l]</th>
<th>0</th>
<th>0.01</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td></td>
<td>A0*</td>
<td>A1*</td>
<td>A2*</td>
<td>A3*</td>
<td>A4*</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>B0*</td>
<td>B1*</td>
<td>B2*</td>
<td>B3</td>
<td>B4</td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>C0</td>
<td>C1</td>
<td>C2</td>
<td>C3</td>
<td>C4</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>D0</td>
<td>D1</td>
<td>D2</td>
<td>D3</td>
<td>D4</td>
</tr>
</tbody>
</table>

*A0-A4 and B0-B2 TiO$_2$/wood samples were not observed with SEM measurements.*

It should be noted that for the C0-C4 samples we wanted to verify the predictions that rutile particles could also be formed from more concentrated aqueous TiCl$_4$ solutions but without added HCl [61, 62]. The investigations of samples A and B were done in order to show that too mild processing conditions did not lead to the formation of particles but merely enabled the impregnation of wood with TiCl$_4$ which is important for enhancing wood dimensional stability and weather resistance [27, 32, 35, 63-67].

2.2. Methods

The presence of rutile particles on wood samples (RxL sections) was assessed using a Perkin-Elmer System 2000 IR spectrophotometer equipped with an attenuated total reflection (FT-IR ATR) cell (SpectraTech) with a diamond crystal (n = 2.0). The spectra were recorded over the range 4000 – 450 cm$^{-1}$.

Raman spectra were recorded on a Bruker Ram II FT Raman spectrometer by application of laser excitation at 1064 nm. Spectra were averaged from 128 interferograms and apodised with a Blackman-Harris 4-Term function. All spectra were recorded in the spectral range between 3500 and 50 cm$^{-1}$, with a nominal resolution of 4 cm$^{-1}$. The laser power used for preliminary studies varied from 50 mW to 500 mW and for all further studies, a laser power of 300 mW was used.
On 100 μm thick slices (RxL section) of the wood specimens, Scanning Electron microscopy (SEM, JEOL 5500 LV, Joel) was used to examine the hydrothermal deposits on the surface and on fractured cross-sections. All samples were coated with a thin film of gold (Sputter Coater SCD 005, Baltec). The specimens were scanned in a high vacuum and an accelerating voltage of 20 kV was used. Quantitative analysis and the concentration profile of titanium in cross-sections for the C0, C1 and C4 samples was performed by Energy Dispersive X-ray spectroscopy (EDX, Oxford Instruments) using INCA software. The real acquisition time for EDX quantitative analyses was approximately 100 s, while for line analyses it was between 400 and 600 s. EDX quantitative analyses were done considering all elements analysis; they were normalised totals. EDX line analyses of Ti were performed for a radial-section (RxL) of the wooden blocks cut from the treated bulk wood (25 mm (radial) × 25 mm (tangential) × 30 mm (longitudinal)) a few mm from the original surface exposed to TiCl₄ solution.

The sessile drop water contact angles (WCA) of *Picea Abies* wood surfaces were measured with a Theta” TITA” optical tensiometer (Attension, Biolin Scientific, Finland).

The colour changes of samples were examined by colour measurements in a CIELab system on an SP62 spectrophotometer (X-Rite GmbH – OPTRONIK™). An average of three colour measurements was calculated for each sample.

\[ L^* – \text{lightness of the colour,} \]
\[ a^* – \text{position of the colour on the red/magenta – green axis,} \]
\[ b^* – \text{position of the colour on the yellow – blue axis.} \]

The total colour difference \( \Delta E^* \) in the CIELab system was calculated by the equation (Eq. 1):

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

\( \Delta E^* \) – total colour difference between the untreated and treated samples,
\( \Delta L^* \) – lightness difference between the untreated and treated samples,
\( \Delta a^* \) – \( a^* \) difference between the untreated and treated samples,
\( \Delta b^* \) – \( b^* \) difference between the untreated and treated samples.

3. Results and discussion
3.1. XRD analysis of TiO₂ powders

From the reaction vessels in which the C0, C1 and C4 samples (Table I) were prepared, the corresponding powders (C0P, C1P, C4P, for short) were collected, washed with water, dried and analysed by XRD. The results of XRD analysis confirmed the expectation that the C0P, C1P and C4P powders consisted entirely of the rutile phase, without any traces of brookite (Fig. 1). Brookite and rutile can form in a certain range of TiCl₄/HCl concentrations [40] or, when the concentration of TiCl₄ precursor in the initial aqueous solution is below a particular value, anatase probably appears instead. The corresponding TiO₂ powders were poorly crystalline. The crystallite size estimated from the various (hkl) peaks (A(101), A(004), A(200) and A(105)) gave nanocrystals with a size of 30-90 nm, forming larger aggregates with a size up to 1-2 μm, as shown from SEM measurements (see below). Examination of the XRD spectra showed that the powders were composed of the rutile phase (JCPDS-ICDD, 1997, File No. 01-087-0710) [68].

![XRD spectra of as-prepared C0P (a), C1P (b) and C4P (c) powders collected from the reaction vessel.](image)

3.2. Optical and SEM analyses

3.2.1. Colour changes from CIELab measurements
Observation of hydrothermally treated wood samples (RxL section) by the naked eye revealed that A and B sets of samples (Table I) looked darker, while the samples from series B and C were of lighter colours, indicating deposited TiO$_2$ particles. This meant that the hydrothermal conditions for processing of samples from sets A and B (Table I) were too mild and times of treatment too short that the TiO$_2$ particles can grow. Instead, the corresponding samples were merely impregnated with titania precursor arising the questions to identify the nature of Ti-O…wood interactions (see below).

As a more objective way of assessing the change of colour ($\Delta E$) that inevitably appeared due to the hydrothermal treatment, and to differentiate between the contributions from the light scattering expressed by $\Delta L^*$ and the colour changes described by $\Delta a^*$ and $\Delta b^*$ values, the change of colour ($\Delta E^*$) values were obtained from the equation (Eq. 1).

The results of the colour measurements were easy to interpret [11, 69]. Hydrothermal treatment of sample A (Fig. 2), selected as a typical example from sets A and B (Table I), became darker and gained a reddish hue, which could be inferred from the decrease of $\Delta L^*$ (-13.4) and increase of $\Delta a^*$ (+3.0). As expected, the changes increased with the time of the hydrothermal treatment, reaching maximum values after 1 h. To conclude, the processing conditions were too mild for growing the particles but solely led to the impregnation of wood.

![Fig. 2. Changes of colour of samples treated for various times under reaction conditions A1 (25 °C, TiCl$_4$ solution mixed with the 0.01 mol/l HCl).](image)
Sample C3 (Table I) served as an example of wood treated at higher temperatures (75 °C) in TiCl₄ solutions with an intermediate amount of HCl (0.5 mol/l). The wood surface reflected slightly more light (ΔL* decreased to -11.1), the reddish colour was lost (Δa* became negative, -4.0) and the blue colour became more expressed (Δb* decreased to -18.7) (Fig. 3). The C0 sample (Fig. 4) was fairly similar, except that the wood became less blue (Δb* became -8.9) and the light scattered more (ΔL* became -2.2). The strongest effect of the hydrothermal treatment was noted for sample C4, which showed the strongest scattering (ΔL* = -10.4) and the bluish colour further increased, i.e., Δb* = -9.2 (Fig. 5). To conclude, deposition of TiO₂ strongly depended on temperature and no appreciable amount of particles formed unless the temperature reached ~75 °C, as noted for the samples from set A (Fig. 3). The time of hydrothermal treatment was also important; saturation of the deposited TiO₂ was already achieved in most cases after 1 h but from more concentrated HCl solutions, saturated deposits were observed after ½ h of treatment.
3.2.2. SEM analyses

In order to correlate the observed CIE Lab values with actual amounts of TiO₂ formed on the wood surfaces as predicted [38-42], SEM analyses were done on samples B2 (Fig. 6), C0 (Fig. 7), C4 (Fig. 8) and C1 (Fig. 9). Examination of the SEM micrographs (Figs. 6-9) confirmed that there was no appreciable amount of TiO₂ formed on the A (not shown here) and B sets of samples, in contrast to samples from sets C and D (D not shown here), on which
the particles could easily be observed. This was expected, since it has not been possible to
obtain TiO$_2$ (rutile) particles from TiCl$_4$ aqueous solutions at ambient temperature in
relatively short period of time (1 or 2 days) [38, 61]. For comparison, SEM micrographs of
untreated *Picea Abies* wood were presented in *Supporting information I (Fig. S1).*

Fig. 6. SEM micrograph of sample B2.

Fig. 7. SEM micrographs of sample C0 at different magnifications.
A closer look at Figs. 7-9 revealed that the C0 and C4 samples exhibited very similar TiO₂ morphology, a similarly high coverage with particles of fairly similar size (~2-3 μm). In contrast, the surface of the C1 sample showed smaller TiO₂ particles (up to 1 μm, although they were fairly uniformly distributed on the surface of wood. This indicated that the efficiency of the deposition strongly depended on the deposition conditions. Namely, C0 coatings made without HCl belonged to the same class as C4 coatings that were made with the highest amount of added HCl, while the C1 samples, as well as the C2 and C3 samples (Table I) prepared, formed another class of TiO₂/wood coatings characterized by smaller TiO₂ grains [38-42].

The identification and concentration profiles of titanium across a few selected lines for the C0, C1 and C4 samples were further analysed by EDX. The line concentration profiles of Ti were determined for a radial-section (RxL) of the wooden block cut from the treated bulk
wood (25 mm (radial) × 25 mm (tangential) × 30 mm (longitudinal)) in order to obtain an RxL surface that had not been directly exposed to the TiCl₄ solution (Figs. 10A). The results of the EDX line analysis for titanium (Fig. 11) confirmed that the precursor solution penetrated into the wood body at least up to 200 μm in depth from the upper surface (i.e., cross-section of the RxT) and that the concentration profiles for the C0, C1 and C4 samples were different. As expected, C0 and C4 samples exhibited higher Ti concentrations up to 200 μm in depth compared to the C1 sample, which agreed with the conditions of the hydrothermal deposition, favouring titania deposition from the more concentrated and more acidic TiCl₄ solutions [38-42].

Fig. 10. SEM micrographs of a radial-section (RxL) of sample C0 at the surface (A) and at a depth of approximately 100 μm (B), sample C1 at the surface (C) and at a depth of approximately 100 μm (D) and sample C4 at the surface (E) and at a depth of approximately 100 μm (F) at different magnifications.
Fig. 11. Depth concentration profile for titanium obtained by EDX of the C0 (A), C1 (B) and C4 (C) samples.

The formation of TiO\textsubscript{2} particles was examined quantitatively up to a depth of 100 \( \mu \text{m} \) in steps of 25 \( \mu \text{m} \) by determining the atomic concentrations of Ti for the C0, C1 and C4 samples, starting at the upper part of the cross-section surface (\( d = 0 \ \mu \text{m} \)) (Fig. 12). Examination of the results shown in Fig. 12 revealed that the Ti concentrations for the C0, C1 and C4 samples dropped fast with depth but did not yet reach zero values at a depth of 100 \( \mu \text{m} \), as also conceived from the EDX line analysis (Fig. 11). As expected, the C0 and C4 samples showed higher Ti concentrations, agreeing with the SEM analysis (Fig. 7-9), which levelled at 100 \( \mu \text{m} \) (3.5 - 3.9 at.\%) with values of approximately 2 at.\% noted for the C1 samples.
To conclude, SEM and EDX analysis did not provide evidence that the TiO$_2$ particles were also deposited in the cell, indicating that complete soaking of the wood with titania typical for vacuum technique [27] and sonification of wood in titanium alkoxide solution [26] was not achieved. However, despite the fairly mild hydrothermal processing conditions, we expected that the TiO$_2$ particles were incorporated in the cell walls because the condensation process of TiCl$_4$ aqueous solutions is generally much slower than the condensation reactions of titanium alkoxides and titanium chelates [70] leaving plenty of time for penetration of precursor solution and in-depth impregnation of wood. Accordingly, IR and Raman spectra analyses were performed in order to establish the interactions of titania particles with the components of wood.

3.3. FT-IR ATR and Raman spectra examinations

3.3.1. FT-IR ATR and Raman spectra of TiO$_2$ powders

Hydrothermal treatment of TiCl$_4$ aqueous solutions in the presence or absence of wood inevitably leads to the formation of hydrated rutile particles with adsorbed water. In order to
understand from the FT-IR ATR spectra how the surface of particles was interconnected to the water system of wood, the IR ATR spectra of TiO$_2$ particles were studied first.

![FT-IR ATR spectra of C0P (a), C1P (b) and C4P (c) TiO$_2$ powders.](image)

Fig. 13. FT-IR ATR spectra of C0P (a), C1P (b) and C4P (c) TiO$_2$ powders.

FT-IR ATR spectra of TiO$_2$ powders, i.e., C0P, C1P and C4P samples collected in the reaction vessel after the hydrothermal treatment of the wood (see Table I), are shown in Fig. 13. The spectra of all three powders were similar, showing the expected broad and strong OH-group stretching modes at 3346 and 3200 cm$^{-1}$ (C0P), 3344 and 3200 cm$^{-1}$ (C1P) and 3344 and 3150 cm$^{-1}$ (C4P), respectively.

The FT-IR ATR spectra of rutile in the spectral region 3500-3100 cm$^{-1}$ have been reported by Bezrodna et al. and Li et al. [59, 71] showing the Ti-OH band at $\sim$3373 cm$^{-1}$, (i.e., the hydroxyl groups located at weak surface active sites to which physisorbed water molecules are bound by weak hydrogen bonds) and the second band at $\sim$3120 cm$^{-1}$ which is associated with water complexes that are strongly bound to the TiO$_2$ surface. The isolated surface OH-group modes at 3665-3725 cm$^{-1}$ [72, 73] could not be observed because the adsorbed water modes are too intense.

The presence of two strong bands in the spectral region 3500-3100 cm$^{-1}$ (Fig. 13) confirmed that the frequency of the OH stretching bands depended on the hydration of the TiO$_2$ surface which was important for the assessment of the interactions of titania crystals with OH bond system of wood [59]. For example, the frequencies and band intensities for the C0P and C1P
samples matched well with the rutile spectra reported by Bezrodna et al. [74], but the frequency of the band at 3150 cm\(^{-1}\) of sample C4P was found at lower frequencies than expected. In addition, the intensity of the latter band was also higher than the band at \(~3344\) cm\(^{-1}\) (Fig. 13). The observed red-frequency shift of the OH stretching band for the C4P sample we explained by protonation of sample C4P at low pH, which shifted the OH mode to 3100 cm\(^{-1}\), as reported by Connor et al. [75]. In the spectral region 1700-450 cm\(^{-1}\) (Fig. 13), deformational O-H-O modes of adsorbed water at 1624-1630 cm\(^{-1}\) and Ti-O and Ti-O-Ti lattice modes at 717 cm\(^{-1}\), 667 cm\(^{-1}\) and 496 cm\(^{-1}\) were noted. Because the corresponding bands could be ascribed to either anatase or rutile, measurements of the Raman spectra were taken (Fig. 14).

Raman spectra of C0P, C1P and C4P TiO\(_2\) powders (Fig. 14) (see Supporting information II) exhibited bands characteristic of the rutile type of TiO\(_2\) at \(~117\) cm\(^{-1}\) (broad), 237-247 cm\(^{-1}\) (weak), 438-447 cm\(^{-1}\) (s) and 602-607 cm\(^{-1}\) (s) [38, 76-78]. Bands typical of anatase at 143-157 (strong), 196, 369, 517 and 639 cm\(^{-1}\) [79] were not observed in the spectra, confirming that the hydrothermal treatment of TiCl\(_4\) aqueous solutions led to the formation of rutile and not anatase.

Finally, the weak bands at 1528, 1440 and 1350 cm\(^{-1}\) were attributed to the modes of adsorbed CO\(_3^{2-}\) and HCO\(_3^-\) species (Fig. 13) [80]. Assignment of these bands was important because they appeared in the same spectral region as the lignin-TiO\(_2\) coordinative bond vibrations [55, 56] and their clear distinction from the H-O-H deformaotional bands was obtained from subtraction spectra (see Supporting information II).
To conclude, the assignment of the modes clearly demonstrated that the processing conditions affected the type of hydroxyl groups on the surface of the TiO₂ powders which changed by the addition of various amounts of HCl in TiCl₄ aqueous solutions. Red-frequency shift of the OH stretching band [81] we used as an indicator for the strength of H-bonding established between the titania and water system of wood (see below) seeming to be stronger for the samples treated at more acidic conditions and at higher TiCl₄ concentrated solutions.

### 3.3.2. FT-IR ATR and Raman spectra of wood and TiO₂/wood samples – identification of rutile

From the analysis of the vibrational spectra of wood (see Supporting information III) and TiO₂/wood we aimed first to prove that the rutile particles formed on wood and secondly to identify the anchoring sites (lignin, hemicellulose, cellulose) of wood and the nature (covalent, coordinative) of titania particles/wood interactions. Subtractive FT-IR ATR and Raman spectra were used for this purpose as shown below.

The assessment of rutile particle layers that form on wood is relatively straightforward from FT-IR ATR and Raman spectra unless the titania layer is too thin (< 200-400 nm) and the bands of wood prevail. On the other hand, too thick titania layers tend to obscure the
vibrational bands stemming from the interfacial layer. In terms of the results obtained from SEM measurements (Fig. 6-9), we focused first on samples in class C (Table I), showing titania particles.

The corresponding TiO$_2$/wood coatings could be ranked into two categories, differing in the amount of deposited titania particles and their size: thicker C0/wood and C4/wood (C0W, C4W, for short) (Figs. 7, 8) and thinner C1, C2 and C3/wood samples (C1W, C2W and C3W) (Fig. 9). The latter group of samples showed smaller titania grains and the layer of particles was much thinner than for the former two samples. FT-IR ATR (Fig. 15) and Raman spectra (Fig. 16) fully supported this classification: the C0W and C4W showed in the FT-IR ATR spectra (Fig. 15 b and f) the strongest rutile bands (561, 515 cm$^{-1}$) compared to the thinner C1W, C2W and C3W samples confirming the predicted massive deposition of TiO$_2$ particles under high acidic conditions (i.e. CW4) [38] and high TiCl$_4$ precursor concentrations (i.e. C0W) [39]. Raman spectra (Fig. 16 b and f) were even more persuasive showing rutile bands (404, 639 cm$^{-1}$) with high intensity in the spectra of the C0W and C4W samples. The rutile bands were not observed in direct Raman spectra of C1W, C2W and C3W samples, which led us search of these bands in the corresponding subtractive spectra as shown below.

Fig. 15. FT-IR ATR spectra of *Picea Abies* hydrothermally treated at 75 °C in aqueous TiCl$_4$ solutions containing various amounts of HCl (in M): W/SDS (a), C0W (0 M) (b), C1W (0.01 M) (c), C2W (0.1 M) (d), C3W (0.5 M) (e), C4W (1 M HCl) (f) (H – hemicellulose, L – lignin, C – cellulose) (see Supporting information III).
Fig. 16. Raman spectra of *Picea Abies* hydrothermally treated at 75 °C (1 h) in aqueous TiCl₄ solutions containing various amounts of HCl (in M): W/SDS (a), C0W (0 M) (b), C1W (0.01 M) (c), C2W (0.1 M) (d), C3W (0.5 M) (e), C4W (1 M HCl) (f) (H – hemicellulose, L – lignin). For enlarged spectrum of W/SDS (a) see Supporting information III.

3.4. Subtraction FT-IR ATR and Raman spectra - interactions of TiO₂ with wood

In order to identify the anchoring sites (lignin, hemicellulose, cellulose) and the nature of Ti-O...wood interactions, the subtractive spectra were constructed and the vibrational bands of wood assigned as reported in literature (see Supporting information III). For easier interpretation of results, the vibrational bands in the FT-IR ATR and Raman spectra were grouped together and considered in regions I, II and III (Fig. 17 and Fig. 18). Region I (spectral region 1800-1450 cm⁻¹) holds the bands belonging to the C=O and C=C modes of hemicellulose and lignin and their interactions. Region II (spectral region 1200-900 cm⁻¹) contains the skeletal modes of cellulose (C-O-C glycosidic groups), while the Region III (spectral region 3500-2800 cm⁻¹) the OH stretching bands (FT-IR ATR) of cellulose and the -OCH₃ modes of lignin (Raman spectra).

For the assessment of interactions between TiO₂ particles and wood, the FT-IR ATR and Raman spectra of wood treated with surfactant (W/SDS) (see Supporting information III) was subtracted from the C0W, C1W, C2W, C3W and C4W spectra (Fig. 15) as shown in Fig. 24.
The FT-IR ATR spectra were normalized with respect to the O-C-O ring mode at 1158 cm\(^{-1}\) the intensity of which remained practically the same for all TiO\(_2\)/wood samples (C0W - C4W). By using the spectrum of wood/SDS as a reference, any changes, such as the possible extraction of hemicellulose [82], were avoided. The subtraction spectra represented the key information about the TiO\(_2\) particles/wood interfacial and interphase Ti-O….wood interactions.

Examination of the FT-IR ATR subtraction spectra (Fig. 17) clearly confirmed the presence of TiO\(_2\) for all samples conceived from the observed Ti-O lattice modes. As expected, the Ti-O lattice modes were much stronger than those noted in the corresponding direct spectra, in which the Ti-O lattice bands were mainly observed for the C0W and C4W samples (Fig. 15), but were difficult to see for the C1W, C2W and C3W samples. The results thus confirmed the deposition of TiO\(_2\) particles, corroborating results of SEM measurements showing that the thickness of the deposited TiO\(_2\) layers depended on the processing conditions, as mentioned above.

Raman spectra of the C0W and C4W samples (Fig. 18) revealed even more clearly strong bands of rutile lattice modes but the corresponding bands were weaker in the spectra of the C1W, C2W and C3W samples agreeing with the fact that the deposition of rutile on wood was more efficient for the C0W and C4W samples than for the other samples. No Raman and FT-IR ATR bands of TiO\(_2\) were observed in the spectra of samples A0-A4 and B0-B2 (Table I).

Fig. 17. FT-IR ATR spectra of W/SDS a) and subtraction spectra of: C0W - W/SDS b), C1W - W/SDS c), C2W - W/SDS d), C3W - W/SDS e), C4W - W/SDS f).
3.4.1. Region I

For the assessment of TiO₂-wood interactions, the bands at 1730, 1655, 1595 and 1507 cm⁻¹ in Region I (see Supporting information III, Fig. S3) were considered first (Fig. 17a). After the subtraction, a negative band at 1736 cm⁻¹ (Fig. 17 c-e) and positive bands at 1706, 1680 and 1635 cm⁻¹ were observed (Fig. 17 c-f). Taking into account the existing assignment of these bands [11, 38, 44, 45, 83-86], the loss of the band at 1735 cm⁻¹ meant that the unconjugated carbonyl moieties of hemicellulose (mainly xylan [82]) were spent for the formation of the new positive band at 1706 cm⁻¹, which we attributed to the crosslinking of the C=O groups of hemicellulose with titanium ions. The red-frequency shift of the C=O stretching band of hemicellulose at 1735 cm⁻¹ to 1706 cm⁻¹ was expected, due to the donation of electron density to the titanium coordination sphere, by which the carbonyls can lose a part of their “carbonyl character” [55, 56].

As expected, the subtraction spectra (C₄W - W/SDS) (Fig. 17 f) and (C₀W - W/SDS) (Fig. 17 b) of much thicker deposited titania layers were similar since they did not show the negative band at 1735 cm⁻¹ but were merely showing strong and unstructured band at ~1622-1628 cm⁻¹ typical for hydrated TiO₂ particles (Fig. 13). The vibrational bands characteristic for the interphase interactions were obscured by the too strong TiO₂ lattice modes stemming from the massive deposition of TiO₂.

The assignment of the positive bands at 1680 and 1635 cm⁻¹ was more problematic because the corresponding positive bands could be attributed to the red-frequency shifted bands of hemicellulose, or to the shifted C=C/C=O stretching mode of lignin at 1664 cm⁻¹ [83] or the H-O-H deformational band at 1624-1645 cm⁻¹ (Fig. 17).

Because the O-H-O deformational modes in Region I weakly scatter Raman light and lignin shows strong bands in Region I, the Raman subtraction spectra were constructed and examined (Fig. 18). The subtractive spectra revealed a distinctive negative band at 1658 cm⁻¹ [87] (C=O mode of coniferyl aldehyde of lignin mixed with C=C mode of coniferyl alcohol), which nearly coincided with the band found in a direct Raman spectra at 1660 cm⁻¹ (Fig. 16) and the positive bands at 1635, 1608 and 1595 cm⁻¹ which substituted strong band at 1600 cm⁻¹ attributed to lignin ring mode [58, 87]. The negative band suggested that the corresponding
lignin moieties were consumed, while the shifts of the positive bands indicated the establishment of bonds to titanium ions. The remaining lignin band at 1505-1515 cm\(^{-1}\) was not observed due to weak Raman scattering, even though the spectra were normalized to the skeletal band of cellulose at 1157 cm\(^{-1}\), as we did in our previous study of TiO\(_2\) finishes on cotton fibres [88].

![Figure 18](image)

Fig. 18. Subtraction of the Raman spectra in the spectral region 3500-2500 cm\(^{-1}\) (A) and spectral region 1900-75 cm\(^{-1}\) (B) of W/SDS a), C0W – W/SDS b), C1W – W/SDS c), C2W – W/SDS d), C3W – W/SDS e), C4W – W/SDS f).

3.4.2. Region II

FT-IR ATR spectra of Region II contained skeletal bands of cellulose [43-47, 49, 89] and hemicellulose [83, 86, 90], ascribed to the vibrations of the glucosidic ring (and pendant alcohol groups) and partially also of lignin (Fig. 17). We attributed strong negative bands observed in our spectra at 1027 and 981 cm\(^{-1}\) to the loss of the bands of the C-O alcohol groups attached to the glucosidic ring, which are common to cellulose and hemicellulose [43-47, 49, 89]. We reported a similar situation recently for the subtraction spectra of cotton subtracted from cotton coated with amorphous TiO\(_2\) layers made of Ti(iOPr)\(_4\) precursors in ethanol solutions [54]. However, the corresponding negative bands [88] were not as strong as the negative bands observed in the subtraction spectra of TiO\(_2\)/wood (Fig. 17), indicating that TiO\(_2\) made from hydrolysed titanium alkoxyde precursor is not bound to cotton [88] as
strongly as hydrothermally synthesized rutile on wood and that the interphase layer was rather thin. Nevertheless, the vibrational bands observed in Region II of the FT-IR ATR spectra fully supported the interactions of hemicellulose with rutile particles concluded from the negative bands noted in Region I (Fig. 17). In other words, the negative bands (Fig. 17) indicated the formation of the TiO₂/wood interface and the direct linking of the particles to the cell walls as we intended to conceive from SEM combined with EDX elemental analysis (Fig. 10 and Fig. 12).

Final confirmation that the TiO₂ was bound to a cellulose (or hemicellulose) skeleton was obtained from Region II of the Raman subtraction spectra (Fig. 18), which revealed a distinct negative band at 1095 cm⁻¹ close to the bands of xylan (1091 cm⁻¹) and glucomannan (1989 cm⁻¹) of hemicellulose, as stated by Agarwal [83]. This assignment ruled out the possibility that only lignin was involved in the interactions, since lignin exhibits relatively weak bands at 975 and 1033 cm⁻¹, i.e., quite apart from the observed negative band at 1095 cm⁻¹. An additional negative but less expressed band at 1171 cm⁻¹ supported the interactions of glucomannan of hemicellulose because the corresponding band in the spectra of glucomannan appeared at 1126 cm⁻¹, while for xylan and lignin the closest bands have been reported at 1128 and 1138 cm⁻¹ [83].

3.4.3. Region III

Because Region III contained OH stretching bands (Fig. 17), the bands in this region were crucial for understanding the anchoring and embedment of hydrated titania particles to either cellulose or hemicellulose. The association of water to cellulose and hemicellulose was reported by Olsson and Salmen [49] and the moisture uptake by Hofstetter et al. [48]. They revealed that the OH stretching band in the spectral region 3500-2900 cm⁻¹ is associated with bands attributed to strongly bound water at ~3200 cm⁻¹, i.e., bound directly by hydrogen bonds to the OH groups of the cellulose and hemicellulose, while the OH stretching band at ~3500-3600 cm⁻¹ is associated with water indirectly bonded to the OH groups via other water molecules.

Growth of titania particles inevitably leads to the consumption of water present in the wood, and to establishment interactions with embedded titania particles as we concluded from the
subtraction FT-IR ATR spectra in the spectral Region III (3500-3000 cm⁻¹) (Fig. 17). Subtraction spectra showed a decrease in the intensity of the OH stretching band of loosely bound water at 3370 cm⁻¹ and an increase of OH absorption at 3215-3086 cm⁻¹ ascribed to stronger bound water to cellulose and its shift to lower wavenumbers (see Supporting information III). For wood modified with tetrabutyl titanate (TBT) by ultrasonic assisted sol-gel method Wang et al. [26] attributed the red-frequency shift of the OH stretching band from 3380 to 3350 cm⁻¹ to the interactions of Ti-OH with OH groups of wood. For the FT-IR ATR spectra of wood impregnated with solution of ZnO nanoparticles Soltani et al. [82] reported the decrease of the intensity of the OH stretching band which they have correlated to the reduction of hygroscopicity of treated wood and its higher anti-swelling efficiency. The reduced hygroscopicity has been reported also by Wang et al. [66] for wood treated with tetrabutyl titanate (105 °C), but the reduced hygroscopicity was not correlated with IR spectra analysis. The corresponding studies are out of the scope of this work.

To conclude, the process of TiO₂ formation on wood, hydrothermally treated in TiCl₄/HCl aqueous solutions, could be roughly visualized as follows. At first, hydrolysis of TiCl₄ leads to the formation of hydroxochloro complexes [TiOH]ₐClₐ(OH₂)ₐ[₄₋ₐ]⁺, in which the number of different ligands depends on the acidity and the concentration of Cl⁻ in the solution [39]. The fact that the H₂O of the precursor or H₂O in wood could act as ligands for the latter, thus assuring plenty of interactive sites for the precursor, is important for this study. During the growth of titania particles, they could easily be attached not only on the wood surface but could also grow inside the wood. At milder conditions (samples A and B, Table I) when the crystallites did not grow at all, the titanium hydroxochloro complex ions also formed coordinative bonds to the functional groups of lignin and hemicellulose [55, 56] what we conceived from the Raman subtraction spectra of the (A0 – W/SDS) and (A3 – W/SDS) samples (Fig. 19) showing nearly identical spectral features as noted for samples C (Table I) (Fig. 18). Quite apparent was the loss of the –OCH₃ band of lignin at 3970 cm⁻¹ observed also for the (C2W – W/SDS) and (C3W – W/SDS) subtraction spectra shown on Fig. 18 d and e. This we expected, because the hydrothermal treatment always started with soaking of wood and the impregnation with titanium hydroxochloro complexes accompanied by the interactions with lignin and hemicellulose and formation of some form of complexes. Because the formation of complexes with wood continued as long as precursors did not condense and the particles formed, better impregnation of wood with aqueous titanium salts and titanium
chelates [70] can be obtained compared to titanium alkoxides which condensation is much faster. Obviously, the depth of impregnation achieved at relatively mild processing conditions used here, could not compete to much better impregnation obtained by the vacuum technique (100-300 Pa and 2 h) and with titanium alkoxide precursor solutions, as reported by Hübert et al. [27] and by sonification of wood in titanium alkoxide solution, as reported by Wang et al. [26]. It should be noted that the hydrothermal treatment developed in the frame of this study, enabled the impregnation of wood and at the same time provided suitable layers of particles, which formed hierarchical structure on the surface of wood needed to achieve repellence of water as described below.

![Raman spectra subtraction](image.png)

Fig. 19. Subtraction of the Raman spectra: W/SDS a), A0W – W/SDS b) and A3W – W/SDS c).
3.5. Water repellent properties of TiO$_2$/wood composites

Despite the evident interactions of complex titanium hydroxochloro complexes with the OH wood system the crosslinking of hemicellulose by titanium ions and complexing of lignin the H-bond system of water in wood was not affected in such an extent to impart wood hydrophobicity (WCA > 90°) which remained hydrophilic (WCA ~10-15°).

However, strong hydrophobicity was noted for wood treated first with SDS and then hydrothermally treated with TiCl$_4$ solutions. The static WCA values of the TiO$_2$/wood/SDS) surfaces increased to 150-155° matching WCA values for TiO$_2$ treated wood with deposited SDS [29-34]. High WCA values we attributed to the hierarchical structure of the deposited TiO$_2$ particles (Fig. 8C) as reported by Zheng et al. [34] and to the of sulphate groups of the dodecylsulphate anions strongly adsorbed on the surface of TiO$_2$ particles. It seemed that during the hydrothermal treatment the hydrophobic part of the dodecylsulphate anions were interacting with complex titania precursor and became adsorbed on the surface of rutile particles. More work is planned in future to understand this effect.
4. Conclusions

We showed in this study that rutile particles can be successfully deposited on *Picea Abies* wood by hydrothermal processing in TiCl$_4$/HCl aqueous solutions at 75 °C and relatively short times (up to 1h). The efficacy of the deposition process was ascribed to the formation of titanium hydroxochloro complexes in the aqueous solutions and their ability to condense and grow within the water system of wood. The hydrothermal treatment exhibited dual functions; impregnated the wood and covered the porous inner and outer surface of wood with rutile particles. The results showed that the amount of deposited particles and the thickness of the particle layers on the wood surface and the surface of cell walls and lumens were higher when more concentrated TiCl$_4$ solutions were used, despite no HCl being added.

FT-IR ATR and Raman subtraction spectra showed that the hydrothermally treated wood exhibited vibrational bands which we attributed to the Ti-O…wood interphase interactions confirming the anchoring sites of titanium ions to hemicellulose, cellulose and lignin. The existence of the interphase was identified for all wood/TiO$_2$ samples; those, with expressed titania particles (SEM) as well as for those samples where due to the too mild processing conditions, the particles’ growth was not noted in SEM but the impregnation was confirmed from the CIELab measurements and subtraction spectra analysis. The combined action of soaking/impregnation of wood with the particle formation on the surface of wood and lumens is important for improving dimensional stability of wood while the formed particles generated the necessary hierarchical structure needed to make surface of wood superhydrophobic. One of the intriguing features which remained to be studied and deserved further investigations was to explain the role of SDS surfactant for achieving water contact angles of our samples above 150°.

To conclude, aqueous TiCl$_4$/HCl solutions were shown to be a versatile and relatively simple system for the deposition of rutile particles, providing controlled growth of particles that adhered very well to the surface due to the abundance of anchoring sites of hemicellulose and lignin and at the same time impregnated wood. More work is planned in the future in order to check the abrasion resistance of the deposited rutile coatings and the degradation and dimensional stability of wood hydrothermally treated with TiCl$_4$ aqueous solutions.
Acknowledgments

This work was supported by the Slovenian Research Agency (Programs P4-0015 and P2-0213). The authors would like to thank Prof. Dr. Barbara Simončič for helpful discussions. M. Mihelčič and U. Novak did this work within the framework of Ph.D. studies at Jožef Stefan International Postgraduate School.

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