

# Vibrational spectroscopy as a tool to monitor the production process of modified wood

Lukas K. Bittner<sup>1</sup>, Christian Lux<sup>2</sup>, Hans Pulker<sup>2</sup> and Christian W. Huck<sup>1\*</sup>

<sup>1</sup>Institute of Analytical Chemistry and Radiochemistry, Leopold-Franzens University, 6020 Innsbruck, Austria

<sup>2</sup>Institute of Ion Physics and Applied Physics, Leopold-Franzens University, 6020 Innsbruck, Austria

\*Corresponding author: christian.w.huck@uibk.ac.at

## Introduction

There is a demand for environment-friendly and cheap ways to treat wood to improve its properties in terms of fire resistance, hardness, weather- and UV-resistance. Therefore, we developed a system to modify the surface of wood based on silica treatment in combination with microwave-assisted drying procedures. The freshly cut wood was firstly dried in a microwave oven before the infiltration process started. After hardening, quality assessments of the final product were performed according to international standards.

In recent years, several silicon-based compounds have been used for wood modification. The earth's crust consists of approximately 25% silicon, which makes it the second most common element on our planet after oxygen. In Nature, it is found as salts of silicic acid, mainly consisting of polymeric  $\text{SiO}_2$  ( $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$  or  $\text{Si}(\text{OH})_4$ ). Silicates as well as most other silicon compounds are generally classified as non-toxic; however, dusts with particles smaller than 5  $\mu\text{m}$  can cause pneumoconiosis.<sup>1</sup>

In a natural process which takes place during the burial of wood over millions of years, the infiltration of silicic acid into the wood tissue forms silicified wood. Polycondensation leads to a silica gel which further reacts to form quartz and opal.<sup>2</sup> Several authors have tried to mimic silicified wood to produce porous ceramics.<sup>3-5</sup> All impregnation techniques showed strong negative moisture-excluding coefficients (MEE) and considerable amounts of the infiltrated materials were washed out, leading to unsatisfactory durability of the products.<sup>4, 5</sup> Therefore, it was of interest to examine if there is evidence of a covalent bond between infiltrated species and wood components in our experiments. Various studies have been performed to deploy NIR spectroscopy for the qualitative and quantitative analysis of wood<sup>6-8</sup>.

During the whole production process of modified wood, vibrational spectroscopic methods such as near infrared (NIR) and mid-infrared (MIR), used both as single point and hyperspectral imaging, play a key role in monitoring the production process and the final product.

## Materials and Methods

### Samples

For this study, alpine spruce and beech samples were used. All samples were selected to be as far as possible free from defects, knots and resin pockets. By default, sample dimensions were 500 x 48 x 76 mm<sup>3</sup>. For hyperspectral imaging, smaller samples (25 x 25 x 25 mm<sup>3</sup>) were chosen while for mechanical tests, sample sizes were selected according to the respective international standards.

### Microwave assisted drying procedure

All experiments were performed using a Linn High Therm MKST-9 microwave oven (Linn High Therm GmbH, Eschenfelden, Germany) equipped with nine magnetrons. The furnace chamber had a length of three metres and an inner diameter of 60 cm. Sample surface temperature was monitored using a pyrometer and the core temperature with a thermometer equipped with a fibre-optic sensor. A vacuum pump (EvoDry 50; Pfeiffer Vacuum, Asslar, Germany) reduced the pressure of the whole microwave chamber down to approximately 200 mbar.

Microwaves are electromagnetic waves similar to radio or infrared waves covering a wavelength range from 1 m to 0.1 cm. They follow the same physical laws and can, after interaction with matter, be reflected, absorbed or transmitted. Metals, for example, reflect microwaves and can therefore not be heated up; this is also the case for microwave transparent materials such as Teflon, quartz glass or polypropylene. Microwave absorbing materials such as water show increased temperatures with longer exposure due to the interaction with microwave radiation. The following formula describes the microwave heating:

$$P = 2 \cdot \pi \cdot f \cdot \epsilon_0 \cdot \epsilon'' \cdot E^2 \cdot V \quad (1)$$

Reference paper as:

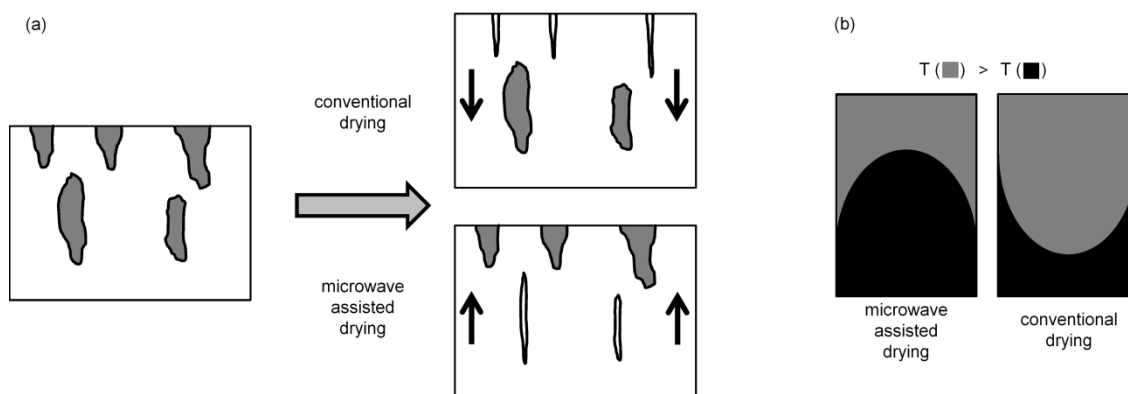
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where  $P$  = power absorbed by the material;  $f$  = frequency;  $\epsilon_0$  = dielectric constant;  $\epsilon''$  = imaginary part of dielectric constant;  $E$  = electric field strength and  $V$  = volume. In this equation, the correlation between microwave heating and microwave frequency, material (dielectric coefficient of the material), microwave power as well as the shape of the material (volume) is demonstrated. The following equation explains the factors on which the penetration depth of microwaves depends:

$$PD = \frac{\lambda_0}{2\pi} \cdot \frac{\sqrt{\epsilon'}}{\epsilon''} \quad (2)$$

where  $PD$  = penetration depth of the microwaves;  $\lambda_0$  = wavelength (vacuum);  $\epsilon'$  = real part of dielectric constant; and  $\epsilon''$  = imaginary part of dielectric constant. The penetration depth is defined as the depth at which the initial field strength is reduced to  $1/e$  (about 37%); this means that heating also takes place below the penetration depth but with much lower energy.<sup>9</sup>

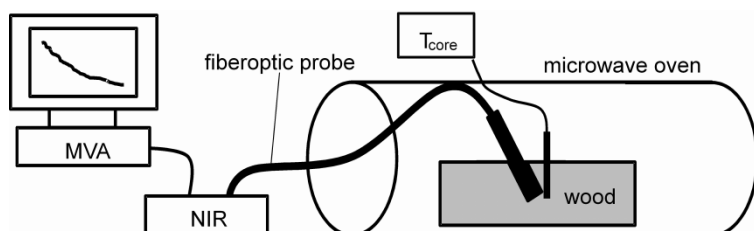
Full penetration results in simultaneous inner and outer heating of the material and, as the surface of the sample radiates heat to the ambient environment, the theoretically homogenous heated material is cooled down on the surface.<sup>6</sup> This leads to an inverse temperature profile comparing to conventional drying processes in an oven. This is a big advantage as the drying process works faster and is more energy efficient. When drying wood in a conventional way, the outer layer dries out first and the pores close; it therefore requires a lot of energy to get the core of the sample dry. Applying microwaves, the inner pores dry out first and it takes considerably less energy to dry the surface. Figure 1 compares conventional drying with microwave-assisted drying of wood and shows the temperature profiles of the two techniques.



**Figure 1.** Conventional vs. microwave drying: schematic of a drying process of (a) wood and (b) temperature profile.

### Near infrared spectroscopy

NIR spectra were recorded using a scanning polarisation interferometer Fourier-transform NIR spectrometer (FT-NIR) (Büchi, Flawil, Switzerland) with a tungsten-halogen lamp and a temperature controlled lead sulphide detector (30°C). The spectral resolution was  $12 \text{ cm}^{-1}$ , the absolute wavelength accuracy  $\pm 2 \text{ cm}^{-1}$  and the relative reproducibility  $0.5 \text{ cm}^{-1}$  between 4000 and  $10\,000 \text{ cm}^{-1}$  (2500–1000 nm). For recording the reflection spectra, a Büchi light fibre probe 93013 was utilised. One spectrum represents the average of 15 scans. Chemometric software NIRCal 4.21 (Büchi) was used for recording the spectra and The Unscrambler X (Camo, Oslo, Norway) software was used for multivariate data analysis. For the development of partial least squares (PLS) regression models, spectra were divided into a calibration set (c-Set, 67 spectra) and a validation set (v-Set, 33 spectra) both consisting of independent samples. The light fibre was mounted along the wall of the microwave oven for as great a distance as possible before being put into a clean bore hole in the sample to reach the core. There was reduced pressure applied (approximately 300 mbar) and the core temperature was regulated at around 65°C. To acquire the respective reference values, the drying process was stopped every 30 min for the first 5 h and then, due to the slower decrease in moisture content, every 60 min. Several runs were executed. Immediate gravimetric analysis of the moisture content was performed. Figure 2 shows the schematic of the coupling of the NIR instrument to the microwave.



**Figure 2.** NIR instrument coupled to an industrial microwave oven.

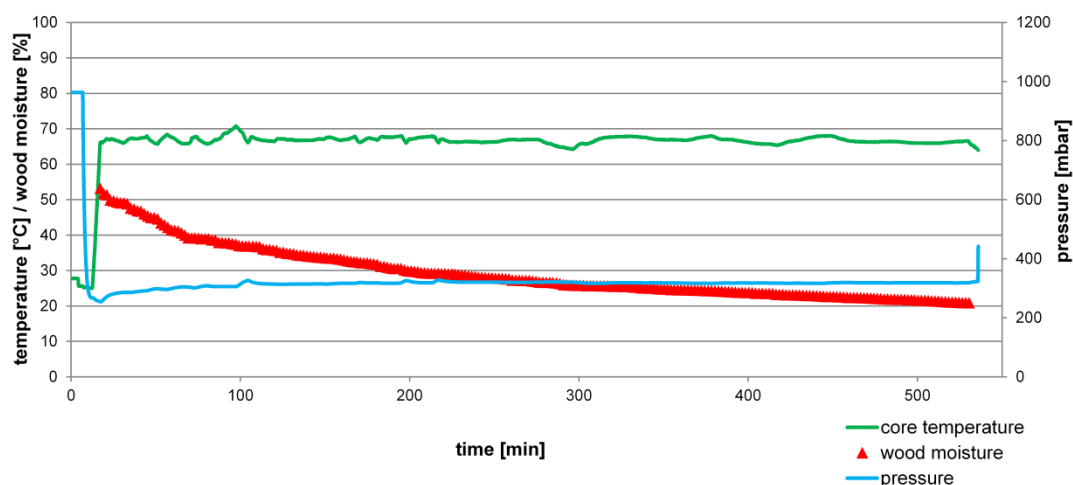
## Hyperspectral imaging

FTIR imaging data were recorded at atmospheric conditions using a Perkin Elmer Spectrum 400 FTIR spectrometer (PerkinElmer, Waltham, MA, USA) coupled with a Perkin Elmer Spotlight 400 microscope, equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) 16-element linear array detector. Samples were measured in NIR and MIR mode with a nominal lateral resolution of  $50\ \mu\text{m} \times 50\ \mu\text{m}$  per pixel for each spot. Reflectance spectra were recorded with 32 co-added scans at  $1.0\ \text{cm.s}^{-1}$  step size. The background spectrum was recorded using a gold-coated slide.

## Results and Discussion

### Microwave assisted pre-drying

To ensure an objective evaluation of the drying process, it is a prerequisite to eliminate defects caused by inherent wood properties such as mechanical properties, density, shrinkage coefficient, fibre orientation, spiral grain, interlocked grain, reaction wood, juvenile wood, knots, growth stresses, ring shake, frost checks or resin pockets. At higher temperatures, changes in wood components occur. Approximate temperatures where changes can be observed are  $130^\circ\text{C}$  for cellulose,  $75^\circ\text{C}$  for hemicellulose,  $100^\circ\text{C}$  for lignin and  $40^\circ\text{C}$  for extractives such as etheric oils<sup>10</sup>. Addressing these facts we performed the drying process at reduced pressure (200 mbar) and at temperatures below  $70^\circ\text{C}$ . Another prerequisite is to have a homogenous microwave field within the oven; this was assured by evaluating the field using thermosensitive paper and liquid crystal films. A PLS calibration model for monitoring the moisture content of alpine spruce in-line during the drying process was established using log  $1/x$  and multiplicative scatter correction (MSC) pretreated spectra. Figure 3 displays an example drying process using NIR for in-line prediction of the wood moisture.



**Figure 3.** Example microwave-assisted drying process of alpine spruce

For quality assessment of the dried samples, the following three European Drying Group (EDG) standard<sup>11</sup> quality classes were used: S (standard), Q (quality dried) and E (exclusive). Factors influencing the classification are variation of the mean moisture content (MC), variation in the differences between  $\text{MC}_{1/2}$  (in the core) and  $\text{MC}_{1/6}$  (near the surface) and deformations caused by case-hardening. Generally, microwave dried samples achieved higher quality classes than conventionally dried ones. If a very high amount of microwave radiation is absorbed, colour changes in the core region occur. NIR spectroscopy was deployed for detection of this phenomenon. In accordance with Schwanninger's work,<sup>12</sup> we observed higher absorptions at wavenumbers above approximately  $7100\ \text{cm}^{-1}$  due to these changes. The band ratio (7640–

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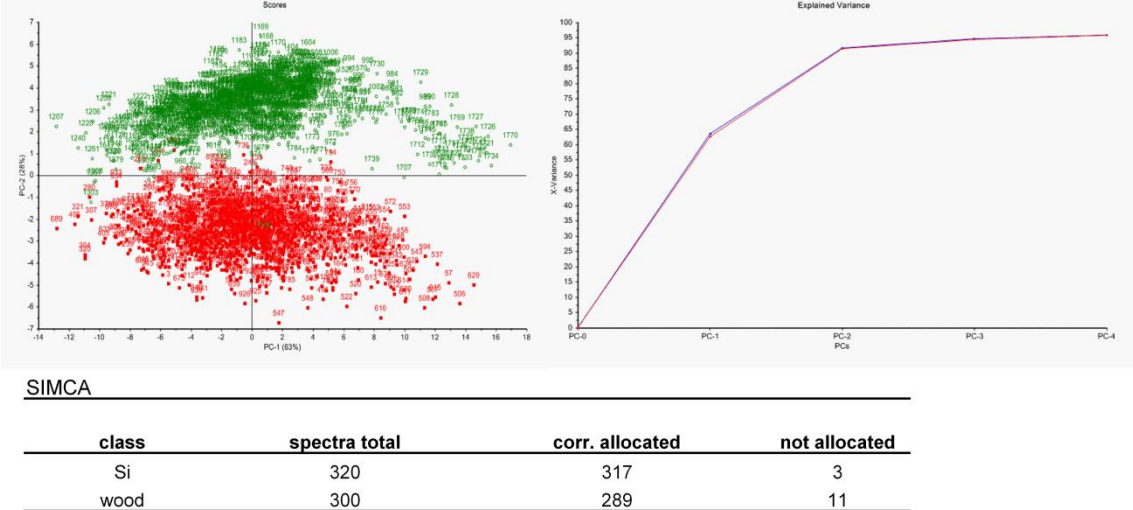
7096 cm<sup>-1</sup>) / (5312–4520 cm<sup>-1</sup>) of log 1/x and standard normal variate (SNV) pretreated spectra was used as a quality parameter addressing the above observation.

### Silica infiltration

For infiltration solutions of lithium and potassium, silicates were used. Typically, water glass is composed of 2–4 mol silicate and 1 mol alkali oxide; due to hydrolysis, water glasses contain mainly hydrogen salts like M<sub>3</sub>HSiO<sub>4</sub>, M<sub>2</sub>H<sub>2</sub>SiO<sub>4</sub> and MH<sub>3</sub>SiO<sub>4</sub> with M being K or Li<sup>13</sup>. The samples were placed in a bath of water glass solution and afterwards microwave dried. Varying concentration, water glasses, ligneous crops and bathing times in the solution were evaluated. After infiltration, the samples were again microwave dried and stored under standardised conditions to reach the equilibrium moisture content. It was observed that the microwave pre-dried samples generally absorbed higher amounts of silicate than the conventionally dried. The following tests were performed on the infiltrated samples according to German industry standards (DIN): Brinell hardness, elasticity modulus, compression strength parallel to the grain, bending strength and shearing strength parallel to the grain. Recent results have shown that infiltrated samples tend generally to perform better than non-infiltrated ones on the tests detailed. Additionally, outdoor weathering, artificial weathering and fire tests are currently being carried out.

MIR imaging spectroscopy was used to show indications of a binding between the silicate and wood components. We noted that the ν(C=O) at 1735 cm<sup>-1</sup> disappeared in the silica infiltrated parts. A possible explanation therefore could be a reaction of a nucleophile O of the water glass with a highly electrophilic carbonyl C in lignin.

MIR imaging was also used to study the penetration depth of the silica. A PCA model was established and, as can be seen in Figure 4, spectra from silica-infiltrated regions and from untreated wood were classified using soft independent modelling of class analogy (SIMCA). Out of 320 silica-infiltrated spectra, 317 were correctly allocated while 289 out of 300 spectra from untreated samples were classified correctly.



**Figure 4.** Classification of infiltrated (Si) and untreated (wood) samples to evaluate the penetration depth using hyperspectral imaging.

### Modification/outlook

Currently, research on modification of silica-infiltrated wood with fullerenes is going on. The reaction mechanism is performed according to Vallant et al.<sup>14</sup> As NIR spectroscopy is highly suitable for the analysis of carbon nano-materials,<sup>15</sup> we expect it to be a useful analytical tool for this question.

### Conclusion

This study demonstrates the applicability of vibrational spectroscopy as a tool for optimisation and monitoring of the microwave-assisted drying process and the silicate-based surface modification of spruce and shows how this technique could be used as a process analytical technology (PAT) tool in the timber industry.

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