Title: Detection and distribution analysis of organosilicon compounds in wood by means of SEM-EDX and micro-CT

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Abstract
This article explores the potential of scanning electron microscopy with an energy dispersive X-ray spectrometer (SEM-EDX) in combination with a new non-destructive 3D visualization technique, X-ray micro-computed tomography (micro-CT), as detection methods for siloxanes/silanes mixtures applied as wood preservatives. In order to have a higher contrast, bromine functional silane was added to the mixture. Scots pine and beech samples were dipped or impregnated with the mixture and subsequently scanned. Both silicon and bromine were easily detectable with both techniques. Dipped siloxanes/silanes covered the cell walls partly in beech, and the lumen partly or completely in Scots pine. Impregnated siloxanes/silanes could be found in the cell walls of both wood species. Out of these results can be concluded that, under the circumstances as described in the article, impregnation with a siloxane is necessary to have cell wall penetration.

The combination of SEM-EDX and micro-CT can offer important information concerning the localization of certain products inside wood. While micro-CT can
monitor changes in 3D, SEM-EDX will give detailed 2D information. Both techniques are complementary and provide important extra information.

**Keywords:** scanning, siloxane, silane, wood modification, microscopy, SEM, micro-CT

**Introduction**

Wood is since long an important building material. The wide variety in appearance, strength properties and the possibility of different dimensions are some of the reasons why wood is still very attractive for this purpose. Besides indoor use of wood, nowadays it is also frequently used as façade panelling or as garden furniture. These outdoor applications require, depending on the wood species, special wood protection. Older wood preservatives often use heavy metals such as copper, chromium and arsenic or are containing polyaromatic hydrocarbons like in creosotes [1, 2, 3, 4]. Health care and environmental considerations make it no longer acceptable to use these preservatives which are based on broad spectrum biocides [1, 2, 3, 4]. New wood preservatives face a lot of challenges: they should be easy applicable, guarantee a long lifetime to the wood and at the same time be easily broken down when released into nature.

Chemical wood modification is a compromising approach, not just to enhance the durability against fungi and insects, but also to improve further material properties such as dimensional stability, strength, moisture sorption, flammability, UV-stability and weathering performance [2, 4, 5, 6, 7, 8].
A group of chemicals which are also suitable for this are the polymers. The idea is that they penetrate the cell wall as monomers and polymerise in situ. Since the cell wall is swollen with polymers, the dimensional stability is enhanced. When on top of that the polymer is not hydrophilic, the rate and ultimate uptake of moisture are both reduced. Finally the ingress of fungal metabolites capable of degrading the wood cell wall polymeric components is reduced or prevented, since the impregnated polymer is able to block the cell wall microporous network through which these agents diffuse [9].

Silicone compounds and more specific silanes and/or siloxanes are already used in many researches as a possible group of suited chemicals [1, 2, 5, 10, 11]. They are frequently used as a water repellent product for natural building stones [12]. Since the localization of these products inside wood is essential in the research of wood protection a first step in the evaluation of these products is to try to localize the silanes and/or siloxanes in treated wood. The object of this study is to evaluate the potential of scanning electron microscopy with an energy dispersive X-ray spectrometer (SEM-EDX) in combination with a new non-destructive 3D visualization technique, X-ray micro-computed tomography (micro-CT), as detection methods for silanes/siloxanes mixtures applied in different types of wood.

X-ray micro-CT, a powerful tool in material research, was already successfully applied within the scope of wood anatomical research by Steppe et al. [13]. Cnudde et al. [14] illustrated the possibility of the visualization of silane-based products inside stone material by means of micro-CT. Since the visualization of the products inside wood is based on the same principle as for the visualization of products inside stone material,
the micro-CT technique was selected for this research. The big advantage of this non-destructive technique, which visualizes the internal microstructure of the scanned samples in 3D, is the fact that it provides the possibility to scan the samples before and after treatment with silanes/siloxanes mixtures. After scanning with micro-CT, the same specimen can be analysed by SEM-EDX to obtain a complete distribution mapping of silicone compounds in wood and to make a firm link between both methods.

**Materials and methods**

**Materials**

Because of the important differences in anatomical structure between softwood and hardwood species, one species of both groups was chosen. Scots pine sapwood and beech, both reference wood species in many European Standards dealing with wood preservation, were used. For every treatment technique one specimen was evaluated.

The siloxane used is a hydroxyterminated polydimethylsiloxane from the company Dow Corning. It is a water dilutable emulsion with an organosilicon content of 60%. This commercial product is also used as a mould release agent and applied in low concentrations by spraying or dipping. In this research it was applied both by dipping and impregnating at a concentration as low as 5% silicone content.

To obtain a high contrast with micro-CT between wood and siloxane, mixing the siloxane was chosen as a possibility to increase this contrast. Based on the previous study of Cnudde et al. [12] on the doping of siloxane mixtures, 3-bromopropyltrimethoxysilane (Figure 1) was selected as possible mixing component for the visualization of the silanes inside the wood material. The presence of the bromine
atom on the 3-bromopropyltrimethoxysilane causes a higher attenuation of X-rays and the wood, resulting in a better contrast on the micro-CT images.

**Treatments**

In a first attempt to localise silica with SEM-EDX a beech and Scots pine sapwood sample with dimensions 40×40×5 mm³ (T×R×L) were impregnated with a 5% concentration of the hydroxyterminated polydimethylsiloxane. Afterwards the sample was divided into 40 small cubes measuring 5×5.6×5 mm³ (T×R×L).

In order to have a bigger contrast between wood and siloxane, samples were treated with an aqueous mixture of 5% siloxane and 20% 3-bromopropyltrimethoxysilane. A first treatment was an immersion of a part of a sample of both wood species with dimensions 30×5×5 mm³ (T×R×L) in the solution. The growth ring orientation was approximately 45°. The lowest 10 mm of the samples were dipped for 1 minute in the aqueous treating solution. Afterwards they were dried upright under atmospheric conditions. The second treatment was a vacuum impregnation in the aqueous treating solution. Specimens’ sizes were 6×6×13 mm (T×R×L) with the growth ring orientation 45°.

**SEM**

A scanning electron microscope (FEI Company Quanta 200F) was used to examine surface details of the scanned wood. By means of an energy dispersive spectrometer (EDAX), qualitative and quantitative compositional analysis could be obtained and precise elemental composition of materials with high spatial resolution was
accomplished. Secondary electron imaging was used to analyse the morphology and the surface topography of the samples, while backscattered electron imaging visualized compositional contrast in detail. SEM was already previously used to scan silica in rattan species [15] and solid wood [16].

To avoid electron loading of the samples, the surface was sputtered with a gold layer. All images were made under high vacuum at a voltage of 20.0 kV with a spot size of 4.0, a dwell of 3000 µs and a working distance of 10 mm.

In order to obtain a surface as smooth as possible, the samples were first scanned with the micro-CT to be sure the borders were included. They were then surface cut with a microtome and subsequently scanned with the SEM-EDX.

**Micro-CT**

An X-ray desktop micro-tomograph Skyscan 1072 was used to scan the small wood cubes of 30×5×5 mm³ (T×R×L). The X-ray source, a Hamamatsu micro-focus tube, has a focal spot size of 10 µm, which limits the spatial resolution of the reconstructed slices to 10 µm in the X, Y and Z directions. The samples were scanned at a voltage of 130 kV, a current at 76 µA and an exposure time of 2.3 ms. A rotation step size of 0.45 °, in combination of random movement and multiple-frame averaging was used to minimise the Poisson noise in the images. The magnification was chosen in such a way that the pixel size reached 10.10 µm. Since this magnification allows visualisation of volumes up to 12 mm long, the dipped samples were divided into three parts: a lower part which was completely dipped in the solution (0-9 mm), a middle part where the bottom was dipped and the top was not (9-18 mm) and an upper part of untreated wood (18-30 mm). The impregnated samples were small enough to be scanned as a whole.
The images were reconstructed with Octopus, which is a server/client tomography reconstruction package for parallel and cone beam geometry [17].

**Results**

**Impregnation with siloxane**

In order to have an idea of the penetration depth of the siloxane into the wood, a corner and central block were scanned with SEM-EDX at all sides. The SEM images give a clear view of the anatomical characteristics of both beech and Scots pine. Tissue types like earlywood, latewood and the characteristic large wood rays of beech can easily be distinguished on the transverse image. Since Scots pine does not have such large wood rays as beech, they can not be spotted, but resin canals on the other hand, can clearly be seen. Even individual cells and bordered pits can be distinguished.

A first glance on the resulting EDX images indicates the silicone, can be found on all sides of the wood cubes over the entire surfaces. For the corner block this seems self-evident. The fact that the same observation is true for the central block indicates the silicone has penetrated even into the heart of the wood block. Moreover, the anatomical structure of the wood is apparent on the EDX images. The explanation for this can be found at larger magnification. At cell level no silicone is detected in cavities, such as the cell lumens, and so they are left dark, whereas cell walls do light up indicating they contain silicone. Beech has larger lumens which are easily detected whereas the lumens of Scots pine tracheids are smaller and a lot of small, darker spots on the EDX images can be seen.
Detection

The main goal of this research is to try to detect siloxanes in siloxane-treated wood. Wood always contains a small amount of silica [18, 19]. A comparison of images of treated and non-treated wood showed this natural amount of silica is too low to detect. Depending on the abundance and form of the siloxanes they can be seen already at magnification 220. Zooming in on the siloxanes reveals the structure consists of a microporous network, this means a 3D structure with pores of varying sizes (Figure 2). The siloxanes are found in different forms and dimensions: ranging from a thin layer on the cell walls to big props filling the lumen. Because of this network EDX-mapping isn’t always necessary to detect the siloxane; the network contrasts very well with the normal wood structure. EDX-mapping showed the network consists of the elements Si (siloxane) and Br (mixing agent).

In siloxane/silane mixture dipped specimens

Transverse scanning of beech reveals a microporous network at the inside of some vessels. This network follows the longitudinal direction and can vary in thickness from less than 1 µm to more than 3 µm. It does not cover the entire area of the cell walls of the vessels, but leaves some parts and bordered pits uncovered (Figure 2). A transverse image of Scots pine seems somehow different from that of beech (Figure 2 and 3). Silica is not evenly distributed over the entire area. Most signals are found in the larger structures: the tracheids of the earlywood and the wood rays. In some tracheids no signal of silica or bromine could be detected. In others a thin film of the microporous network covers the cell wall, and in again some others the microporous networks fills the lumen partly or even completely. The walls of most wood rays are covered by the
The props formed by siloxanes in the lumen of tracheids are not indissoluble connected to the cell walls. Moreover, some props loosened (maybe due to microtoming) and formed new cavities. The cell walls themselves only seem to have taken up the bromine and silicon in small contents. At higher magnification no silicon can be found in the middle lamella.

The resolution of the micro-CT is not high enough to distinguish the siloxane/silane mixture inside the wood in the same detail as SEM-EDX (Figure 4, 5 and 6). On the other hand, the images derived from the micro-CT indicate a global overview of the sample in 3D with the distribution of the mixed product. More than 1000 cross-sections with an in between distance of 10.10 µm are obtained from each scanned wood sample, offering the possibility to look inside the wood in a non-destructive way. Additionally, since the sample sides need to be cut with a microtome before scanning with the SEM, information of siloxanes at the sides can only be derived from the micro-CT images. Looking at the 3D reconstructions after micro-CT, the transitional part of the sample (where the bottom was dipped and the top was not) offers some very interesting information. Figure 4 and 5 show a part of this transition zone for beech. Migrating from the exterior to the interior a decrease in siloxane is observed. As figure 5 illustrates, most siloxane/silane can be found at the borders and the penetration of the mixture took mainly place in the longitudinal direction. These images are thus a confirmation of the SEM-images.

The penetration front of the siloxane/silane mixture in Scots pine is distinct on figure 6. The figure clearly shows some tracheid lumens are filled with the mixture, whereas
others are not. As in beech micro-CT seems a complementary technique in evaluating penetration depth and patterns in treated wood.

**Siloxane/silane mixture-impregnated specimens**

As in the dipped samples silicon and bromine are easily detectable with SEM-EDX. In contrast although, the elements are not found as a thin layer on the cell walls or in the lumens, but inside the cell walls themselves (Figure 7 and 8). Remarkable is the fact that silicone and bromine do not always appear to be on the same spots. So it must be concluded there was no homogenous mixture of the hydroxyterminated polydimethylsiloxane and the 3-bromopropyltrimethoxysilane. Better formulations could be evaluated to resolve this problem.

One vessel of beech shows an interesting detail (Figure 9). Zooming in at magnification 4000 reveals a bubbled layer on the inner surface. A possible explanation of this peculiar phenomenon is that the layer itself is a siloxane (proved by SEM-EDX) formed due to the impregnation. However volatile compounds included in the cell wall, like water vapour, came out of the cell wall afterwards and formed bubbles under the siloxane layer.

The 3D reconstructions after micro-CT scanning show the siloxane/silane mixture can be found all through the samples of beech and Scots pine (Figure 10 and 11). Just like in dipped beech, Figure 10a and b indicate most siloxane/silane in impregnated samples is to be found at the borders of the sample. The vessels stay open, but the cell walls contain the mixture. The wood rays of Scots pine seem to contain more siloxane/silane
than the surrounding tissues (Figure 11a and b). This is a confirmation of the SEM-EDX results.

**Conclusion and discussion**

SEM is able to give a clear view of the anatomical structure of wood. Mapping with EDX makes it possible to see with very good detail where silicon, originating from siloxanes, can be found. This is mainly in the lumen for dipped wood and in the cell wall for wood impregnated with the hydroxyterminated polydimethylsiloxane. X-ray micro-computed tomography is indeed a powerful tool in getting a 3D image of the structure of (non-)treated wood. The border between treated and non-treated wood is very clear and an idea about the concentration can be derived based on the intensity of the gray values. The combination of SEM-EDX and micro-CT can offer important information concerning the localization of certain products inside wood. While micro-CT can monitor changes in 3D, SEM-EDX will give detailed 2D information. Both techniques are complementary and using both techniques provides important extra information. Since technology is improving fast, micro-CT which is still limited by its resolution, will be enhanced by the development of nano-CT, with a resolution up to 400 nm. This technique is still in its early development, but will turn out to be very useful for more detailed 3D research.

From the experiment results it can be concluded that, under the circumstances as described in the article, impregnation with a siloxane is necessary to have cell wall penetration. This is an important factor to keep in mind when trying to achieve wood preservation with siloxanes.
Acknowledgments

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Figure 1: Chemical structure of 3-bromopropyltrimethoxysilane

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\begin{align*}
\text{CH}_3 & \quad \text{O} & \quad \text{Si} & \quad (\text{CH}_2)_3 & \quad \text{Br} & \quad + & \quad \text{H}_2\text{O} & \quad \rightarrow & \quad \text{HO} & \quad \text{Si} & \quad (\text{CH}_2)_3 & \quad \text{Br} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{O} & \quad \text{O} & \quad \text{CH}_3
\end{align*}
\]

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