WOOD RESEARCH doi.org/10.37763/wr.1336-4561/66.6.900911
e-ISSN 2729-8906
66(6): 2021 900-911 pp.

COMPREHENSIVE APPROACH TO ENSURE DURABILTY OF EXTERNAL WOODEN STRUCTURES

PETR KUKLÍK, ZDENĚK PROŠEK, ANNA GREGOROVÁ
CZECH TECHNICAL UNIVERSITY IN PRAGUE
CZECH REPUBLIC

(RECEIVED MARCH 2021)

ABSTRACT

The article deals with durability of wood, durability of wooden structures and surface modification of wood. We are trying to eliminate the factors causing degradation of wood with the use of photocatalytic materials. Those materials are efficient UV absorbers and they are able to destroy biological aggressors also. The planar particles of titanium oxide TiO_2 were chosen for the purpose of our research and applied on a wooden surface. In our case, we used a water solution of TiO_2. The main goal of our work was to study the interaction between planar particles of TiO_2 and wood matter. The samples of pine wood (*Pinus sylvestris*) were monitored for 255 days and subsequently evaluated using an electron microscope. The use of TiO_2 was compared with reference material and a reference commercial coating.

KEYWORDS: Wood, durability of wood, protection of wood, wooden structures.

INTRODUCTION

Wood is the oldest building material capable of transferring both tension and compression (Thelandersson et al. 2003). Wood also has a very good strength to weight ratio. The problem is biological degradation of wood as a natural material (Blass et al. 1995). Due to that durability considerations are important in ensuring an appropriate life for wooden structures. Durability issues imply that the designer has an expectation of performance of the wooden structures for a given number of years - usually the service life of the structure. Responsible design is focused to appropriate wooden species, sizes that allow the satisfactory performance and appropriate treatment. The protection of wood takes many forms including proper detailing. They are mainly directed towards the prevention of moisture access.

Although wood as raw material has wide utilisation in many industrial sectors, its use is compromised in some applications due to some draw-backs resulting from its variability both between and within wood species as well as its inherent physical-chemical properties

(e.g. anisotropy, hygroscopicity). Wood performs variably in density, strength and durability, while it is susceptible to degradation by UV-light, chemicals, fungi and insects when in humid environments. Moreover, wood lacks dimensional stability because of its property to swell and shrink when being in variable moisture conditions, caused by the large number of hydroxyl groups in the wood structure (Blass et al. 1995). Protective systems ensuring durability of wooden structures take many forms: *a)* design for durability, *b)* chemical treatment where natural durability is not enough, or *c)* maintenance and monitoring (visual, semi-destructive). Nevertheless, it is also necessary to take into account that preservative treatment may affect the strength and stiffness properties of wood (Blass et al. 1995).

One of the semi-destructive methods for evaluation of wooden structures is based on measurement of material resistance against penetration of an indenter. The damage of a wooden structural member is small after the tests. One of the well-known devices is Pilodyn 6J Forest that penetrates the surface layers of wooden element by a short pin with the help of an internal spring. It is possible to determine wood density and even the related mechanical properties based on the input of the depth of the pin penetration (Hasníková et al. 2014).

Wood density is determined by several factors, e.g. cell diameter and cell wall thickness, proportions of earlywood and latewood, cellulose and lignin content etc. Density has a significant influence on mechanical properties of wood (Kasal et al. 2004).

One of the innovative methods particularly suitable for long-term continuous monitoring of stress in wooden structure is the use of a fibre optic sensor. The technology of Fibre Bragg Grating (FBG) sensor is an optical system used for the same purposes as strain gauge sensors. However, unlike strain gauges, deformation measurements and information transmission are realized by means of light. Energy requirements of the system are therefore reduced and the system is significantly more resistant to most potential sources of interference, including electromagnetic interference. The fibre optic sensor is essentially an optical fibre equipped with a special grating (the so-called Bragg grating), which is produced for example by UV laser firing during fibre production. It is a very small, germanium doped portion of the optical fibre which, in the case of joining this fibre with the stretched body, changes its optical properties in a defined manner, and thus it is possible to measure very precisely the elongation of the body. On one fibre there can be several independent FBG sensors, each measuring a different place on the construction and working at a different wavelength. The fibre is equipped with a polymeric sleeve covering which acts as a fibre protection against moisture and mechanical damage. The FBG sensors are based on a principle of reflection of central wavelength of light by the Bragg grating. A part of the emitted light signal passes through the grating and a part of the light spectrum is reflected back. In the measuring unit, it is compared to the reference (unloaded) grating tuned to the same wavelength, the deformation is obtained from the difference of values. In the case of a newly made wooden member, the sensor can be inserted into its body. If an existing wooden member or even historical structure is to be monitored, the sensor can be attached to its surface (Velebil et al. 2016).

Durability of wood

Under ideal conditions wooden structures can be in use for centuries without significant biological deterioration (Thelandersson et al. 2003). However, when conditions are not ideal, many of wood species need a preservative treatment to be protected from the biological agents responsible for wood degradation, mainly fungi and insects. There is also one simple rule for design of wooden structures - "keep wood dry". In this case, the good detailing can be used to reduce biological hazard. Maintenance is also very important during the service life of the structure.

Each type of biological hazard has its own set of conditions that increase the risk of deterioration. Many of them include high levels of moisture. For example, fungal attack on wood is accelerated by the following conditions: moisture content between 20% and 25%, freely available oxygen, temperature range in 5°C to 40°C (ideally 25-40°C), a ready supply of food containing sugars and carbohydrates (i.e. the wood itself, particularly sapwood) (Blass et al. 1995).

Wood and wood-based products shall either have adequate natural durability for the particular application, or be given some preservative treatment. The new EN 335: 2013 gives general definitions of Use classes (previously called Hazard classes) for different service situations to which wood and wood-based products can be exposed.

Surface modification of wood

From a chemical point of view, the wood consists of cellulose, hemicellulose and lignin, while the wood cells also contain at a lesser extent other components like tannins, resins, oils, fats, terpenes, flavonoids, quinines and alkaloids (Hunt et al. 1938). The properties of wood surfaces are influenced by polymer morphology, extractive chemicals and processing parameters and conditions in end-uses. In the case of wood, the cell wall polymers are the main components which must be modified to change the properties of wood.

Generally timber protection materials should prolong lifetime of wooden structures. The main role of the group protective materials based on photocatalysis is to protect wood before color changing, moulds and fungus. The most spread photocatalytic materials for wood protection are TiO_2, ZnO, CeO_2 (Šubrt 2014) and WO_3 (Paola el al. 2012). Photocatalytic materials are applied in nanoform and usually used as a transparent coating. There are two ways to apply, particle of photocatalytic material can be directly mixed with the solution (Allen et al. 2002) or encapsulated into porous, resistant material (Minabe et al. 2000). Furthermore, the article deals with the use of TiO_2 because it is the most available material with photocatalytic properties (Chen et al. 2009).

Material for chemical protection of wood by TiO_2 was chosen planar particles of TiO_2 because it is possible to prepare as photoactive (crystalline) and non-photoactive (amorphous) (Bahtat et al. 1992). We are expecting that the use of the planar particles of TiO_2 (Fig. 1) could be one of the method to ensure durability of wood and wooden structures during their planned service life. This will strengthen the confidence of users (e.g. engineers and architects) and boost the use of wood also in conventional fields of application like building structures etc. The goal of our work is study interaction between planar particles of TiO_2 and wood matter. In our study, we want to observe the direct interaction between wood tissue and particle of

TiO_2, so we used an aqueous solution of TiO_2. We assume that water evaporates and the particles are bonded by Van der Waals forces directly to wood tissue (Hu et al. 2014).

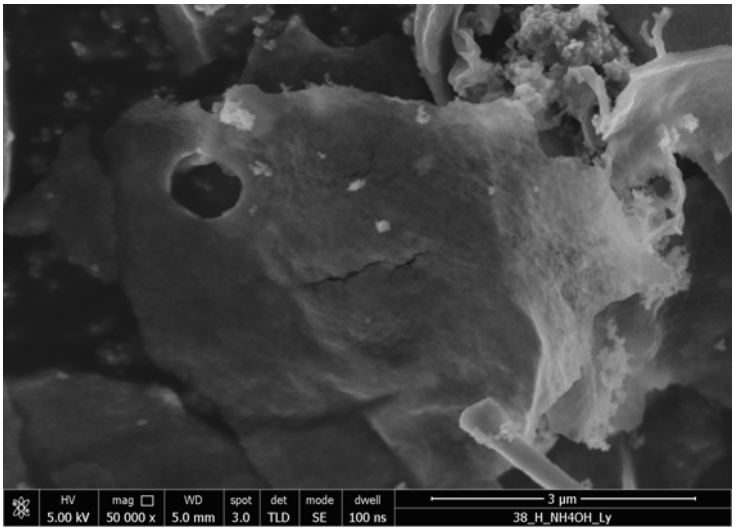

Fig. 1: Planar particle of amorphous TiO_2 (Photo: electron microscopy CTU, Prague).

After the application of TiO_2, the planar morphology was proved by electron microscopy (Fig. 1). On the picture is possible to see that the surface of the particle is not plain but wavy and also it is not completely continuous. The holes cover 20% of the surface and aggregates cover 10%. Holes and aggregates in this amount have no negative impact on the UV absorption of the material as was proven by UV-VIS spectroscopy.

In the next part of the article is presented the use of chemical protection of wood in the form of TiO_2 in comparison with the commonly used commercial protection of wood and unprotected wood.

MATERIAL AND METHODS

Materials

The tested wood was pine (*Pinus sylvestris*) from the forest area in Central Europe. The wood was protected in the form of a coating. Planar TiO_2 particles were used as chemical protection of wood. It was a 3% aqueous solution of TiO_2, which was evenly applied on the wood surface. The preparation of TiO_2 itself was taken from the article by Svora et al. (2020), where elemental composition and structural characterization are also described. Alkyd stain SynolacTM 6005 W from Cray Valley Ltd. was chosen as a representative of commercial chemical protection of wood and was chosen for comparison according to EN 927-3: 2002. Alkyd stain SynolacTM 6005 W with a solids content of 65% uses iron catalysis (bispidon) as drier.

Samples preparation

Three sets of samples were used to describe the effect of wood protection using TiO_2, which were exposed to the outside environment for 255 days. Each set contained six pine samples measuring 20 x 40 x 400 mm, which were placed external environment on the grounds of the University Centre of Energy Efficient Buildings. Tab. 1 shows the identification of individual samples with methods of protection. The samples were continuously visually monitored (Fig. 2) and subsequently, after 255 days, smaller samples were taken from the surface for microscopic sections.

Tab. 1: Methods of UV protection of samples.

Set	UV protection method
1	without protection
2	alkyd stain
3	3% TiO_2 solution

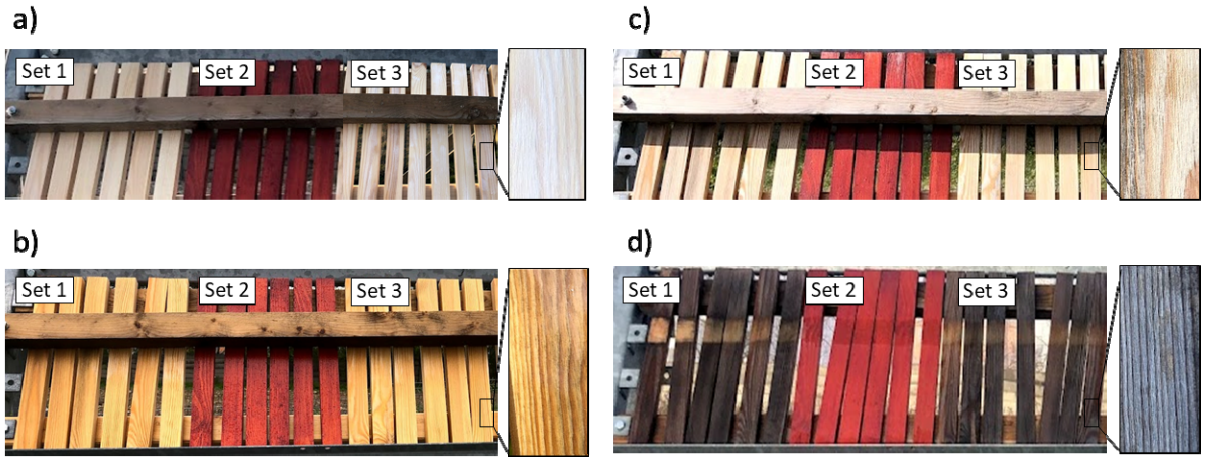

Fig. 2: Visual monitoring of the samples during exposure to the external environment: a) exposure time 0 days, b) exposure time 44 days, c) exposure time 83 days, d) exposure time 255 days.

Microscopic sections were used for electron microscopy. A small portion of the sample was taken from the wood surface and enclosing in epoxy resin (EpoFix kit from Struers). Subsequently, the sample was ground and polished to achieve the required roughness for electron microscopy and elemental microanalysis. In the first step, silicon carbide foils with a roughness of 500 grains·cm^{-2} were used for 2 min, followed by foils with a roughness of 1200 grains·cm^{-2} and 2000 grains/cm^2 for 4 min and 4000 grains·cm^{-2} for 12 min. The entire preparation was performed on Tegramin 25 from Struers with a pressure on samples of 5 N and performed without the use of water as a wetting agent. The sample thus prepared reached the flatness required for analysis. Finally, the samples were sputtered with 3 nm platinum. Platinum created a conductive layer on the surface of the wood, thus eliminating the charging effect that occurs when using the high current required for elemental microanalysis.

Experimental methods

The experimental methods used describe the surface and microstructure of the tested wood. The article uses a combination of optical and electron microscopy with elemental microanalysis. The experiments methods were performed in the Laboratory of Electron Microscopy and Micro-analysis at the University Centre for Energy Efficient Buildings in Buštěhrad. The Axio Zoom.V16 microscope from ZEISS was used for optical microscopy. This is a stereo zoom microscope and a large field was used to study and describe the surface of the tested samples.

The electron microscopy was performed using the scanning electron microscope (SEM) with a Schottky cathode FEG SEM Merlin from ZEISS. Energy dispersive spectrometer (EDS) from Oxford Instruments was used for qualitative elemental microanalysis of the tested samples. The EDS microanalysis was performed using the element maps of the microstructure and point ID of individual coating. During the SEM analysis, the microscope settings were as follows: resolution 1024 × 768 pixels with an average time per pixel of 9 µs, a working distance of 8.5 mm, acceleration voltage 20 kV, current 2 nA, and EDS setting were as follows: resolution 2048 pixels, frame live time 79 seconds, frame count 4, process time 3 and the pixel dwell time 25 µs.

RESULTS AND DISCUSSION

Optical microscopy

The surfaces of the tested samples can be seen in Fig. 3. The color of the wood surface can be seen with a protective coating for set of samples 2 and 3. Sample with a commercial protection (Set 2) shows no changes during exposure to the external environment. The surface of the sample without protection against UV degradation (Set 1) shows color changes which are caused degradation of wood by external environment. The color of wood changed from yellow (natural color) to brown for latewood and silver patina acquires on the surface of earlywood.

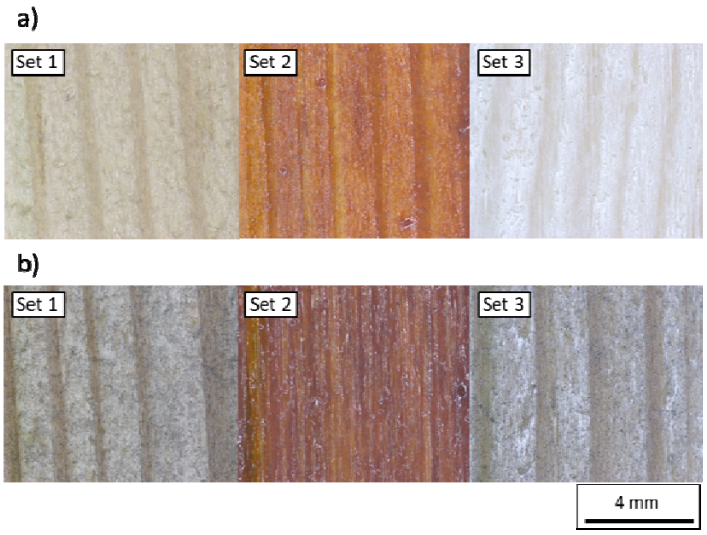

Fig. 3: Optical images of the sample surface: a) exposure time 0 days, b) exposure time 255 days, magnification 10x.

The differences between earlywood and latewood were caused by different bulk densities. The earlywood is more degraded than latewood due to its lower density and thus, a deeper light penetration into wood. A smaller color change effect can also be observed for a sample with TiO_2 protection (Set 3). These results are consistent with other studies dealing with UV degradation of wood (Cogulet et al. 2016). However, it must be noted that these findings were reached for the white spruce (*Picea glauca*) and samples were exposed in a QUV accelerated weathering tester from Q-Lab (USA) for 2000 h.

Electron microscopy

Electron microscopy images of the microstructure (Figs. 4-6) confirmed the results from optical microscopy. The microstructure is composed of 90% by volume of cells, which divide earlywood tracheids or latewood tracheids according to the period in which they grew (Prošek et al. 2015). The remaining microstructure is made up of parenchymal cells and resin channels.

Change in the microstructure of sample without UV protection (Set 1) due to degradation by UV radiation can be seen (Fig. 4). The receding part of earlywood can be seen in the microstructure of the sample, which is more susceptible to UV degradation of wood. In addition, the loss of lignin by means of UV radiation thins the cell walls in the case of an earlywood cell and their impaired connection through the middle lamella, which is rich on lignin. The same effect of UV radiation is described in a study by Rowell (2005).

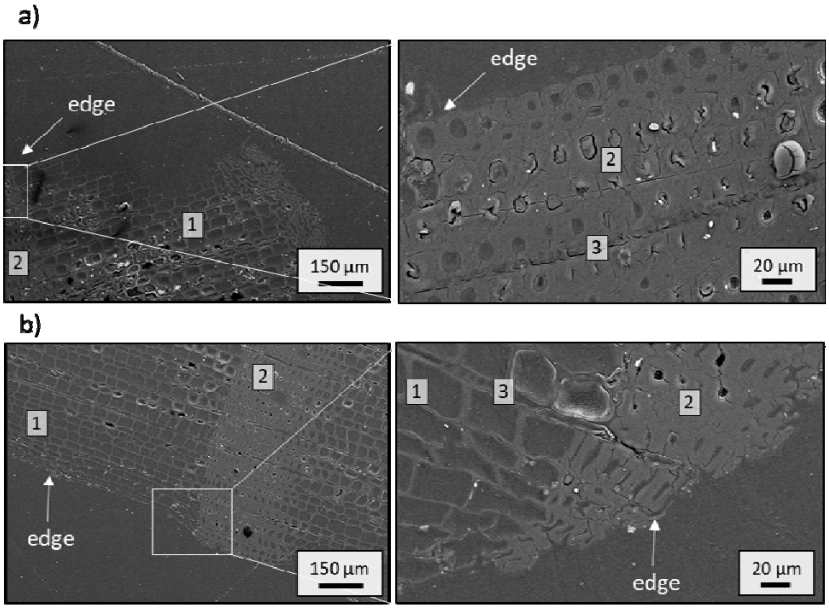

Fig. 4: SEM images of reference sample without a protective layer (Set 1), cross-section, magnification 250 × and for cutout 1k ×: (1) earlywood tracheid, (2) latewood tracheid, (3) parenchymal cell, a) exposure time 0 days, b) exposure time 255 days.

The UV protective coating can be seen in the microstructure (Fig. 5) of samples with commercial protective layer (Set 2). The protective layer is approximately 10 µm thick. The microstructure does not show any significant changes in the cells due to the protective coating and thus UV radiation did not cause degradation of the material. Protective layer,

opaque pigmented coatings, act as very effective UV radiation screen. This is an effect that has been described in several studies (George et al. 2005).

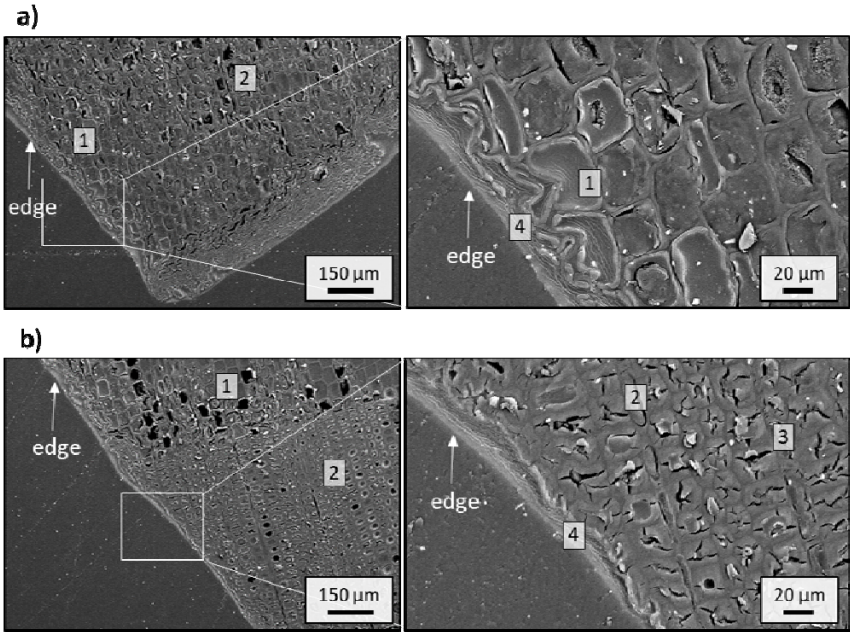

Fig. 5: SEM images of sample with a commercial protective layer (Set 2), cross-section, magnification 250 × and for cutout 1k ×: (1) earlywood tracheid, (2) latewood tracheid, (3) parenchymal cell, (4) protective layer, a) exposure time 0 days, b) exposure time 255 days.

Sample with protection layer of TiO_2 (Set 3) can be seen on Fig. 6. Protection layer of TiO_2 has a thickness of approximately 5 µm. The protective layer of TiO_2 is not visible in the microstructure after exposure to the external environment for 255 days and damaged wood cells of earlywood tracheid can be seen in the microstructure.

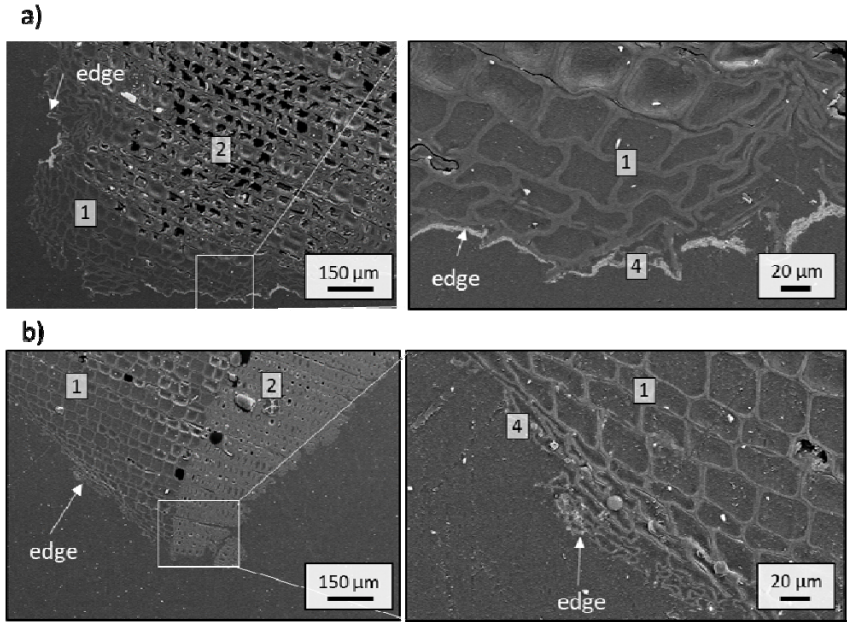

Fig. 6: SEM images of sample with TiO_2 protective layer (Set 3), cross-section, magnification 250 × and for cutout 1k ×: (1) earlywood tracheid, (2) latewood tracheid, (3) parenchymal cell, (4) protective layer, a) exposure time 0 days, b) exposure time 255 days.

Elemental microanalysis

The element map determined by EDS can be seen in the Fig. 7. The commercial protective layer and the 3% aqueous TiO_2 solution layer were rich in iron and titanium, respectively. Therefore, these chemical elements were examined in the microstructure.

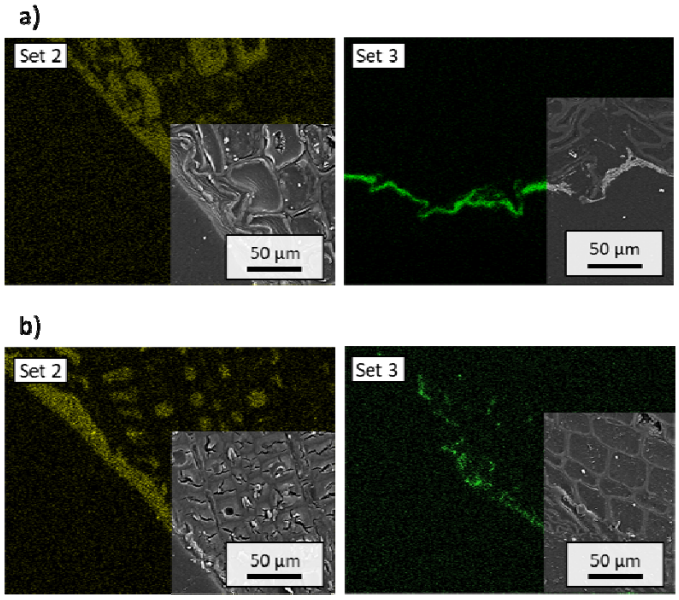

Fig. 7: Elemental microanalysis of samples with a protective layer – BSE detector magnified 1k × with EDS element maps (yellow – iron, green – titanium), a) exposure time 0 days, b) exposure time 255 days.

The high iron (drier) content can be seen in the protective layer with a thickness of 10 µm for the sample with the commercial protective layer (Set 2). In addition, a high content of iron in the cell cavities of the so-called lumen can also be seen, which indicates that the wood is impregnated to a depth of 100 µm and thus reliably protected the wood cells. The depth of impregnation of 100 µm was also confirmed in the work of Rijckaer et al. (2001) who tested Scots pine sapwood in this way.

Samples with a protective TiO_2 layer (Set 3) show a high titanium content in the layer with a width of approximately 5 µm. Furthermore, there is no titanium in the lumen and in the entire microstructure, which means that the wood has not been impregnated. The TiO_2 protective layer is not integral after exposure of the sample to the external environment and this results in a partial degradation of the wood cells. This is the effect of a weak connection between the TiO_2 layer and the wood surface. An aqueous solution of TiO_2 was used because after evaporation of the water, the TiO_2 particles are bonding by Van der Waals forces (Hu et al. 2014). The Van der Waals forces have a low binding effect and, as a result, TiO_2 particles are gradually leached out of the sample surface by rain. This statement is in agreement with the knowledge about the weak connection of particles by Van der Waals forces (Santamarina 2003, Santos et al. 2020).

CONCLUSIONS

Durability of wooden structures is one of the critical limit states which should be considered. Wood protection should be carried out in accordance with the requirements for the specific applications. The protection of wood takes many forms including proper detailing. The effect and interaction between wood mass and amorphous titanium dioxide TiO_2 were investigated in order to improve the quality of surface finish of wooden structures. Coatings with planar particles of titanium dioxide were used for dispersions applied on wooden surface in a transparent layer. The researched wood was pine (*Pinus sylvestris*), which was exposed to the external environment for 255 days and compared with a reference sample and a commercial coating. Based on the results, it can be concluded that: *(1)* the cells of the reference wood were destroyed by the external environment for 255 days, *(2)* commercial protective coating reliably protected wood, *(3)* the protective layer of 3% TiO_2 water solution was not integral and thus the wood cells were damaged, *(4)* the low integrity of the TiO_2 protective coating was caused by the lower bonding of the resulting Van der Waals forces.

Work in progress deal with testing new wood samples, which are protected by TiO_2 coating in a solution of water glass and acrylate. In the case of a water glass solution, the inorganic porous structure is created and particles are surrounded by silicate chains. In the case of acrylic solution, the organic porous structure is created.

ACKNOWLEDGMENT

This work was financially supported by the Czech Science Foundation research project Interactions between wooden surface and planar particles of TiO_2, N^o. 18-26297S. The authors also thank the Laboratory of Electron Microscopy and Microanalysis at University Centre for Energy Efficient Buildings, Czech Technical University in Prague.

REFERENCES

1. Allen, N.S., Edge, M., Ortega, A., Liauw, C.M., Stratton, J., McIntyre, R.B., 2002: Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings. Polymer degradation and stability 78(3): 467-478.
2. Bahtat, M., Mugnier, J., Lou, L., Serughetti J., 1992: Planar TiO_2 waveguides by the sol-gel process: The relationship of structure to properties. Sol-Gel Optics II 1758: 173-183.
3. Blass, H., Aune, P., Choo, B., Görlacher, R., Griffiths, D., Hilson, B., Racher, P., Steck, G., 1995: Timber Engineering. Centrum Hout. Almere, The Netherlands, 427 pp.
4. Chen, F., Yang, X., Wu, Q., 2009: Antifungal capability of TiO_2 coated film on moist wood. Building and Environment 44(5): 1088-1093.
5. Cogulet, A., Blanchet, P., Landry, V., 2016: Wood degradation under UV irradiation: A lignin characterization. Journal of Photochemistry and Photobiology B: Biology 158: 184-191.

6. EN 335, 1992: Durability of wood and wood-based products - Use classes: definitions, application to solid wood and wood-based products.
7. EN 927-3, 2002: Paints and varnishes. Coating materials and coating systems for exterior wood. Part 3: Natural weathering test.
8. George, B., Suttie, E., Merlin, A., Deglise, X., 2005: Photodegradation and photostabilisation of wood – the state of the art. Polymer Degradation and Stability 88(2): 268-274.
9. Hasníková, H., Kuklík, P., 2014: Various non-destructive methods for investigation of timber members from a historical structure. Wood Research 59(3): 411-420.
10. Hunt, G., Garrett, G., 1938: Wood preservation. McGraw-Hill, Book Company, Inc. New York and London, First Edition, 457 pp.
11. Hu, Z., Zhang, X., Liu, Z., Huo, K., Chu, P.K., Zhai, J., Jiang, L., 2014: Regulating water adhesion on superhydrophobic TiO_2 nanotube arrays. Advanced Functional Materials 24(40): 6381-6388.
12. Kasal, B., Anthony, R., 2004: Advances in situ evaluation of timber structures. Progress in Structural Engineering and Materials 6: 94–103.
13. Maddox, J., Kuklík, P., 2016: Non-destructive testing methods for determining material characteristic values of historic timber structures. In: FORDE CARILLION, MC, ed. Structural Faults & Repair - 2016. 16th International Conference and Exhibition. Edinburgh, 17.05.2016 - 19.05.2016. Edinburgh: Engineering Technics Press Edinburgh.
14. Minabe, T., Tryk, D.A., Sawunyama, P., Kikuchi, Y., Hashimoto, K., Fujishima, A., 2000: TiO_2-mediated photodegradation of liquid and solid organic compounds. Journal of Photochemistry and Photobiology A: Chemistry 137(1): 53-62.
15. Nikolic M., Lawther J.M., Sanadi A.R., 2015: Use of nanofillers in wood coatings: a scientific review. Journal of Coatings Technology and Research 12: 445-61.
16. Paola, A.D., García-López, E., Marcì, G., Palmisano, L., 2012: A survey of photocatalytic materials for environmental remediation. Journal of hazardous materials 211: 3-29.
17. Prošek, Z., Králík, V., Topič, J., Nežerka, V., Indrová, K., Tesárek, P., 2015: A description of the microstructure and the micromechanical properties of spruce wood. Acta Polytechnica 55(1): 39-49.
18. Rijckaert, V., Stevens, M., Van Acker, J., de Meijer, M., Militz, H., 2001: Quantitative assessment of the penetration of water-borne and solvent-borne wood coating in Scots pine sapwood. European Journal of Wood and Wood Products 59(4): 278-287.
19. Rowell, R.M., 2005: Handbook of wood chemistry and wood composites. Taylor & Francis. London, 487 pp.
20. Santamarina, J.C., 2003: Soil behavior at the microscale: Particle Forces. Soil behavior and Soft Ground Construction. Pp 25-56.
21. Santos, T.P. , Cunha, R.L., Tabeling, P., Cejas, C.M., 2020: Colloidal particle deposition on microchannel walls, for attractive and repulsive surface potentials. Physical Chemistry Chemical Physics 30: 17236-17246.
22. Svora, P., Ecorchard, P., Pližingrová, E., Komárková, B., Pawełkowicz, S.S., Murafa, N., Maříková, M., Smržová, D., Wagner, B., Machálková, A., Bezdička, P., 2020: Influence of

inorganic bases on the structure of titanium dioxide-based microsheets. ACS omega 5(37): 23703-23717.
23. Šubrt, J., Pulišová, P., Boháček, J., Bezdička, P., Pližingrová, E., Volfová, L., Kupčík, J., 2014: Highly photoactive 2D titanium dioxide nanostructures prepared from lyophilized aqueous colloids of peroxo-polytitanic acid. Materials Research Bulletin 49: 405-12.
24. Thelandersson, S., Larsen, H., 2003: Timber Engineering. John Wiley & Sons. Chichester, 446 pp.
25. Velebil, L. , Zelený, R., Včelák, J., Dvořák, M., Kuklík, P., Terebesyová, M., Olbrich, M., 2016: Optical fibre sensors as a potential solution for monitoring wooden structures**.** In: WCTE 2016 CD-ROM Proceedings, Vienna.

PETR KUKLÍK*, ZDENĚK PROŠEK, ANNA GREGOROVÁ
CZECH TECHNICAL UNIVERSITY IN PRAGUE
UNIVERSITY CENTRE FOR ENERGY EFFICIENT BUILDINGS
TŘINECKÁ 1024, 273 43 BUŠTĚHRAD
CZECH REPUBLIC
*Corresponding author: kuklik@fsv.cvut.cz