Research final report

OTKA PD116635

With the help of research funding OTKA PD 116635, I have presented the research work from 1 October 2015 to 30 September 2018 in 4 scientific publications and at 2 national and 8 international conferences with oral presentations (and 8 related citable abstract or conference paper at the conferences). Further publications are currently being prepared to present the research results not yet published. In the research proposal, after the detection and selection of the nanoparticles suitable for use and the preliminary experiments I focused on three main areas of my work. On the one hand, I studied the effect of different nanoparticles on wood-water relations (dimensional stability, water absorption, water vapour permeability, etc.). On the other hand, I analyzed the effect of the selected nanoparticles on the biological resistance of the wood, and thirdly, the effect on UV resistance (color durability). As far as possible, I tried to support the experimental concept and results with the help of as many tests as possible.

1 Preliminary tests

According to the work plan, firstly, the selection of nanoparticles considered suitable for the improvement of the technical characteristics of wood material was carried out, but the scope of these studies has been continuously expanded with the progress of the tests. Determination of optimal treatment (impregnation) parameters (concentration, pressure, temperature, duration, carriers, additives) in pre-experiments to fit selected nanoparticles and wood properties (dimensional stability, UV protection, fungal resistance). Among the preliminary experiments, I performed scanning electrone microscopic studies to determine the possible tissue changes of the wood to check the nanoparticle recording. Primary physico-mechanical tests were also carried out in connection with preliminary experiments. These tests have been ongoing due to the treatments that were subsequently examined.

In all cases, I have chosen beech and scots pine wood, because they have a significant economic role in the field of wood industry. On the other hand, they can easily be saturated, which is essential to carry out the intended treatments, by filling wood with nanoparticles by impregnation.

1.1 Mechanical tests

When examining the mechanical properties of different nanoparticle-treated wood, it has been found that none of the treatments significantly influences the most important characteristics (compressive strength, bending strength, surface hardness) (Fig. 1-3.). This is most important because many of the methods used to modify wood (eg heat treatment) either significantly reduce individual strength values in exchange for increased dimensional stability or biological durability.

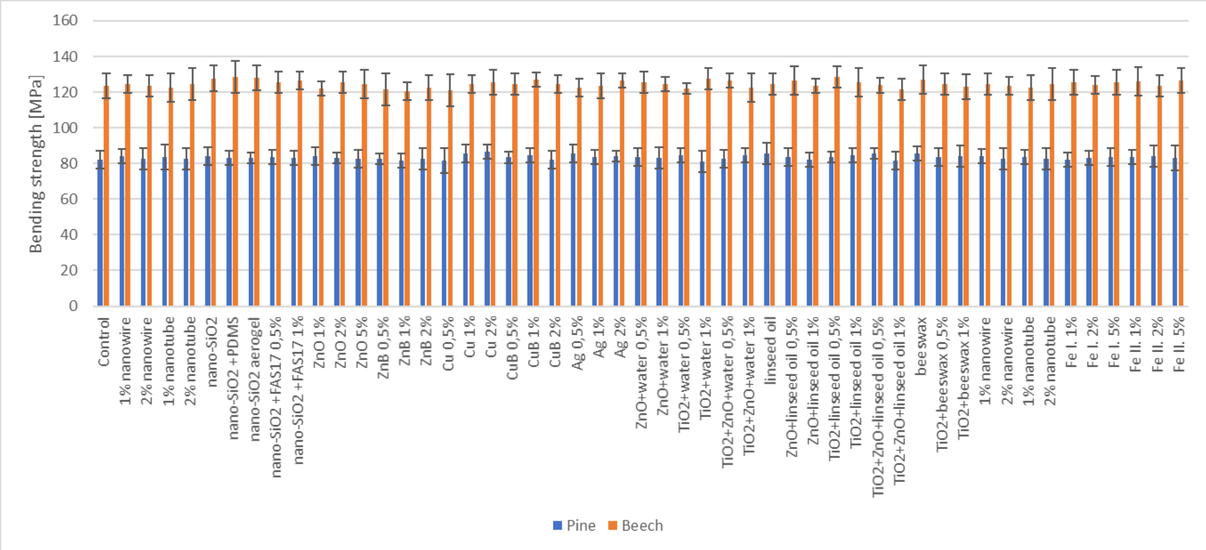

Fig. 1. Effect of the investigated nanoparticle treatments on the bending strength of beech and pine wood

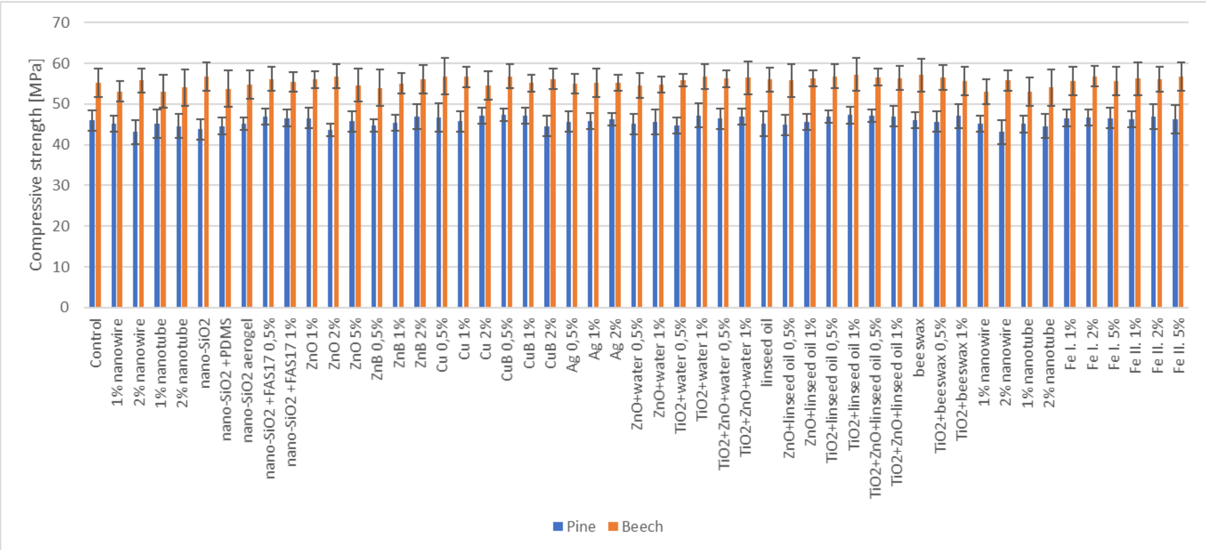

Fig. 2. Effect of the investigated nanoparticle treatments on the compressive strength of beech and pine wood

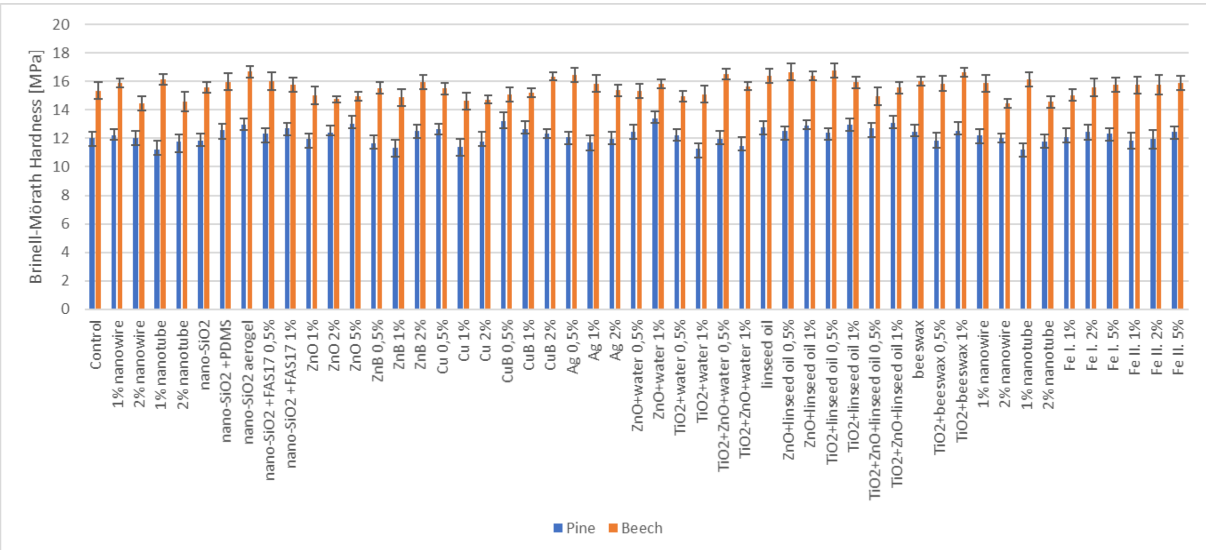

Fig. 3. Effect of the investigated nanoparticle treatments on the Brinell-Mörath hardness of beech and pine wood

1.2 FT-IR tests

Presence of the nanoparticles was firstly tested with the use of infrared spectroscopy. Usually this method is suitable for the detection of the nanoparticles on the surface, because the chemical bonds of them are in the detectable region with this technique (commonly between 400-1100 in case of metal oxides), according to some earlier tests:

- In case of ZnO the sharp peak around 450 cm^{-1} can be attributed due to Zn-O stretching vibrations, but depending on synthesis and other experimental conditions, weak bands positioned at 520 cm^{-1}, 560 cm^{-1} and 660 cm^{-1} are also possible to appear in FT-IR spectrum
- The FT-IR spectrum of TiO_2 might show various characteristic peaks. The intense peak around 400 cm^{-1} is assigned to the Ti-O stretching band which is the characteristic peak of TiO_2
- Iron-oxide: It displays several bands at 460, 560 cm^{-1}. The vibration bands may be assigned to Fe–O–Fe stretching vibration.
- CuO: The FTIR absorption peaks in the infrared spectrum of CuO at low frequencies below 700 cm^{-1} are due to Cu-O vibrations.
- SiO_2: The absoprption peak at 1020-1110 cm^{-1} is assigned tot he Si-O-Si asymmetric stretching vibration, and the peaks at 960 cm^{-1} are ascribed tot he asymmetric bending and stretching vibration of Si-OH respectively.

Mostly our measurements were supported by the the literature data, but in some cases it was not possible to detect them with this technique (Fig. 4-6). This might be because of the use of different origin and preparation methods of the investigated nanoparticles, that might shift the characteristic peaks out of the range of this technique. Therefore, the characterisation was continued by another techniques, namely SEM imaging and EDX analysis (electrone dispersive X-ray spectroscopy).

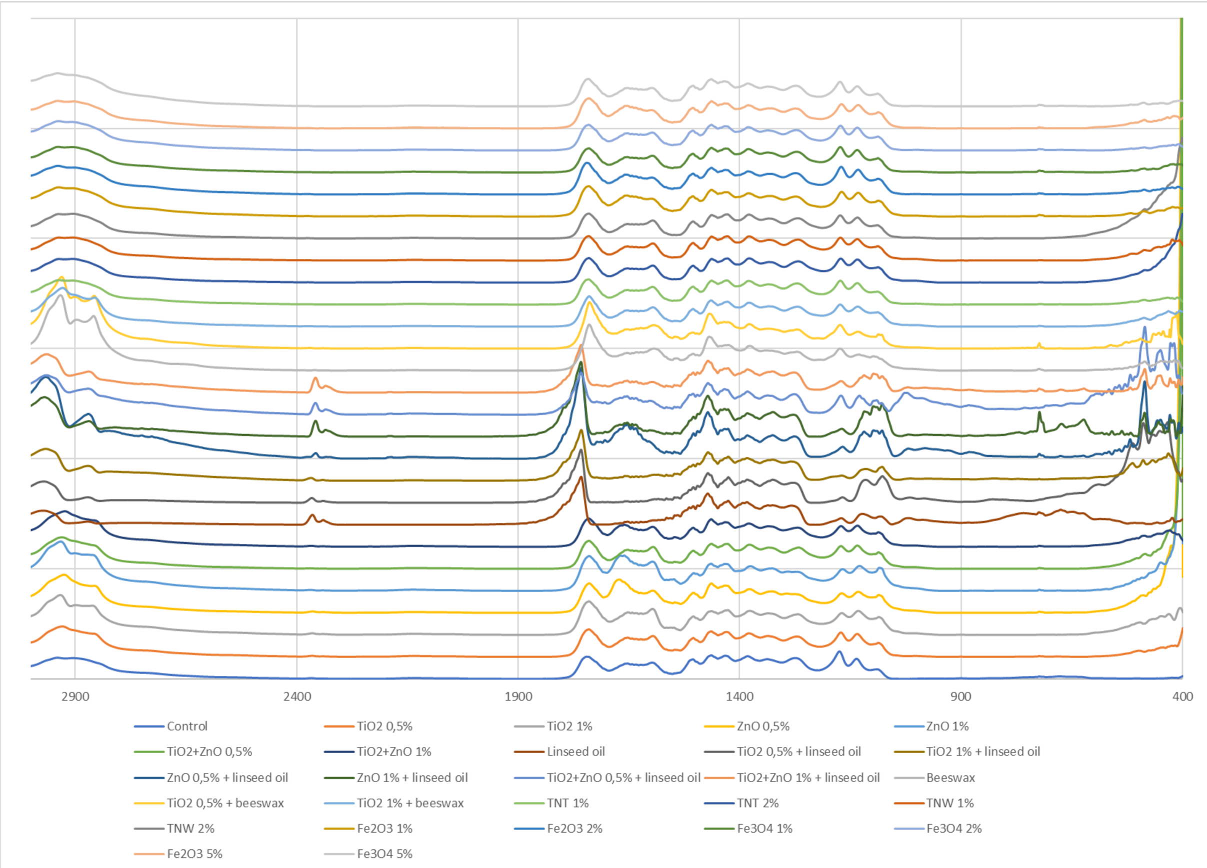

Fig. 4. FT-IR spectra of the wood samples treated by different nanoparticle systems to improve weathering resistance

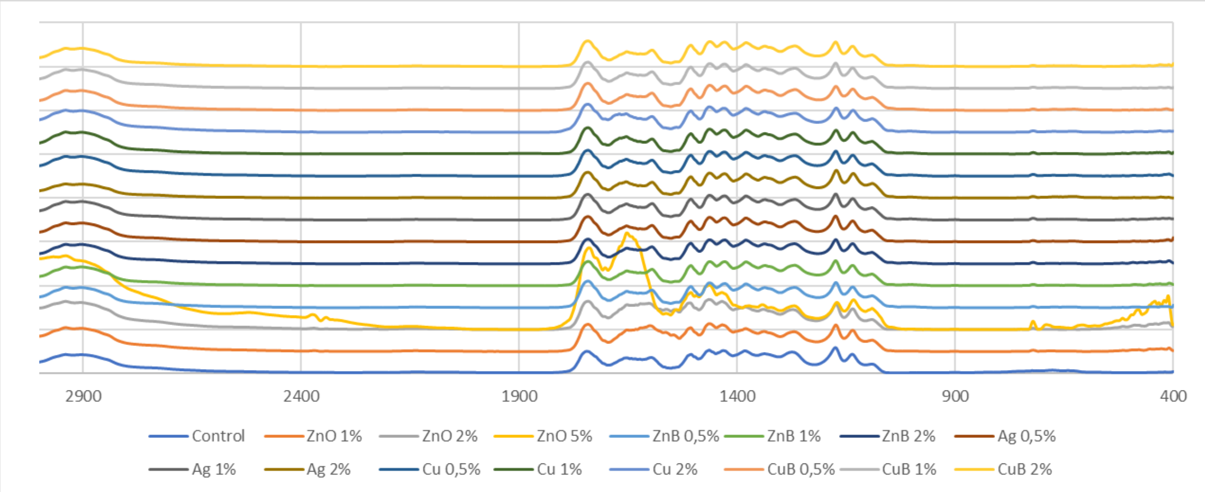

Fig 5. FT-IR spectra of the wood samples treated by different nanoparticles to improve decay resistance

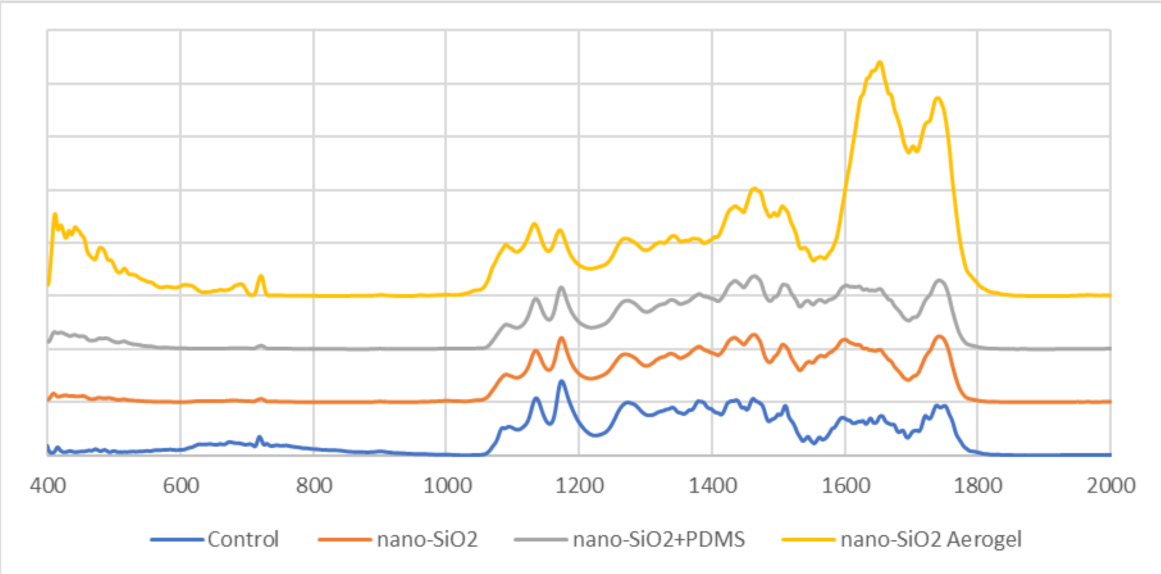

Fig. 6. FT-IR spectra of the wood samples treated by different nanoparticles systems to improve dimensional stability

1.3 Scanning electrone microscope characterization

1.3.1 SEM imaging

The efficiency of the nanoparticle based treatments, the distribution of the particles in the wood and their occurrence was determined by scanning electron microscopy (Fig. 7.). It has been found that the nanoparticles used have appropriately penetrated into the structure of the wood and are typically distributed evenly on the surface of the cell walls. This supports the efficiency of the saturation procedures used. However, there have been several cases of partial agglomeration of particles, which also resulted in the blockage of cellular cavities. This phenomenon, though not desirable, did not inhibit the achievement of the goals to be achieved. The formation of UV protection was not compromised by these agglomerates, and the dimensional stability was improved by blocking the movement of water in the wood by clogging the cell lumens. The agglomerates also had a positive effect on the development of biological durability since the cell lumens were blocked by the spread of the fungal hyphae in the wood.

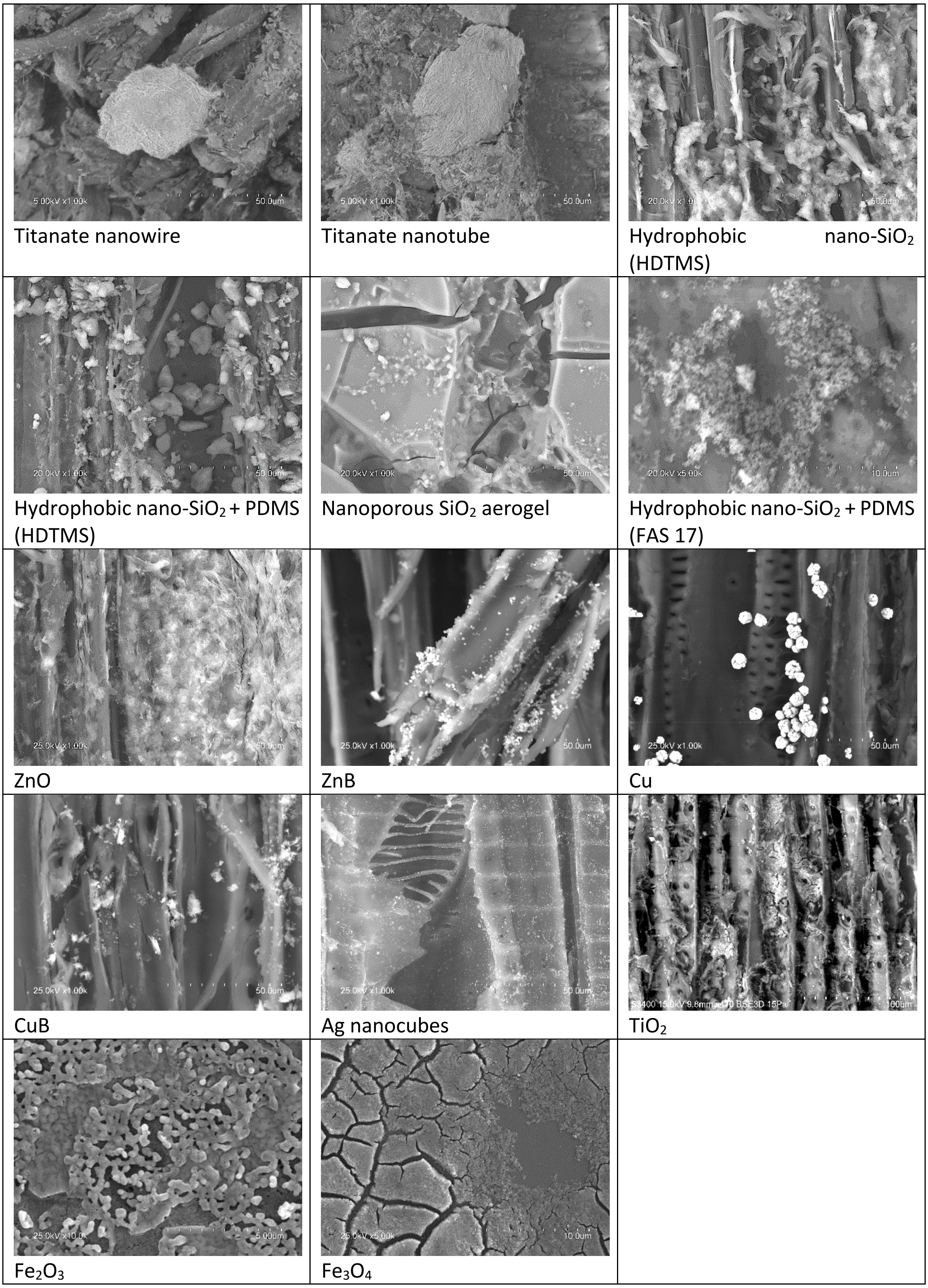

Fig. 7. SEM images of the investigated nanoparticles and their distribution on wood surfaces

1.3.2 SEM-EDX analysis

Parallel tot he SEM imaging, the EDX analysys of the samples was done as well to get more detailed information about the location and the distribution of the nanoparticles. These results supported the data from SEM imaging, as it showed usually also even distribution of the particles, beside some agglomerations (Fig. 8.).

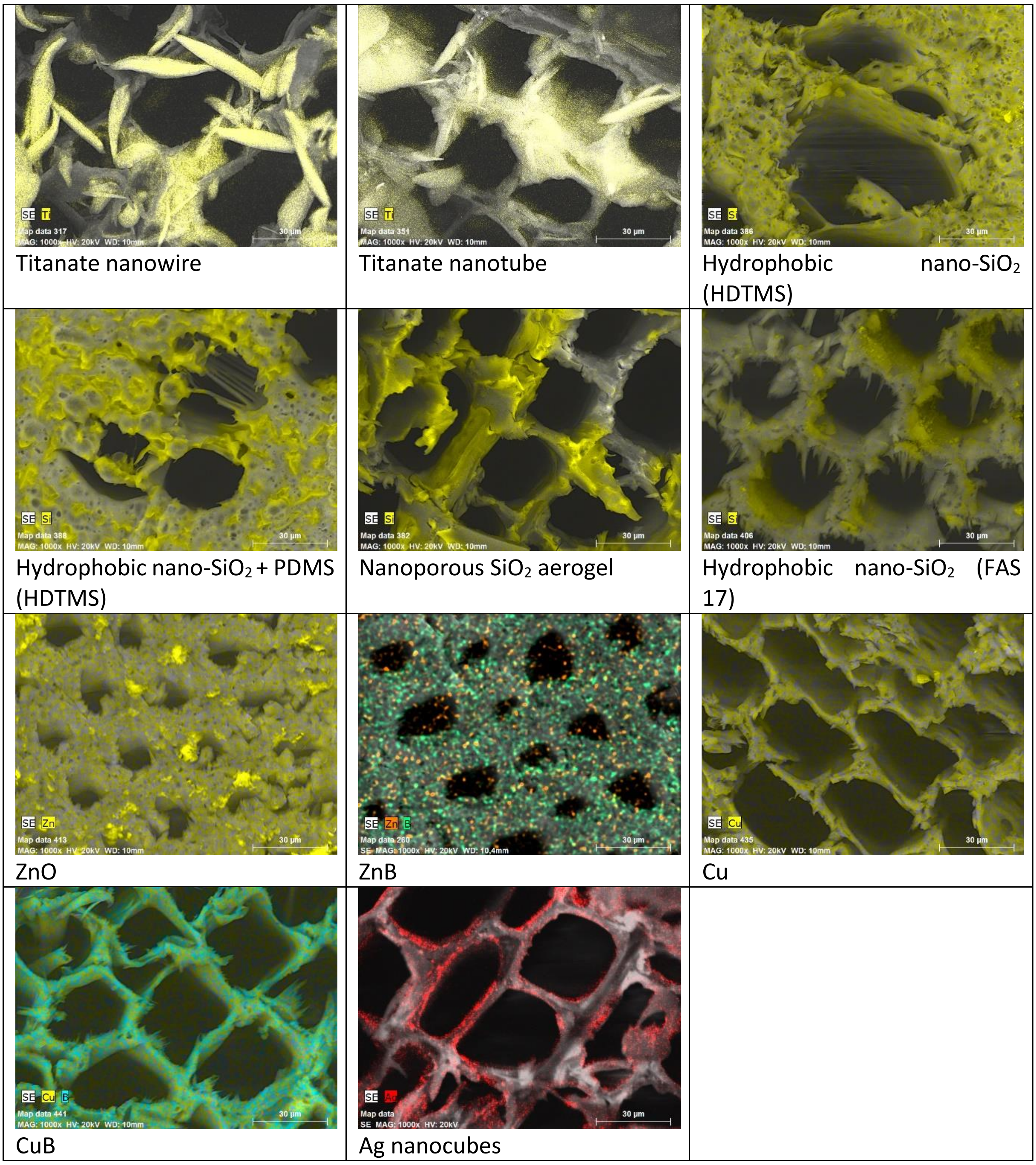

Fig. 8. SEM-EDX maps of the investigated nanoparticles on wood surfaces

2 Wood-water relation based tests

The hydrophilic nature of the wood can be converted to be hydrophobic when the hydroxyl groups on the surface of the micelles forming the cell walls are made unavailable by hydrophilic nanoparticles. With the so-modified wood, the change of the environmental parameters (temperature and humidity) will have a smaller effect, that is, the shrinkage or swelling of the wood will be smaller, which will ultimately result in an increase in dimensional stability.

Nanoparticles selected for the treatment of wood are as follows (concentrations of carriers and suspensions in parentheses):

- Titanium based particles:
  - hydrophobic titanate nanotube - HTNT (Nanobakt Kft.) (distilled water, 1%, 2%)
  - hydrophobic titanate nanowire - HTNW (Nanobakt Kft.) (distilled water, 1%, 2%)
- Silicium based particles:
  - hydrophobized silica
    - by hexadecyltrimethoxysilane (HDTMS) (ethanol, 5%)
    - by HDTMS + Poly(dimethylsiloxane) (PDMS) bonding agent (tetrahydrofurane, 5%)
    - by FAS 17 (1H,1H,2H,2H-Perfluorodecyltriethoxysilane) (etanol, 0,5%, 1%)
  - nanoporous silica aerogel (ethanol/distilled water, 35%)

2.1 Titanate nanoprticle based treatments

This part of the research work was published in the journal Pro Ligno in 2017 (see list of publications). Additionally presented at 2 international conferences with oral presentation. This part of the research has been done in cooperation with the company Nanobakt Kft., as they offered the production and supply of the nanoprticle suspensions for the treatments.

A slight colour change could be observed as a result of nanoparticle impregnation. Total colour change values were in the range of 2,5 - 5,5, which is a region of slightly visible to well visible for the naked eye. The colour change was visible as a fading (whitening) of the initial colour.

Shrinking/Swelling coefficient decreased as a result of nanoparticle impregnation. No correlation could be found between the efficiency and the concentration of the nanoparticles in the suspension. However, the retention of the samples showed the same ratio than the ratio between the initial concentrations (~2). The used nanoparticles are relatively large in one dimension (length is 100-500nm for HTNT and 1-10µm for HTNW), so they have a stick-like shape. On the one hand, the dimensions of the particles are probably too large for a good penetration into micro- and nanopores of the cell wall. On the other hand, the shape of the particles is not optimal for the penetration into the micro- and nanopores of the cell wall. This can lead to an uneven distribution of the nanoparticles in the wood material, and especially a weak penetration into the cell wall, which would be a key factor for a better efficiency.

Water uptake decreased as a result of the nanoparticle treatments, where the effectiveness was better in case of tangential surface (water uptake in radial direction). HTNT impregnation was more effective then impregnation with HTNW. The difference between the different concentrations was not significant. The hydrophobic property of the nanoparticles can keep away the water from the cell wall, but these results showed again the possible uneven distribution of the nanoparticles in the cell wall. There was no significant difference between the equilibrium moisture content of the treated and untreated samples. This result shows, that however the nanoparticles used are hydrophobic and can the liquid water keep away from the cell wall, the access of water vapour to it is not blocked.

2.2 Silica nanoprticle based treatments

2.2.1 HDTMS modified nanoparticle treatments with or without bonding agent (PDMS)

This part of the research work was published in the journal Wood Material Science and Engineering in 2018 (see list of publications). Additionally presented at 4 international conferences with oral presentation.

In this part of the research work, silica nanoparticles were prepared by hydrolysis and condensation of TEOS at high pH. This step of preparing hydrophilic spherical nanoparticles was followed by a modification step with hexadecyltrimethoxysilane (HDTMS), resulting in the grafting of long-chain alkyl groups onto the surface of the nanoparticles to make them hydrophobic. To get better bonding to the wood surface, PDMS was used as a bonding agent between the HDTMS-coated silica nanoparticles and wood. The novelty of this research is the application of such nanoparticles not only as a surface coating, but a full cross-section impregnation, which utilization form in case of wood material was not investigated yet. The planned treatment will likely elongate the lifetime of the wood-based products, because the wood–water relations are essential at all utilization fields. The expected positive effect of the investigated treatments is the improvement of the dimensional stability of wood as a result of impregnation with hydrophobic silica nanoparticles. Another goal was to improve the effect of the treatment by the use of polydimethylsiloxane (PDMS) as the bonding agent between the nanoparticles and the wood surface.

With the use of the modified hydrophobic silica nanoparticles (SiO_2), it is possible to improve the dimensional stability of wood. Shrinking and swelling properties decreased remarkably, depending on wood species and treatment type. The anti-swelling-efficiency (ASE) was similar in radial and tangential direction for both beech and pine, however, a slight, statistically significant difference could be observed in the results between the different wood species. Application of PDMS did not provide better dimensional stability compared to the treatment without it, which is explained by the lower amount of hydrophobic nanoparticles in this case, but compensated by the hydrophobic properties of PDMS itself. Swelling anisotropy was increased slightly, but insignificantly as a result of the treatment, as slightly higher ASE was observed in the radial direction, compared to tangential. With the use of PDMS slightly lower EMC and highly lower water uptake compared to the basic “nano-SiO_2” treatment was observed. The improved hydrophobicity of the cell wall surfaces through the deposition of silica nanoparticles make the investigated treatments more effective against liquid water, compared to water vapour. SEM imaging showed that the distribution of the nanoparticles is mostly even on the cell wall surfaces, but some deposits and agglomerations were found as well. As a side effect of the treatments, a well visible colour change in the form of darkening/fading occurred.

2.2.2 FAS 17 modified nanoparticle treatments

This part of the research has not been published yet, as it was started at the end of the research period. In this part of the research work, silica nanoparticles were suspended in ethanol. This was followed by a modification step with FAS 17 (1H,1H,2H,2H-perfluorodecyltriethoxysilane), resulting in the grafting of long perfluoro chains onto the surface of the nanoparticles to make them hydrophobic. The novelty of this research is the application of such nanoparticles not only as a surface coating, but a full cross-section impregnation, which utilization form in case of wood material was not investigated yet. The planned treatment will likely elongate the lifetime of the wood-based products, because the wood–water relations are essential at all utilization fields. The expected positive effect of the investigated treatments is the improvement of the dimensional stability of wood as a result of impregnation with hydrophobic silica nanoparticles.

With this method, weight percent gain (WPG) of 0,8-1,2% could be reached for both beech and pine wood. This is the result of the very low concentration (1%) of the silica nanoparticles used in case of this treatment. Additionally, a different amount os FAS17 was added tot he treatment system (0,5% or 1%). The porous structure of wood is the main channels for SiO_2 sol into the wood tissue. It is obvious that no compound was detected in any part of the untreated woodblocks. The samples treated with FAS17 hydrophobized SiO_2 nanoparticles, many agglomerates can be found in the cell lumens and pores. To confirm the presence of SiO_2 nanoparticles inside the cell of wood, SEM-EDX mapping was carried out. SEM-EDX map for the untreated and treated blocks indicates that there is no functional element except the basic elements of wood such as C and O. Additionally, the SEM-EDX images of the samples treated with SiO_2 particles indicate that the Si element exist in the wood cell. This means that SiO_2 nano-treatment can reside in the wood since wood itself does not have Si elements at this level. As the samples were obtained from the middle of the wood samples, it can be concluded that SiO_2 particles is easy to be brought by water into the wood tissue.

Shrinking and swelling properties decreased remarkably, between 50-60% depending on the treatment used (Fig. 9.). The ASE was similar in radial and tangential direction as well for both beech and pine wood. FAS17 modified nano-SiO_2 treatment resulted in slightly, but significantly higher ASE in case of pine wood, compared to beech. These results show that wood species has some effect on the efficiency of the investigated treatments. This is related to the differences in the anatomical structure that leads to different permeability of beech and pine in the different anatomical directions. There was only a slight improvement observed in the ASE as the ratio of FAS17 was increased. As this nano-SiO_2 treatment caused filling of the cell lumens, the affinity of water for the cell wall decreased. As a result, dimensional stability increased due to less available space in the cell lumens for water.

Behind the result that, despite of the low hydrophobic nanoparticle amount in wood ASE shows these good results, must be the reduced hygroscopicity of the treated wood material. The sites that enable bonding of water molecules are excluded by the hydrophobic nanoparticles. According to Donath et al. (2004) the treatment of wood with different alkoxysilanes (tetraethoxysilane, methyl triethoxysilane, propyl triethoxysilane) might result in 20-35% ASE, while other authors reported 8-69% ASE with other alkoxysilanes (ethyltriethoxysilane, diethyldiethoxysilane) at relatively high WPG values (16-65%). While in this case, ASE values ranged between 50-60% as already reported, but only at 0,8-1,2% WPG.

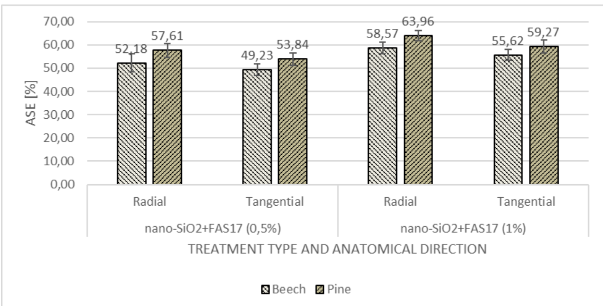

Fig. 9. ASE of nano-silica treatments on beech and scots pine wood (whiskers showing standard deviation of the results).

Similar ASE values were observed in radial and tangential direction. Therefore, swelling anisotropy did not changed (Fig. 10). Therefore, the values of swelling anisotropy are in case of all treatments and both wood species under the value of 2, which is the theoretical limit for wood materials regarding the tending to the warping and deformations. Over the value of 2, the wood material is highly capable for warping and deformations related to the changes in the wood-water relations.

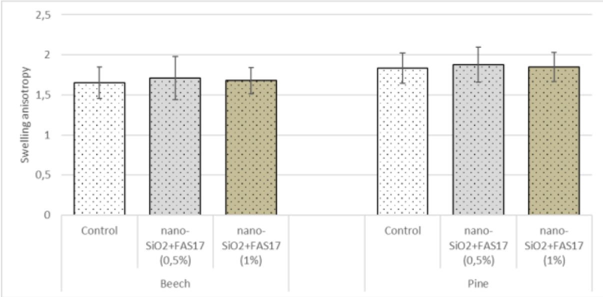

Fig. 10. Effect of nano-silica treatments on the swelling anisotropy (whiskers showing standard deviation of the results)

EMC decreased slightly, but significantly as a result of the investigated nanoparticle treatment (Fig. 11). With other words, the uptake of water vapour is decreased by these nano-SiO_2 treatments. This means that the investigated treatment did not only result in highly hydrophobic characteristic of the treated wood, but decreased additionally the ability of wood to absorb moisture.

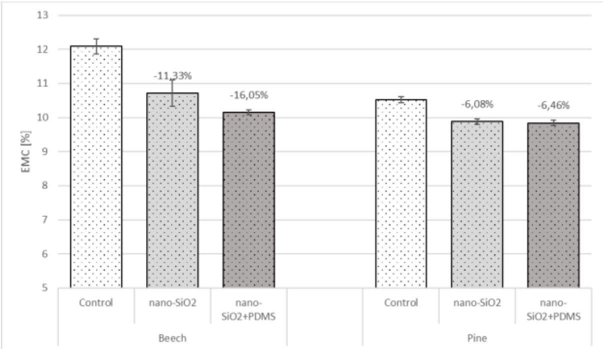

Fig. 11. Effect of nano-silica treatments on the equilibrium moisture content of beech and scots pine wood (percentages showing the difference to the control and whiskers the standard deviation of the results)

Water uptake decreased significantly as a result of the treatments. In radial and also tangential direction, treatment resulted in statistically significant decrease in case of beech and pine samples compared to the control (Fig. 12-13). These results indicated that a large amount of nano-silica particles successfully attached to the wood cell walls, impeding access of water to cell lumens in the treated wood samples. Thus, presence of nanoparticles leads to lower water uptake capacity. Furthermore, the nanoparticles increasingly block the pits and micropores of the cell wall. As a result of the treatment, a packed layer is deposited on the cell lumen surface. Because of the roughness of this layer, the surface free energy is reduced as well. This is the so called “lotus effect” that is common in nature. Water uptake decreased in a much higher ratio compared to the water vapour uptake. Highly decreased water uptake shows that besides a decreased ability of wood to absorb moisture, there is also a hydrophobization effect present, caused by the investigated nanoparticle based treatment. This hydrophobization effect of the used silica nanoparticles is responsible for the difference between the uptake of liquid water and water vapour. The improved hydrophobicity of the cell wall surfaces through the deposition of silica aerogel make the investigated treatment more effective against liquid water, compared to water vapour.

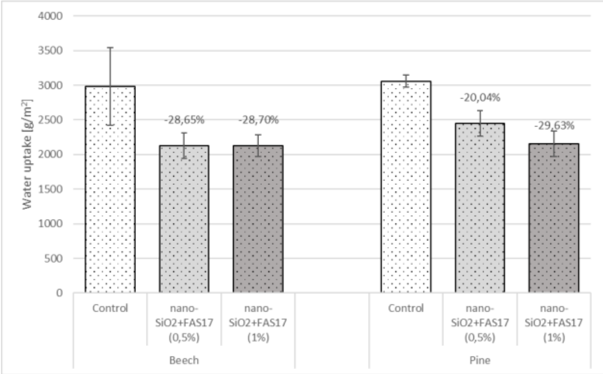

Fig. 12. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in radial direction (percentages showing the difference to the control and whiskers the standard deviation of the results)

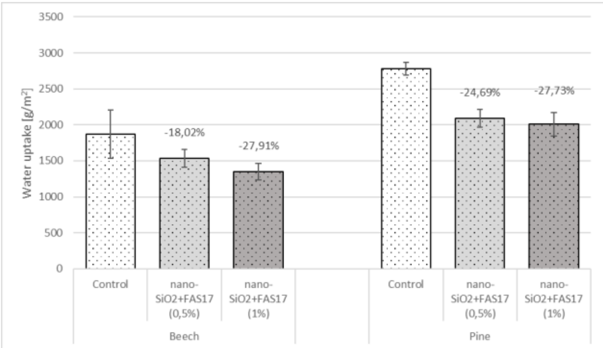

Fig. 13. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in tangential direction (percentages showing the difference to the control and whiskers the standard deviation of the results)

2.2.3 Nanoporous silica aerogel treatments

This part of the research has not been published yet, as it was finished at the end of the research period. The nano-SiO_2 aerogel with nanoporous network structure was made by sol-gel method. The tetraethyl orthosilicate (TEOS)/ethanol/H_2O with a molar ratio of 1 : 5 : 8 were poured into the reaction system. To promote the hydrolysis process, HCl was added until the pH value was 3. The mixture solution was stirred at 50°C for 60 min until the solution was clear. With this ratio, a nano-silica sol with 35%m/m concentration was prepared. As a next step, the wooden samples were impregnated with the nano-silica sol, using 100 mbar prevacuum for 60 min, followed by a 2 hours impregnation step at atmospheric pressure. No overpressure was necessary, as small samples were used (20×20×30 mm for swelling and EMC tests, 10×50×50 for water uptake test). After that, they were placed in an oven controlled at 60°C for 24 h and at 105°C for another 24 h to age the gels until nano-SiO_2 aerogel formed in the cell lumen of wood.

With this method, weight percent gain (WPG) of 18-20% could be reached for both beech and pine wood. The porous structure of wood is the main channels for SiO_2 sol into the wood tissue. It is obvious that no compound was detected in any part of the untreated woodblocks. The samples treated with SiO_2 sol, many agglomerates can be found in the cell lumens and pores. This is because the fluid can diffuse, resulting in the impregnation of agents into the wood. To confirm the presence of SiO_2 sol inside the cell of wood, SEM-EDX mapping was carried out. SEM-EDX map for the untreated and treated blocks indicates that there is no functional element except the basic elements of wood such as C and O. Additionally, the SEM-EDX images of the samples treated with SiO_2 sol indicate that the Si element exist in the wood cell. This means that SiO_2 sol can reside in the wood since wood itself does not have Si elements at this level. As the samples were obtained from the middle of the wood samples, it can be concluded that SiO_2 sol is easy to be brought by water into the wood tissue.

Shrinking and swelling properties decreased remarkably (Fig. 14). The ASE was similar in radial and tangential direction as well for both beech and pine wood. Nano-SiO_2 aerogel treatment resulted in slightly, but significantly higher ASE in case of beech wood, compared to pine. These results show that wood species has some effect on the efficiency of the investigated treatments. This is related to the differences in the anatomical structure that leads to different permeability of beech and pine in the different anatomical directions. As nano-SiO_2 aerogel caused filling of the cell lumens, the affinity of water for the cell wall decreased. As a result, dimensional stability increased due to less available space in the cell lumens for water.

Behind the result that, despite of the lower hydrophobic nanoparticle amount in wood while using PDMS as bonding agent ASE is not decreasing, must be the reduced hygroscopicity of the treated wood material (Kumar et al. 2016). The sites that enable bonding of water molecules are replaced partly by PDMS layers. According to Donath et al. (2004) the treatment of wood with different alkoxysilanes (tetraethoxysilane, methyl triethoxysilane, propyl triethoxysilane) might result in 20-35% ASE, while other authors reported 8-69% ASE with other alkoxysilanes (ethyltriethoxysilane, diethyldiethoxysilane) at relatively high WPG values (16-65%). In our case, ASE values ranged between 17-33% as already reported, but only at 3,5% and 4,6% WPG in case of “nano-SiO2” treatment for beech and pine respectively, furthermore, 3,75% and 4,72% WPG in case of “nano-SiO2+PDMS” treatment for beech and pine respectively.

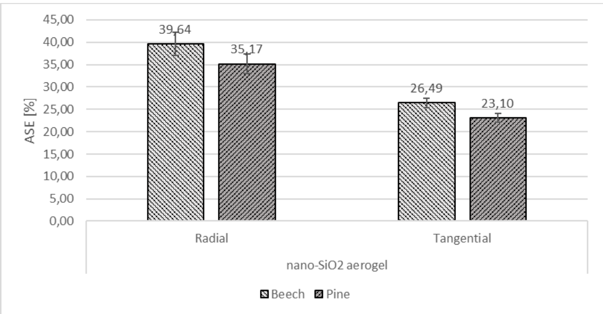

Fig. 14. ASE of nano-silica treatments on beech and scots pine wood (whiskers showing standard deviation of the results).

Significantly higher ASE values were observed in the radial direction, compared to the tangential direction. Unfortunately, this effect increased the swelling anisotropy slightly, but statistically in a insignificant ratio (Fig. 15). This phenomenon might lead to the increased capability of cracks, deformations and warping. However, the values of swelling anisotropy are in case of all treatments and both wood species under the value of 2, which is the theoretical limit for wood materials regarding the tending to the warping and deformations. Over the value of 2, the wood material is highly capable for warping and deformations related to the changes in the wood-water relations.

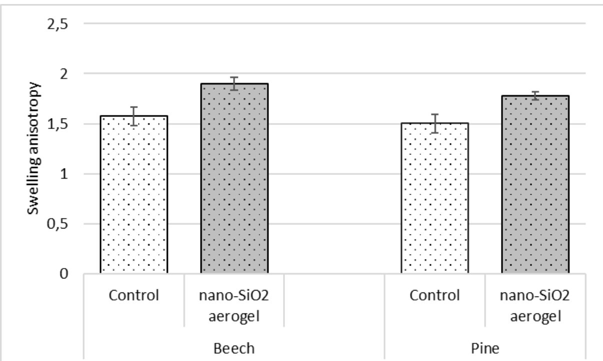

Fig. 15. Effect of nano-silica treatments on the swelling anisotropy (whiskers showing standard deviation)

EMC decreased significantly as a result of the investigated nanoparticle treatment (Fig. 16). With other words, the uptake of water vapour is decreased by the nano-SiO_2 treatment. This means that the investigated treatment did not only result in highly hydrophobic characteristic of the treated wood, but decreased additionally the ability of wood to absorb moisture.

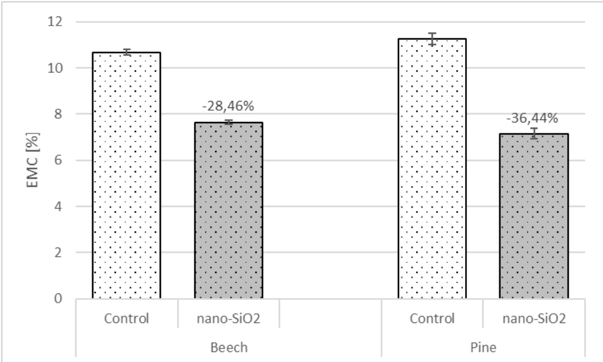

Fig. 16. Effect of nano-silica treatments on the equilibrium moisture content of beech and scots pine wood (percentages showing the difference to the control and whiskers the standard deviation of the results)

Water uptake decreased significantly as a result of the treatments. In radial and also tangential direction, treatment resulted in statistically significant decrease in case of beech and pine samples compared to the control (Fig. 17-18). These results indicated that a large amount of nano-silica particles successfully attached to the wood cell walls, impeding access of water to cell lumens in the treated wood samples. Thus, presence of nanoparticles leads to lower water uptake capacity. Furthermore, the nanoparticles increasingly block the pits and micropores of the cell wall. This kind of treatment of wood samples showed lower water absorption compared to that of hydrophobic silica treatments, likely due to the additional water impeding effect of the nanoporous aerogel aggregates that is filling the void spaces and blocking more effective the water absorption. As a result of that, a packed layer is deposited on the cell lumen surface. Because of the roughness of this layer, the surface free energy is reduced as well. This is the so called “lotus effect” that is common in nature. Water uptake decreased in a much higher ratio compared to the water vapour uptake. Highly decreased water uptake shows that besides a decreased ability of wood to absorb moisture, there is also a hydrophobization effect present, caused by the investigated nanoparticle based treatment. This hydrophobization effect of the used silica nanoparticles is responsible for the difference between the uptake of liquid water and water vapour. The improved hydrophobicity of the cell wall surfaces through the deposition of silica aerogel make the investigated treatment more effective against liquid water, compared to water vapour.

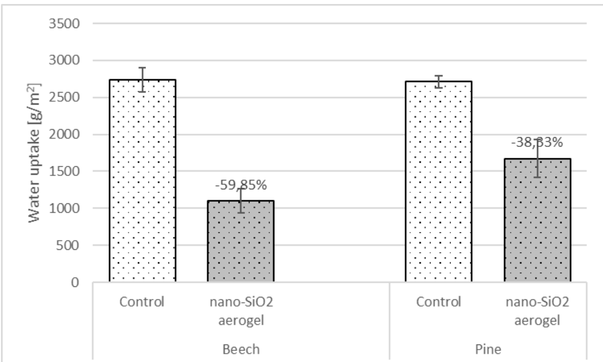

Fig. 17. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in radial direction (percentages showing the difference to the control and whiskers the standard deviation of the results)

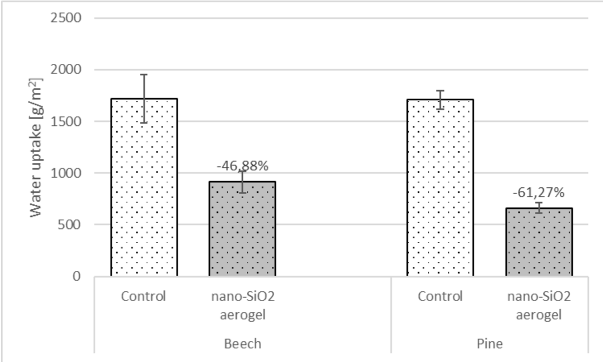

Fig. 18. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in tangential direction (percentages showing the difference to the control and whiskers the standard deviation of the results)

As a side effect of the treatments, a well visible colour change in the form of darkening was visible as well. The value of total colour change was similar in case of both beech and pine. The reason for the colour change is on one hand the leaching effect of the organic solvent as carrier material (ethanol), on the other hand the use of elevated temperature during the curing step of the treatments and the low pH (3) of the sol.

2.2.4 Effect of the treatments on the water vapour diffusion

The results of these tests are under publication recently. Density of water vapour flow rate was measured with dry-cup test. The density of water vapour flow rate was tested in case of all titanate and silica nanoparticle treatments. Untreated specimens served as control. Specimens were tested for each treated and control wood, in both tangential and radial direction. Samples were climatized at normal climate (T= 20°C, ϕ= 65%) before the test. Thickness of the samples was 10mm, with a diameter of 88mm. The samples had a clear radial or tangential surface. Water-free calcium-chloride was used as a desiccant to ensure the 0% relative humidity (RH) in the testing cup. The testing cups were placed in a climatic chamber with 20°C temperature and 65% RH. Cups were weighed once a day to determine the mass of the moisture transport through the wood specimens.

Tests showed the important result, that except two cases (nano-SiO2+HDTMS+PDMS and nano-SiO_2 aerogel), the water vapour permeability (δ) did not decreased as a result of the treatments used on wood for dimensional stabilization (Tab. 1-4). In case of those two treatments the reason behind the results is the polimerization of the treatment systems (PDMS or the aerogel) on the cell lumen surfaces. This leads to the inhibition of the water vapour transport tot he wood tissue. However the decrease of water vapour permeabilty is significant, there is only a slight decrease observed. This is an importan result, as during the utilization of wood as a building material, the good water vapour permeability is a positive property. Additionally the treatments did not influence the ratio of water vapour permeability between radial and tangential direction. As expected, the water vapour permeability was higher in radial direction, compared tot he tangential. This is because of the presene of rays in radial direction, that are improving the permeability.

Table 1. Water vapour diffusion properties of pine wood in radial direction as a result of the different investigated nanoparticle treatments (legend: Δm: mass change rate; g: density of water vapour flow rate; W: water vapour permeance; Z: water vapour resistance; δ: water vapour permeability)

Radial direction	Δm [kg/s]	g [kg/(m^2·s)]	W [kg/(m^2·s·Pa)]	Z [m^2·s·Pa/kg]	δ [kg/(m·s·Pa)]
1% Ti-nanowire	2,05E-09	3,41E-13	1,21E-10	8,30E+09	1,25E-09
2% Ti-nanowire	1,72E-09	2,92E-13	1,04E-10	9,68E+09	1,06E-09
1% Ti-nanotube	2,01E-09	3,34E-13	1,19E-10	8,64E+09	1,22E-09
2% Ti-nanotube	1,99E-09	3,39E-13	1,21E-10	8,40E+09	1,23E-09
nano-SiO_2+HDTMS	1,81E-09	3,04E-13	1,08E-10	9,26E+09	1,12E-09
nano-SiO_2+HDTMS+PDMS	1,46E-09	2,52E-13	9,00E-11	1,12E+10	9,26E-10
nano-SiO_2 aerogel	1,49E-09	2,51E-13	8,97E-11	1,12E+10	9,33E-10
Control	1,76E-09	2,98E-13	1,06E-10	9,43E+09	1,07E-09

Table 2. Water vapour diffusion properties of pine wood in tangential direction as a result of the different investigated nanoparticle treatments (legend: Δm: mass change rate; g: density of water vapour flow rate; W: water vapour permeance; Z: water vapour resistance; δ: water vapour permeability)

Tangential direction	Δm [kg/s]	g [kg/(m^2·s)]	W [kg/(m^2·s·Pa)]	Z [m^2·s·Pa/kg]	δ [kg/(m·s·Pa)]
1% Ti-nanowire	9,84E-10	1,61E-13	5,76E-11	1,75E+10	5,81E-10
2% Ti-nanowire	9,84E-10	1,65E-13	5,90E-11	1,70E+10	5,94E-10
1% Ti-nanotube	1,06E-09	1,76E-13	6,30E-11	1,60E+10	6,35E-10
2% Ti-nanotube	1,37E-09	2,24E-13	7,99E-11	1,26E+10	8,09E-10
nano-SiO_2+HDTMS	1,33E-09	2,23E-13	7,94E-11	1,29E+10	8,31E-10
nano-SiO_2+HDTMS+PDMS	8,63E-10	1,45E-13	5,18E-11	1,99E+10	5,40E-10
nano-SiO_2 aerogel	1,09E-09	1,85E-13	6,62E-11	1,52E+10	6,82E-10
Control	1,05E-09	1,74E-13	6,22E-11	1,66E+10	6,32E-10

Table 3. Water vapour diffusion properties of beech wood in radial direction as a result of the different investigated nanoparticle treatments (legend: Δm: mass change rate; g: density of water vapour flow rate; W: water vapour permeance; Z: water vapour resistance; δ: water vapour permeability)

Radial direction	Δm [kg/s]	g [kg/(m^2·s)]	W [kg/(m^2·s·Pa)]	Z [m^2·s·Pa/kg]	δ [kg/(m·s·Pa)]
1% Ti-nanowire	3,68E-09	6,20E-13	2,21E-10	4,52E+09	2,26E-09
2% Ti-nanowire	3,62E-09	6,10E-13	2,18E-10	4,59E+09	2,22E-09
1% Ti-nanotube	3,54E-09	5,96E-13	2,13E-10	4,70E+09	2,17E-09
2% Ti-nanotube	3,17E-09	5,33E-13	1,90E-10	5,26E+09	1,94E-09
nano-SiO_2+HDTMS	1,52E-09	2,56E-13	9,12E-11	1,11E+10	9,48E-10
nano-SiO_2+HDTMS+PDMS	7,81E-10	1,36E-13	4,85E-11	2,07E+10	4,90E-10
nano-SiO_2 aerogel	7,84E-10	1,33E-13	4,73E-11	2,12E+10	4,88E-10
Control	3,08E-09	5,18E-13	1,85E-10	5,41E+09	1,89E-09

Table 4. Water vapour diffusion properties of beech wood in tangential direction as a result of the different investigated nanoparticle treatments (legend: Δm: mass change rate; g: density of water vapour flow rate; W: water vapour permeance; Z: water vapour resistance; δ: water vapour permeability)

Tangential direction	Δm [kg/s]	g [kg/(m^2·s)]	W [kg/(m^2·s·Pa)]	Z [m^2·s·Pa/kg]	δ [kg/(m·s·Pa)]
1% Ti-nanowire	2,30E-09	3,77E-13	1,34E-10	7,45E+09	1,39E-09
2% Ti-nanowire	2,27E-09	3,69E-13	1,31E-10	7,61E+09	1,35E-09
1% Ti-nanotube	2,21E-09	3,61E-13	1,29E-10	7,81E+09	1,31E-09
2% Ti-nanotube	1,98E-09	3,25E-13	1,16E-10	8,65E+09	1,17E-09
nano-SiO_2+HDTMS	7,89E-10	1,31E-13	4,66E-11	2,24E+10	4,89E-10
nano-SiO_2+HDTMS+PDMS	9,23E-10	1,58E-13	5,64E-11	1,80E+10	5,42E-10
nano-SiO_2 aerogel	6,22E-10	1,05E-13	3,75E-11	2,68E+10	3,54E-10
Control	1,93E-09	3,12E-13	1,11E-10	9,03E+09	1,12E-09

2.2.5 Hydrophobization effect of the treatments

The results of these tests are under publication recently. Contact angle (CA) measurements were performed on a goniometer (68-76 PocketGoniometer PGX+) with de-ionised water. The water droplet volume was ~4 μl. CA was measured at intervals of 120 ms for the 1st s and at 5, 10, 20, 30, 60, 120, 240, 360, 480 and 570 sec. At least 20 CA determinations were made at different locations on the surface for each specimen.

Results showed high hydrophobization effect as a result of the different silica-based nanoparticle treatments (Fig. 19-20). The initial contact angle (at time = 0 s) of the untreated wood material was around 65° for both wood species. In contrast to that, significantly higher contact angles were observed for the SiO_2 nanoparticle treated wood surfaces, between 130-145°. This is very close to the superhydrophobic region (>150°). The highest initial contact angle was observed in case of the treatment using hydrophobized SiO_2 nanoparticles by 1% FAS17. The lowest value was observed in case of nanoporous silica aerogel treatment, with the valu of 135°. The treatments are not only providing high hydrophobicity for wood, but they also provide long lasting effect, as the contact angle is only slightly decreasing with time. The most stable treatment was the hydrophobic silica nanoparticle treatment (nano-SiO_2) and the nanoporous silica aerogel. Unfortunately, the most promising treatments according tot he initial CA seemed not to be that stable, as in case of the nano-SiO_2+FAS17 treatments the CA decreased remarkably tot he value of 80-85°. These results are supporting the conclusions taken related to the dimensional stabilization and water-uptake decreasing effect of the investigated treatments. One of the main reasons, why these treatments are improving these properties of wood is the long-lasting hydrophobization effect of the treatments.

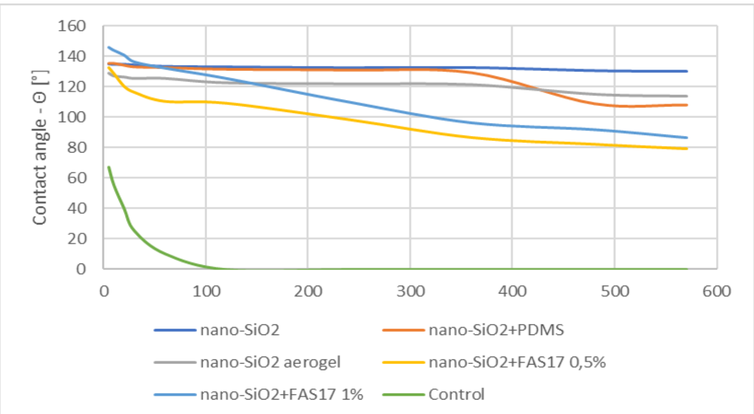

Fig. 19. Change of the water droplet contact angle as a function of time on the investigated beech wood surfaces

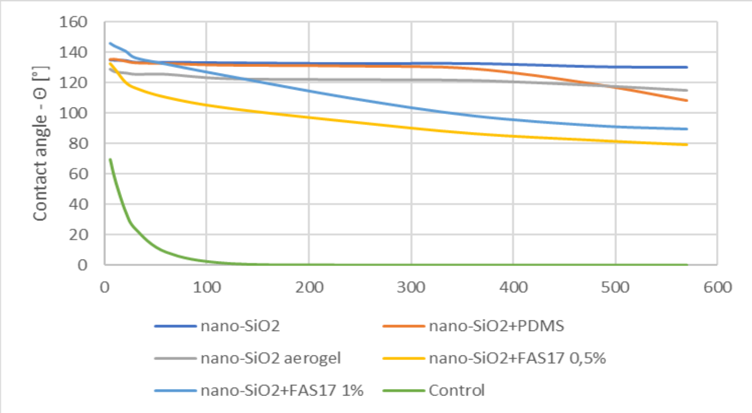

Fig. 20. Change of the water droplet contact angle as a function of time on the investigated pine wood surfaces

3 Biological resistance related investigations

This part of the research work was published in the journal BioResources in 2018 (see list of publications). Additionally presented at 1 international conference with oral presentation. To improve wood properties, immersion and impregnation are the most adequate processes. In the case of some nanoparticles, it is not yet clear whether they are applicable and effective for improving wood properties. The mode of nanoparticle preparation may also influence the efficiency because of different particle sizes and formulations. For that reason, it is necessary to analyze the relationship between these nanoparticles and wood. Nanoparticles have to be in a liquid medium, either dispersed or suspended, for the impregnation of wood to be possible; therefore, the base materials may also be an influencing factor.

Assuming that zinc, copper, silver, and boron nanoparticles show original properties, they may be a tool in developing new wood protection systems. Preparations of nano-metals may possess unique characteristics that are very different from the characteristics of the elemental metal. The objective of this study was to evaluate the preparation of different metal nanoparticles to prevent decay by the brown rot fungus *Coniophora puteana* and the white rot fungus *Coriolus versicolor*. The goal of the planned research was to investigate different nanoparticles and their effect on the durability of wood. Nanoparticle treatments were prepared by using nanoparticles directly from their preparation solutions, without precipitating or re-dispersing them. An important goal of this study was to investigate the leaching resistance of the nanoparticles from the wood material. Instead of surface treatments, a full cross-section treatment was performed, which could make the service life of wooden products longer. An important objective was the improvement of the durability of European wood species.

In some cases, one of the investigated fungi showed a significantly higher tolerance to the investigated nanoparticles; thus, these treatments are not recommended for general use, and only for use at higher concentrations (zinc-oxide, silver nanocubes, and copper). The generally effective nanoparticle treatments were the combinations containing borate in its chemical composition, and zinc-oxide. Only the zinc-oxide, copper, and silver nanoparticles showed a remarkable leaching resistance. The zinc-borate and copper-borate nanoparticles provided the greatest efficiency against the decaying fungi, but they were not resistant to leaching. The best results were found with the zinc-oxide nanoparticle treatment, as it showed a low percentage weight loss for both fungi and a strong leaching resistance. Also, the copper nanoparticles showed potential as an effective treatment at higher concentrations. The investigated nanoparticle treatments provided greater resistance against *Coriolus versicolor* compared with *Coniophora puteana*.

4 UV stabilization related investigations

The results of these tests are under publication recently. Colourfastness characterizes a material's colour's resistance to fading or running. It is an important factor in the evaluation of wood, but unfortunately the colour of the most wood species is not stable under outdoor conditions, it is mainly degraded by UV-radiation. The final result of outdoor weathering on unprotected wood surfaces is the well-known greying effect. To protect the colour of wood material, only surface protection is available nowadays, but in case of surface damages (scratching, cracks, etc.) this protection is not adequate. The impregnation of wood in the whole cross section with UV-stable nanoparticles can protect the wood long lasting. Most promising results can be found in the literature about the utilization of TiO_2, ZnO and Fe_3O_2 nanoparticles to protect the wood against UV-radiation. The advantage of using nanoparticles for wood protection against UV irradiation is that this treatment usually remains the initial colour of wood unchanged, or there is only a slight change in colour.

For the stabilization of the nanoparticles on the wood surfaces, different treatment systems were developed. For this reason, different carrier materials were used, like distilled water, linseed oil and beeswax emulsion. Different concentrations were used as well. Beeswax/ZnO combinations were not tested, as during the preparation of these treatment systems the beeswax was permanently precipitating, thus the preparations was not possible. In summary, 27 different treatment systems were investigated (Tab. 5). Additionally, the UV-resistance and weathering properties of the nanoparticle treated (impregnated) samples were tested with and without surface coating. Natural weathering and artificial ageing of the samples was done as well. Natural weathering was done for 13 months (01.09.2017 – 30.09.2018) with southern inclination. Colour measurement was done at every 30th day. The advantage of artificial ageing is the reproducibility of the measurements, the constant settings and the short testing time. In these tests, artificial light sources like a xenon lamp, a mercury-vapour lamp, etc., are used. Unlike weather exposure, only photodegradation occurs during artificial ageing. The artificial ageing was carried out in an ageing machine at the Department of Physics and Electronics at the University of Sopron. There were two mercury-vapour lamps used (800 Watt), which were 64 cm above the samples. The temperature of the equipment was set to 50°C. The samples were of 10 mm × 50 mm × 50 mm (thickness × width × length) with planed, smooth, tangential surface. The colour and FTIR measurement was determined after 0-6-12-24-48-72-144-200 hours of irradiation.

Table 5. Treatment combinations related to the weathering and artificial ageing tests

Nanoparticle							NP conc.	Carrier material		
TiO_2	ZnO	TiO_2+ZnO	Fe_3O_4	Υ-Fe_2O_3	TNT	TNW	C_{nano} (m/m%)	Dist. Water	Linseed oil	Beeswax
---	---	---	---	---	---	---	0	X	---	---
X	---	---	---	---	---	---	0,5	X	---	---
X	---	---	---	---	---	---	1	X	---	---
---	X	---	---	---	---	---	0,5	X	---	---
---	X	---	---	---	---	---	1	X	---	---
---	---	X	---	---	---	---	0,5	X	---	---
---	---	X	---	---	---	---	1	X	---	---
---	---	---	---	---	---	---	0	---	X	---
X	---	---	---	---	---	---	0,5	---	X	---
X	---	---	---	---	---	---	1	---	X	---
---	X	---	---	---	---	---	0,5	---	X	---
---	X	---	---	---	---	---	1	---	X	---
---	---	X	---	---	---	---	0,5	---	X	---
---	---	X	---	---	---	---	1	---	X	---
---	---	---	---	---	---	---	0	---	---	X
X	---	---	---	---	---	---	0,5	---	---	X
X	---	---	---	---	---	---	1	---	---	X
---	---	---	---	---	X	---	1	X	---	---
---	---	---	---	---	X	---	2	X	---	---
---	---	---	---	---	---	X	1	X	---	---
---	---	---	---	---	---	X	2	X	---	---
---	---	---	X	---	---	---	1	X	---	---
---	---	---	X	---	---	---	2	X	---	---
---	---	---	X	---	---	---	5	X	---	---
---	---	---	---	X	---	---	1	X	---	---
---	---	---	---	X	---	---	2	X	---	---
---	---	---	---	X	---	---	5	X	---	---

4.1 Natural weathering

The most promising result was found in case of the treatment systems using TiO_2 especially those using linseed oil or beeswax emulsion for stabilization of the nanoparticles (Fig. 21-22). Furthermore, the system using Fe_3O_4 provided also promising outdoor colur performance. The use of surface coating improved only slightly the colourfastness of the specimens, which means that the nanoparticles were well stabilized on the wood surface, and only slight leaching happend because of rain and condensed water.

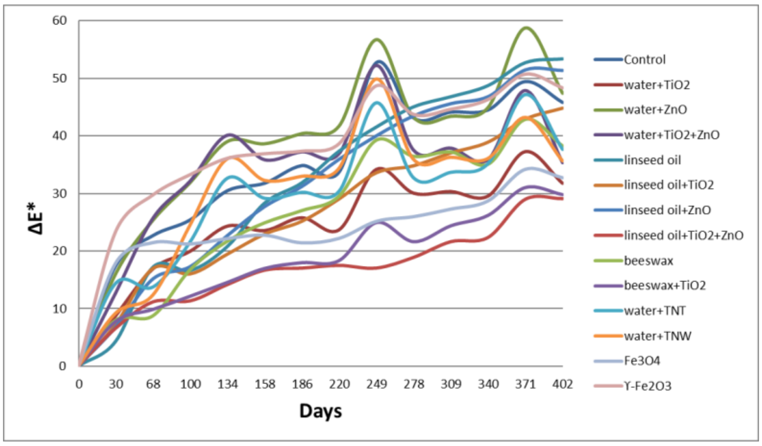

Fig. 21. Total colour change of uncoated scots pine samples during outdoor weathering

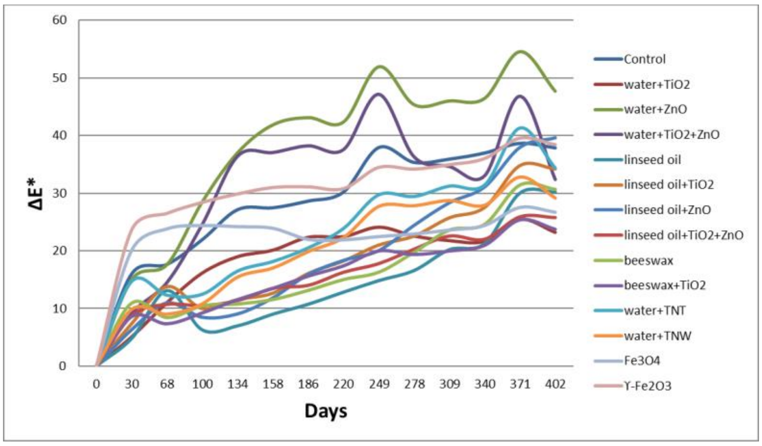

Fig. 22. Total colour change of coated scots pine samples during outdoor weathering

4.2 Artificial ageing

During artificial ageing, similar results to the natural weathering were found, as the titania-based and the Fe_3O_4-based treatmens showed better performance (Fig. 23-24). The total colour change was significantly lower compared tot he natural weathering. The colour change induced by natural weathering and artificial ageing (mercury-vapour lamp) has similar results or tendency, but in case of weather exposure, the colour is influenced by many other factors besides UV radiation. The exposure to real conditions is more useful for industry rather than for laboratory tests, which lack these factors. On the other hand, the weathering tests are non-repeatable and uncontrollable, which makes it difficult to compare results. The sunlight (UV radiation) causes the greatest change in the colour and the surface. The mercury-vapour lamp can help study the photodegradation mechanism in wood, but it cannot simulate natural sunlight. During irradiation, the leaching of lignin and extractives does not take place, which greys the surface. The colour obtained after 200 hours of irradiation is obtained in less than 1 month of weather exposure.

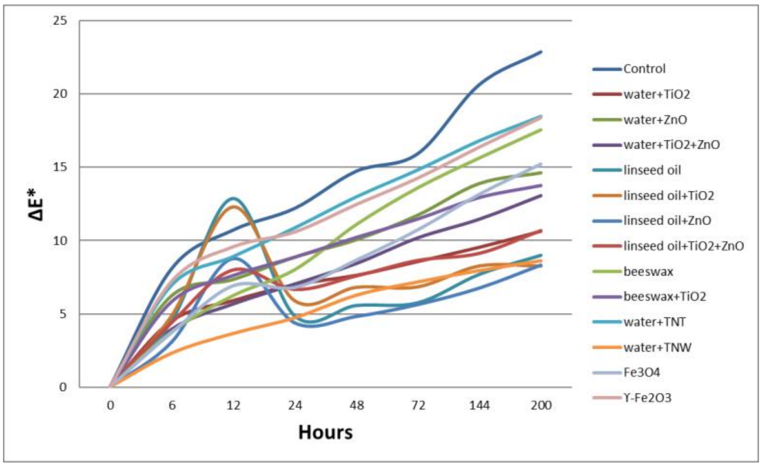

Fig. 23. Total colour change of uncoated scots pine samples during artificial weathering

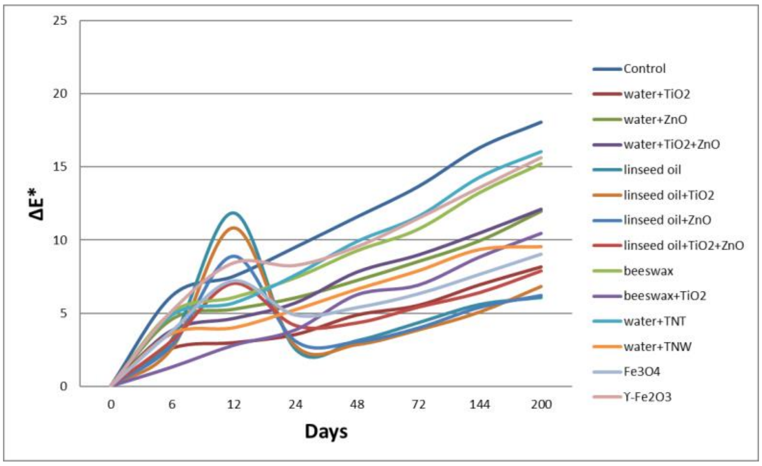

Fig. 24. Total colour change of coated scots pine samples during artificial weathering

5 Publications related to the research work

Published articles:

Charalampos Lykidis, Miklós Bak, George Mantanis, Róbert Németh (2016): Biological resistance of pine wood treated with nano-sized zinc oxide and zinc borate against brown-rot fungi. EUROPEAN JOURNAL OF WOOD AND WOOD PRODUCTS **74**:(6) pp. 909-911.

Bak Miklós, Németh Róbert, Molnár Ferenc (2017): Effect of nanoparticles on the wood-water relations. PRO LIGNO **13**:(4) pp. 308-315.

Bak Miklós, Németh Róbert (2018): Effect of different nanoparticle treatments on the decay resistance of wood. BIORESOURCES **13**:(4) pp. 7886-7899.

Bak Miklós, Molnár Ferenc, Németh Róbert (2018): Improvement of dimensional stability of wood by silica nanoparticles. WOOD MATERIAL SCIENCE AND ENGINEERING, available online: https://doi.org/10.1080/17480272.2018.1528568

Articles under press:

Bak Miklós (accepted, under press): Possibilities of using nanotechnology in wood colour protection. ÓBUDA UNIVERSITY E-BULLETIN

Abstracts, conference papers:

Bak Miklós, Molnár Ferenc (2017): Decreasing the hygroscopicity of wood with nanoparticles In: Svetozar Madjov (Editors) COST FP1303 - Design, application and aesthetics of biobased building materials. Konferencia helye, ideje: Szófia, Bulgária, 2017.02.28-2017.03.01., Sofia University Press, pp. 90-91. (ISBN:978-619-160-758-7)

Bak Miklós, Molnár Ferenc, Németh Róbert (2017): Improvement of dimensional stability of wood by silica-nanoparticles. In: Vjekoslav Zivkovic, Dennis Jones (Editors) Building with bio-based materials: Best practice and performance specification. Konferencia helye, ideje: Zágráb, Horvátország, 2017.09.06-2017.09.07., University of Zagreb, pp. 83-84. (ISBN:978-953-292-051-2)

Bak Miklós, Németh Róbert, Molnár Ferenc (2017): Effect of nanoparticles on the wood-water relations. In: Lidia Gurau, Mihaela Campean, Mihai Ispas (Editors) Proceedings of the 11th edition of the International Conference "Wood Science and Engineering in the third Millenium". Konferencia helye, ideje: Brasov, Románia, 2017.11.02-2017.11.04. Transilvania University of Brasov, pp. 421-428.

Bak Miklós, Molnár Ferenc, Németh Róbert (2017): Modification of wood by silica nano-particles. In: Ivica Župčić, Vjekoslav Živković, Josip Miklečić (Editors) Proceedings of the 28th International Conference on Wood Science and Technology (ICWST). Konferencia helye, ideje: Zagreb, Croatia, 2017.12.07-2017.12.08. University of Zagreb

Bak Miklós, Németh Róbert (2018): Improving the decay resistance of wood by nanoparticles. In: Marius C. Barbu, Alexander Petutschnigg, Eugenia M. Tudor (Editors) Proceedings of the 5th International Conference on Processing Technologies for the Forest and Bio-based Products Industries (PTF BPI 2018). Place and date of the conference: Freising/Munich, Germany, September 20-21, 2018. pp. 175-182.

Németh Róbert, Csóka Levente, Bak Miklós (2018): Achievements of nanotechnology in the wood industry. In: Ivana, Radojcic Redovnikovic; Tamara, Jakovljevic; Vlatka, Petravic Tominac; Manuela, Panic; Renata, Stojakovic; Dina, Erdec; Kristina, Radosevic; Visnja, Gaurina Sarcek; Marina, Cvjetko Bubalo (Editors) Natural resources green technology & sustainable development: Book of Abstracts. Place and date of the conference: Zagreb, Croatia, June 5-8, 2018. p. 184.

Bak Miklós, Németh Róbert (2018): Improvement of the dimensional stability of wood by nanosilica treatments. In: Németh Róbert, Alfred Teischinger, Peter Rademacher, Bak Miklós (Editors) Hardwood Conference Proceedings Volume 8. ISBN: 978-963-359-095-9. Place and date of the conference: Sopron, Hungary, October 25-26, 2018. pp. 125-126.

Bak Miklós; Molnár Ferenc; Németh Róbert (2018): Dimensional stabilization of wood using silica nanoparticles. In: Lars, Berglund; Ingo, Burgert (Editors) Book of Abstracts of the Wood Nanotechnology Conference 2018. Place and date of the conference: Ascona, Switzerland: September 02-05, 2018. p. 42.

6 Other achievments

During the research period, I had the possibility to work together with BSc students on the selected topics. The outcomes of this work are as follows:

- István Molnár helped during the laboratory work, the preparation of the nanoparticle treatment systems and the treated material for UV-resistance tests
- Ferenc Molnár was working on the topic of wood-water relations, and based on this work, he did the following achievements:

    - 2× special prize (2016, 2017) at the Scientific Students' Associations Conference (TDK) of the Simonyi Károly Faculty
    - participation at the National Scientific Students' Associations Conference in 2017 (OTDK)
    - Finishing a BSc thesis in 2017 with the title: „Effect of nanoparticles on the wood-water relations - Nanorészecskék hatásának vizsgálata fa-víz kapcsolatokra”
- Dávid Takács was working on the topic of UV-stabilization of wood by nanoparticles, and based on this work, he did the following achievements:
    - finishing a BSc thesis in 2018 with the title: „Improving the colorfastness of wood by nanoparticles - Faanyagok színállóságának növelése nanorészecskékkel”

7 References

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Donath, S., Militz, H., Mai, C. (2004). Wood modification with alkoxysilanes. *Wood Science and Technology*, **38**(7), 555–566.