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EFFECT OF NANOPARTICLES ON THE WOOD-WATER RELATIONS

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Abstract:

Results of an experimental research about the effect of different titanate nanoparticles on the wood-water relations are shown in this paper. Different wood species were used for the experiments. Treatment of wood with the nanoparticles was performed by impregnation method. Different concentrations of nanoparticles were used. Investigated properties after treatment were shrinking/swelling coefficient, equilibrium moisture content (EMC), water uptake and moisture permeability. Beside these, colour change (CIELab) and mechanical properties (compression strength and surface hardness) were investigated as well. Overall, we can state according to our investigations so far, that the impregnation with nanoparticles was successful. Shrinking and swelling properties decreased remarkably in case of all the four investigated wood species. As a side effect of the treatments, a slight colour change could be observed as well. No effect on the mechanical properties could be found as a result of the treatment.

Key words: *nanoparticles; shrinking/swelling; water uptake; EMC; colour change.*

INTRODUCTION

Wood is in contact with air humidity in all utilization fields. In many cases, wood elements are used as space border. Furthermore, during the processing wood undergoes a drying process. In these cases, it is important to know the sorption and diffusion properties of the wood to be able to understand the expected moisture transport processes in the wood during utilization. Diffusion properties of wood are strongly dependent on wood species and anatomical directions, but climatic conditions and sample size are also important factors (Jalaludin et al. 2010, Pfriem et al. 2010).

Moisture uptake in wood occurs through diffusion and capillary flow. Below the fibre saturation point moisture can transported as water vapour in the lumens, or as bound water in the cell walls with the diffusion. In this phase of moisture movement can be modelled successfully with a diffusion front moving through the wood, causing smooth moisture content gradients in the different cardinal direc-tions (Droin-Josserand et al. 1988). However, in reality the moisture transport in wood is suspected to be more difficult (Absetz and Koponen 1997).

The characteristic of modified woods' sorption behaviour usually includes slower reaction to relative humidity changes than natural wood; therefore, the moisture uptake is lower and slower (Hill 2006). Changes in wood-water relations due to modification are also strongly influenced, however, by the wood species. The phenomenon of modification is even more complicated, as usually all of the treatment parameters have influence on the wood-water relations (WPG, concentrations, temperature, duration, etc.). The moisture uptake rate can therefore be different after various treatments.

The utilization of nanoparticles to improve the properties of wood is not widely investigated recently. On the other hand, a lot of promising results were achieved with the use of nanoparticles in relation to the mechanical, combustion, hydrophobic and some other properties of different polymers, papers or textiles (Wang et al. 2006; Csóka et al. 2007; Chen and Yan 2012; Nypelö et al. 2012; Jiang et al. 2011; Sun et al. 2007; Textor and Mahltig 2010). Recently there is only limited information available about the utilization of nanoparticles to improve the wood properties, but all results are positive. With the use of different nanoparticles the moisture uptake is reducible, UV-protection, mechanical properties and durability is improvable (Rassam et al. 2012; Niemz et al. 2010; Yu et al. 2011; Mahltig et al. 2008). In some cases, fire resistance could be improved as well (Shabir Mahr et al. 2012). According to the careful examination of the results mentioned above, for the research received nanoparticles can be selected (different titanate nanotubes and nanowires, nanozinc, titan dioxide, montmorillonite and other nanoclays, etc.).

The novelty of the planned research is to investigate some nanoparticle, which effect on wood properties and the applicability on wood is not known until yet. Instead of surface treatments a full cross-section treatment is planned which could make the service life of wooden products longer. The utilization of wood contributes to the sustainable development. The technical properties of most of the European wood species are in many respects behind some competing materials, which are originating from sources that are disadvantageous in aspect of sustainability (endangered tropical wood species, plastics). An important objective is the expressive improvement of the properties of European wood species.

OBJECTIVE

The main goal of this investigation was to determine the influence of nanoparticle impregnation on the wood-water relations. This is relevant because it results in improvement of dimensional stability – but is also important during the utilization. During the service life of a product the surrounding climate is regularly changing, thus the EMC, and therefore the dimensions, are changing too. Short time exposure to extreme climates (either high or low relative humidity) will not result in pronounced dimensional changes if the moisture uptake is damped. The nanoparticle impregnation is a promising method to reduce the shrinking and swelling and therefore investigations are necessary to prove the effect of the treatment on the water-related properties of wood.

MATERIAL, METHOD, EQUIPMENT

Pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) wood was used for the tests. For the impregnation of wood, two types of aqueous emulsions were used, namely hydrophobic titanate-nanowire (HTNW) and hydrophobic titanate nanotube (HTNT). Both emulsions were used with two different concentrations, namely 1 wt% and 2 wt%. This resulted in four different treatments. The emulsions are proprietary formulas of NanoBakt Kft. (Budapest, Hungary). The nanowires were comprised of particles with dimensions of 50-100 nm in diameter and 1-10µm in length, furthermore the nanotubes 5-8 nm in diameter and 100-500 nm in length. Their specific size distribution was not available.

The samples were weighed as a first step. The impregnation was carried out according to the full-cell process in a vacuum chamber at 20°C. The impregnation process involved an initial vacuum phase at 100 mbar for 30 min. The chamber was then pressurised at atmospheric pressure for 60 min. The surfaces of the specimens were then gently rinsed with water to wash away residual material and conditioned at a temperature of 20°C and a relative humidity of 65% for 20 days. Consequently, the final weight was measured and the weight percent gain (WPG, %) for each specimen was calculated according to equation (1):

$$WPG = \frac{m_{imp} - m_{initial}}{m_{initial}} \times 100\ [\%] \qquad (1)$$

where:
$m_{initial}$: weight of the sample before impregnation [g]
m_{imp}: weight of the sample after impregnation [g]

Colour Change

Colour measurements were carried out with a colorimeter (Konica-Minolta 2600d). The CIELab colour coordinates were calculated based on the D65 illuminant and 10° standard observer with a test-window diameter of 8mm. The relatively large window was chosen to measure the average colour of earlywood and latewood regions combined. The radial surface of the sample was used for colour measurement. The colour of randomly chosen 3 points were measured on each sample. Measurements on samples were carried out before and after impregnation., and the total colour change (ΔE^*) was calculated.

Shrinking and swelling

Samples with the dimensions of 20×20×30mm (rad×tang×long) were used. 20 samples for each treatment, and 20 untreated samples served as control. After the impregnation, the samples were climatized at 20°C and 65% relative humidity until constant mass. After climatization samples were dried at 103±2°C. Radial and tangential dimensions of the samples were measured before and after the drying. Also weighing of the samples was carried out before and after the drying. From these data the shrinking coefficient was calculated in both radial and tangential direction, according to equation (2):

$$SH_{coeff} = \frac{l_{wet} - l_{dry}}{l_{dry} \times U} \times 100 \qquad (2)$$

where:
l_{wet}: radial or tangential dimension before drying [mm]
l_{dry}: radial or tangential dimension after drying [mm]
U: moisture content of the sample [%]

After drying, the same samples were immersed into water for 10 days. Radial and tangential dimensions of the samples were measured before and after the immersion. Also weighing of the samples was carried out before and after the immersion. From these data the swelling coefficient was calculated in both radial and tangential direction, according to equation (3):

$$SW_{coeff} = \frac{l_{wet} - l_{dry}}{l_{wet} \times U} \times 100 \tag{3}$$

where:
l_{wet}: radial or tangential dimension after immersion [mm]
l_{dry}: radial or tangential dimension before immersion [mm]
U: moisture content of the sample [%]

Water uptake

Samples with the dimensions of 10×50×50 mm (rad or tangential×tang or radial×long) were used. 20 samples for each treatment, and 20 untreated samples served as control. Water uptake through both radial and tangential surface was measured. After the impregnation, the samples were climatized at 20°C and 65% relative humidity until constant mass. Samples were sealed at the edges and at one radial/tangential surface and weighed. Samples were then immersed to water with the unsealed surface and weighed at 2, 4, 8, 24, 48 and 72 hours. Water uptake was calculated according to equation (4):

$$W = \frac{m}{A} \quad \left[\frac{g}{m^2}\right] \tag{4}$$

where:
m: mass of the samples [g]
A: radial or tangential surface area of the samples [mm^2]

Equilibrium moisture content (EMC)

Samples with the dimensions of 20×20×30mm (rad×tang×long) were used. 5 samples for each treatment, and 5 untreated samples served as control. Samples were dried at 103±2°C and weighed, then climatized at 20°C and 65% relative humidity until constant mass. After climatization, the samples were weighed again. EMC was calculated according to equation (5):

$$EMC = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \tag{5}$$

where:
m_{wet}: wet weight of the samples
m_{dry}: dry weight of the samples

RESULTS AND DISCUSSION

Retention

The amounts of chemical retention for tested specimens are shown in Fig. 1. There were no notable differences in chemical retention based on wood species, but significant differences based on nano-suspension concentration. The retention was increasing quite proportionately with the preservative concentration as the mean ratio of retention is 1,96 - 2,12, depending on wood species and nanoparticles type. This result complied with the ratio of nano-suspension concentrations used during our experiments 2. It showed that the decay specimens effectively absorbed the nano-suspensions.

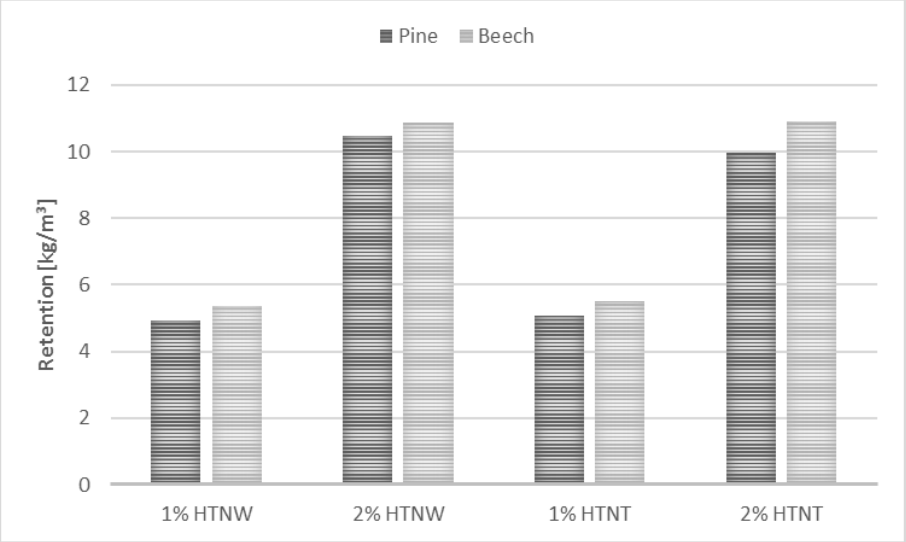

Fig. 1.
Retention of nanoparticles as a result of impregnation.

Colour Changes

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 (Fig. 2.). However, only the treatment with 1% HTNW resulted in a well visible colour change. In case of pine no significant differences in colour change could be found between the different impregnations. In case of beech, the increasing concentration of the nanoparticles resulted in decreasing colour change. The colour change was visible as a fading (whitening) of the initial colour.

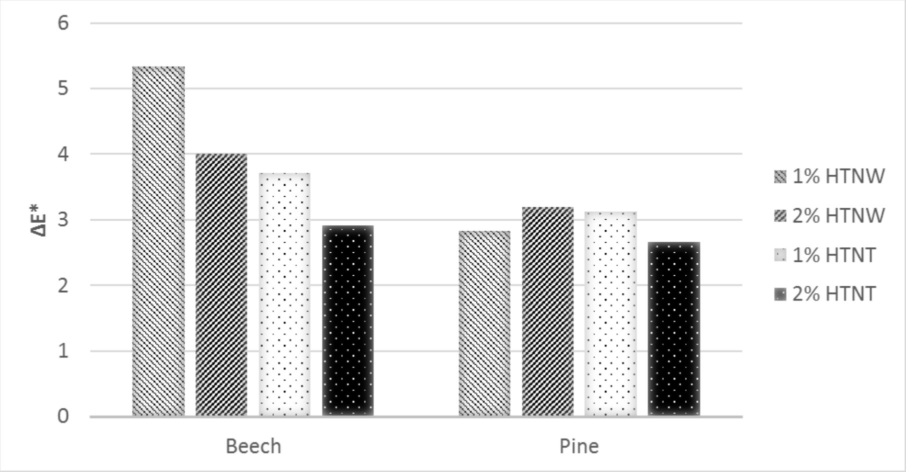

Fig. 2.
Colour change as a result of nanoparticle treatment.

Shrinking and swelling

Shrinking coefficient decreased in most cases as a result of nanoparticle impregnation. An interesting result is that the treatment decreased the shrinking coefficient more effective in radial direction, compared to the tangential direction (Fig. 3.). A possible reason for that can be a better penetration of the nanoparticles in radial direction, through the rays. 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.

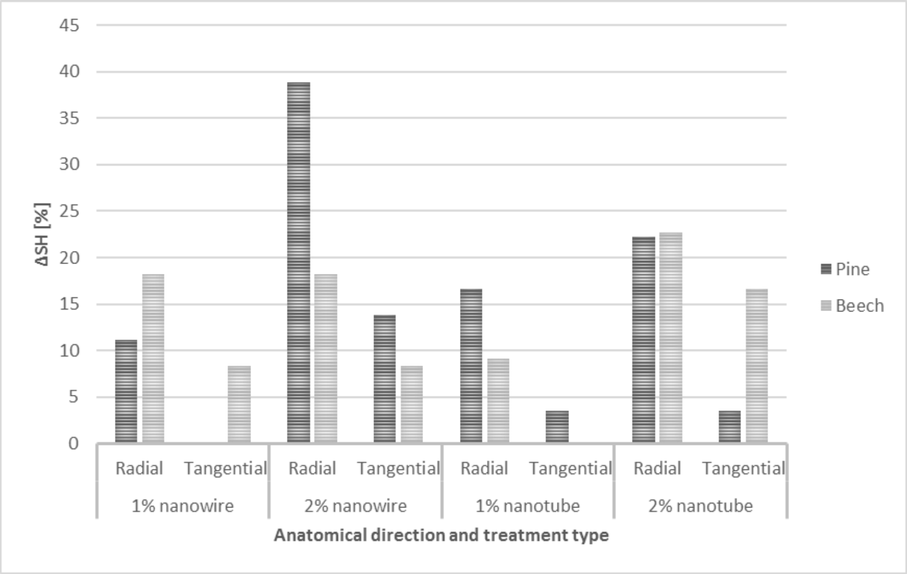

Fig. 3.
Decrease in the shrinking coefficient as a result of nanoparticle treatment.

After the shrinking test, the same samples were immersed to water to accomplish the swelling test. The efficiency of the treatment increased after this step in radial direction in case of the most treatments (Fig. 4.). In tangential direction, it remained unchanged or increased slightly as well, which might be a result of a leaching effect. This phenomenon is explained by the hydrophobic properties of the used nanoparticles. After the cell wall dried, the nanoparticles kept away the water more efficiently and this resulted in a lower swelling.

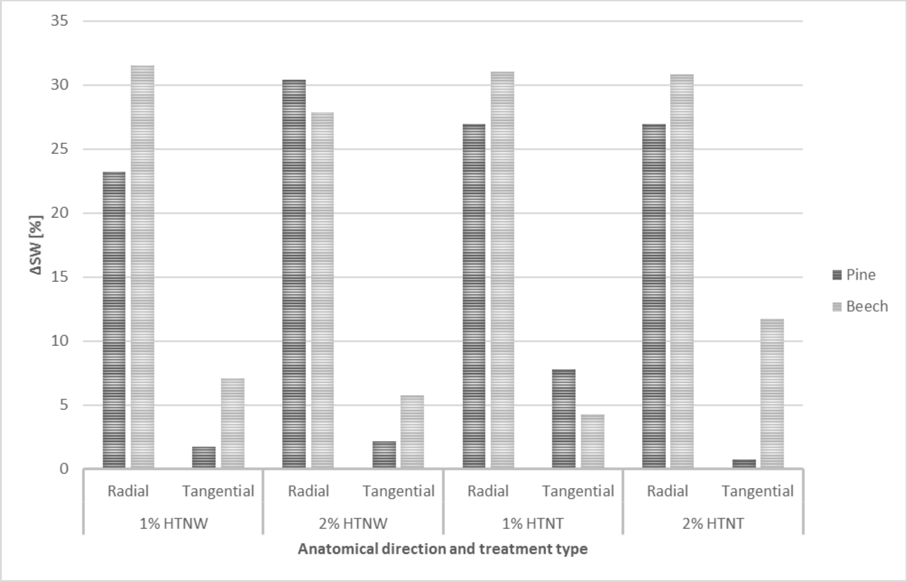

Fig. 4.
Decrease in the swelling coefficient as a result of nanoparticle treatment.

Water uptake

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) (Fig. 5-6.). 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.

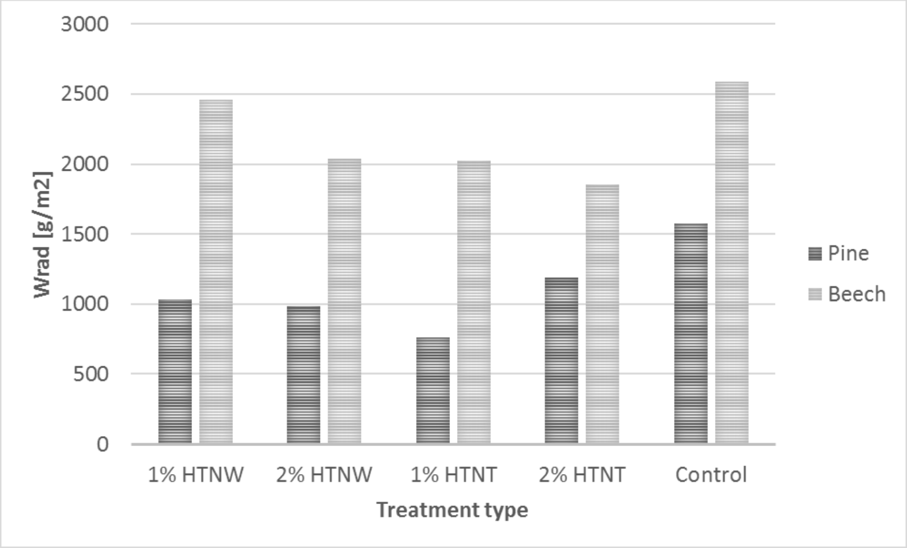

Fig. 5.
Water uptake during 72 hours immersion in water in radial direction.

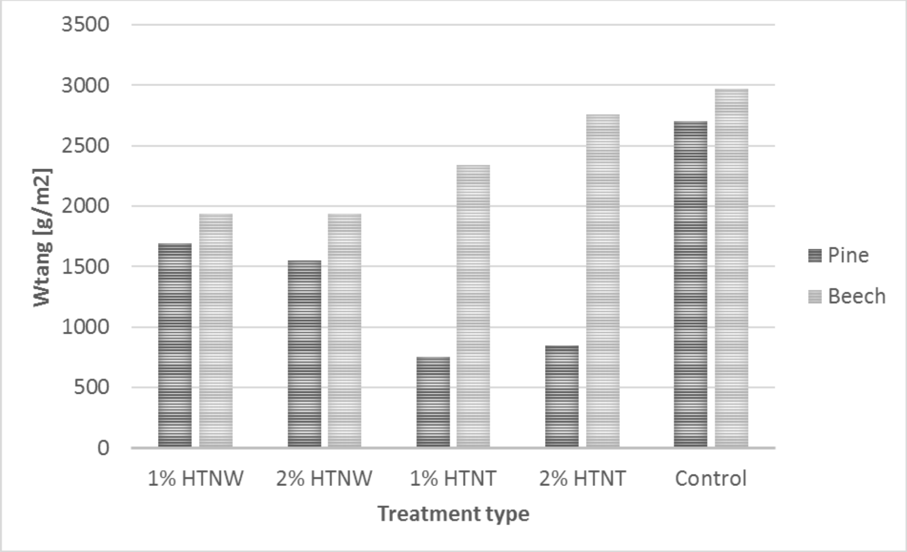

Fig. 6.
Water uptake during 72 hours immersion in water in tangential direction.

Equilibrium moisture content

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.

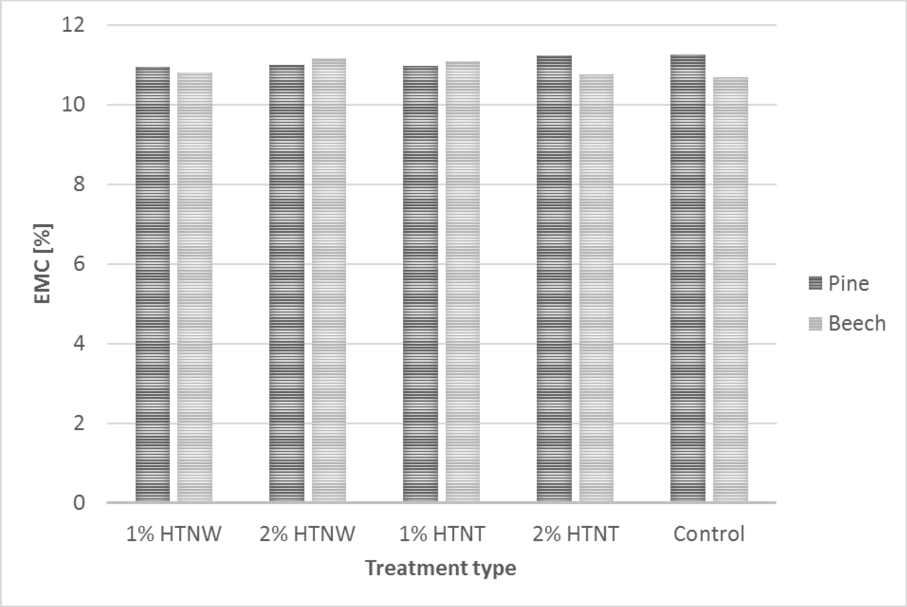

Fig. 7.
Equilibrium moisture content of the impregnated and control samples.

CONCLUSIONS

A slight colour change could be observed as a result of nanoparticle impregnation. The colour change was visible as a fading (whitening) of the initial colour. Shrinking and swelling could be decreased by the treatments, but there are differences in the effectiveness between the anatomical directions. A possible reason for that can be a better penetration of the nanoparticles in radial direction, through the rays. Furthermore, the distribution of the nanoparticles seems to be uneven in the cell walls, due to the unoptimal shape and length of the particles. Water uptake decreased as well and HTNT treatment was more effective compared to HTNW treatment. EMC remained unchanged after treatments.

The treatments gave an effective protection against shrinking and swelling, but the water uptake decreased only slightly in most cases and the EMC remained unchanged. Taking into consideration these results, we can state that the mode of action of the impregnation with HTNW and HTNT particles is a physical blocking of the penetration of liquid water into the cell wall, which is a physical bulking effect supplemented by the hydrophobic properties of the particles.

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REFERENCES

Absetz I, Koponen S (1997) Fundamental diffusion behaviour in wood. Procceedeings of Interna-tional Conference of COST Action E8, Mechanical Performance of Wood and Wood Products. 16-17 June 1997, Copenhagen, Denmark.

Chen J, Yan N (2012) Hydrophobization of bleached softwood kraft fibers via adsorption of organo-nanoclay. BioResources 7(3):4132-4149.

Droin-Josserand A, Taverdet JL, Vergnaud JM (1988) Modeling the absorption and desorption of moisture by wood in an atmosphere of constant and programmed relative-humidity. Wood Science and Technology 22:299-309.

Hill CAS (2006) Wood Modification – Chemical, thermal and other processes. John Wiley and sons Ltd., 30-36.

Jalaludin Z, Hill CAS, Xie Y, Samsi HW, Husain H, Awang K, Curling SF (2010) Analysis of the water vapour sorption isotherms of thermally modified acacia and sesendok. Wood Material Science and Engineering 5(3-4):194-203.

Jiang X, Tian X, Gu J, Huang D, Yang Y (2011) Cotton fabric coated with nano TiO_2-acrylate copolymer for photocatalytic self-cleaning by in-situ suspension polymerization. Applied Surface Science 257(20):8451-8456.

Mahltig B, Swaboda C, Roessler A, Böttcher H (2008) Functionalising wood by nanosol application. Journal of Materials Chemistry 27(18):3180-3192.

Niemz P, Mannes D, Herbers Y, Koch W (2010) Untersuchungen zum Verhalten von mit Nanopartikeln imprägniertem Holz bei Freibewitterung. Bauphysik 32(4):226–232.

Nypelö T, Pynnönen H, Österberg M, Paltakari J, Laine J (2012) Interactions between inorganic nanoparticles and cellulose nanofibrils. Cellulose 19(3):779-792.

Pfriem A, Zauer M, Wagenführ A (2010) Alteration of the unsteady sorption behaviour of maple (*Acer pseudoplatanus* L.) and spruce (*Picea abies* (L.) Karst.) due to thermal modification. Holzforschung 64(2):235-241.

Rassama G, Abdib Y, Abdia A (2012) Deposition of TiO_2 nano-particles on wood surfaces for UV and moisture protection. Journal of Experimental Nanoscience 7(4):468-476.

Shabir Mahr M, Hübert T, Schartel B, Bahr H, Sabel M, Militz H (2012) Fire retardancy effects in single and double layered sol–gel derived TiO_2 and SiO_2-wood composites. Journal of Sol-Gel Science and Technology 64(2):452-464.

Sun Q, Schork FJ, Deng Y (2007) Water-based polymer/clay nanocomposite suspension for improving water and moisture barrier in coating. Composites Science and Technology 67(9):1823-1829.

Textor T, Mahltig B (2010) A sol–gel based surface treatment for preparation of water repellent antistatic textiles. Applied Surface Science 256:1668–1674.

Wang Z, Han E, Ke W (2006) An investigation into fire protection and water resistance of intumescent nano-coatings. Surface and Coatings Technology 201:1528-1535.

Yu X, Sun D, Li X (2011) Preparation and characterization of urea-formaldehyde resin-sodium montmorillonite intercalation-modified poplar. Journal of Wood Science 57(6):501-506.