Report on the Troëdsson Postdoc-project 2013–2015

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Funktionella ytbeläggningar på trä/ Functional multilayer coatings to improve properties of wood

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The target of the postdoc-project was to develop new type of multifunctional coatings for wood in order to improve its properties (liquid repellence, antifungal properties and repellence against UV-radiation and severe climate conditions) and eventually its performance in end-use applications. The postdoc-project was a continuation to the research exchange (year 2012) of Dr. Mikko Tuominen, where the key technologies and application areas of SP Chemistry, Materials and Coatings and Tampere University of Technology (TUT) were studied. The Postdoc-project "Functional multilayer coatings to improve properties of wood" was granted from Nils and Dorthi Troëdsson Foundation for Scientific Research at the beginning of 2013 and the work started in August 2013. The partners participating in the research were Prof. Jyrki Mäkelä (TUT), Dr. Stig Bardage (SP), Prof. Magnus Wålinder (KTH) and Prof. Agne Swerin (SP).

The multifunctional coating on wood was created using two state of the art techniques, i.e. liquid flame spray (LFS) and plasma deposition. The created TiO_2-PFH coating was superamphiphobic, since it repelled both water and oil. To our knowledge, this was the first time superamphiphobicity was shown for renewable bio-based material, such as wood. The coating had high transparency and it did not change color of wood. The self-cleaning on wood surfaces was demonstrated by using water and oil. The coating showed good resistance in water droplet impact test, but it had limited durability against severe climate conditions, i.e. rain and UV-illumination cycles in Weatherometer test. In addition, the coating showed fungal resistance as long as the coated wood did not get wetted. The most likely reason for the loss of liquid repellence of the coating is the repeatable wetting and drying of wood during the Weatherometer test, which causes mechanical deformation and eventually leads to cracking of coated wood surface. From the industrial point of view the key question is the durability of the coatings. In outdoor applications, the coated wood have to perform against several deteriorating factors, such as UV, moisture, fungal and water simultaneously. One of the main observation in the research was the poor correlation between lab-scale spontaneous wetting tests (e.g. contact angle measurements) and forced wetting test (e.g. Weatherometer test). There is an evident need to develop lab-scale measurement technique for force wetting, which can predict the performance of coating in severe climate conditions.

The research work will be published in three scientific papers: Paper 1: Superamphiphobic coating for wood (submitted to Applied Surface Science), paper 2: Climate protective coating for wood (all research is performed and manuscript in preparation), paper 3: Antifungal coating for wood (all research is performed and manuscript in preparation). In addition, the postdoc-project includes three joint publications with former PhD students Maziar Sedighi, Golrokh Heydari Hamedani and Lina Ejenstam.

Key words: liquid flame spray (LFS), plasma deposition, wood, wetting, liquid repellence, superamphiphobic, superhydrophobic, superoleophobic, water repellence, oil repellence, self-cleaning, antifungal properties, UV-repellence, biobased material, nanoparticle, perfluorohexane.

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1 Summary

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2 Postdoc-project: Functional multilayer coatings to improve properties of wood

2.1 Partners involved

The applicant, i.e. Dr. Mikko Tuominen, worked the year 2012 at SP as a visiting researcher from Tampere University of Technology (TUT). The research exchange was part of the Nanorata-project (TEKES/Finnish national funding). The target of the research exchange was to increase the knowledge in the research field of thin functional coatings, and furthermore to enhance the co-operation between the SP and TUT. The main target of visit was to combine the key technologies of TUT and SP, i.e. LFS and plasma deposition techniques. In addition, these techniques were studied on the key research areas of SP, i.e. ice free surfaces, wood surfaces, and anti-corrosive surfaces. Based on the results of the research visit the Postdoc-project "Functional multilayer coatings to improve properties of wood" was successfully applied from Nils and Dorthi Troëdsson Foundation for Scientific Research at the beginning of 2013 and the work started in August 2013.

The partners involved in the Postdoc-project were:

- Prof. Agne Swerin, Research Director at SP and Troëdsson Professor in Forest-based Surface Chemistry at KTH.
- Prof. Jyrki Mäkelä, Aerosol physics laboratory at TUT, Finland.
- Dr. Stig Bardage SP Technical Research Institute of Sweden, Sustainable Built Environment, Biobased Materials and Products
- Prof. Magnus Wålinder, KTH Royal Institute of Technology, Department of Civil and Architectural Engineering, Building Materials

The postdoc-project combined knowledge and partners from different research areas, i.e. LFS and plasma coating technologies, wood coatings, wood as building material, antifungal and climate testing, etc. Collaboration between (former) PhD students, i.e. Lina Ejenstam, Golrokh Heydarihamedani and Maziar Sedighi at SP and KTH Surface and Corrosion Science continued. Discussions with potential industrial partners started (Stora Enso Building and Living/Platform director Janne Pynnönen), but no concrete actions were taken.

2.2 Research plan

The research was planned for two years. The budget included one full year's personnel costs and two years' research and travelling costs. The remaining personnel costs were covered from other projects. The research plan, i.e. application, substrates, coatings and characterisation is presented in Table 1.

Table 1. *Research plan for 2 years; applications, substrates, coatings and characterization.*

Application	Substrate	Coating	Characterization
Testing of LFS-precursors and optmization of LFS-parameters	Wood: birch, spruce, wood laminates, etc.	LFS: TiO_2, SiO_2, CeO_2, etc.	Contact angles, (water, oil, hexadecane), SEM
Testing of plasma coatings	Wood: birch, spruce, wood laminates, etc.	Plasma deposition: fluorine (PFH), siloxane (HMDSO), etc.	Contact angle (water, oil, hexadecane), XPS
Amphiphobic coating	Wood: birch, spruce, wood laminates, etc.	LFS (optmized) + Plasma deposition (optmized)	Contact angle (water, ethylene glycol, dioodomethane, oil, hexane, paint, ink, etc.)
UV-repellence and enviromental testing	Wood: birch, spruce, wood laminates, etc.	LFS (optmized) + Plasma deposition (optmized)	Transmission analyses, visual light/UV-exposures, XPS and Contact angles
Antibacteria/ antifungal properties	Wood (birch, spruce, etc.) and wood laminates	LFS (optmized) + Plasma deposition (optmized)	Bacterial inoculation with e.g. E. coli and B. subtilis with evaluation of relative growth from optical density measurements. Fungal activity after inoculation by T. versicolor according to EN 252 or ASTM standards
Self-cleanability	Wood (birch, spruce, etc.) and wood laminates	LFS (optmized) + Plasma deposition (optmized)	Self cleanability test, optical microscope
Other properties: e.g. water droplet durability.	Wood (birch, spruce, etc.) and wood laminates	LFS (optmized) + Plasma deposition (optmized)	water droplet and sand tests, SEM, AFM, XPS

The LFS and plasma coatings were performed at TUT and SP, respectively. The wetting tests, XPS, self-cleaning, SEM, lab-scale UV-illumination, water droplet durability tests were carried out at SP Chemistry and Materials and Surfaces. Antifungal and Weathero-meter tests were performed at Sustainable Built Environment, Biobased Materials and Products in the guidance and supervision of Dr. Stig Bardage. The research work will be published in three scientific papers:

- Paper 1: Superamphiphobic coating for wood
    - submitted to Applied Surface Science
- Paper 2: Climate protective coating for wood
    - All research is performed and manuscript is still in preparation
- Paper 3: Antifungal coating for wood
    - All research is performed and manuscript is still in preparation

Unfortunately, the schedule of the original publication plan delayed due of fundamental work and understanding of liquid repellence, i.e. the required overhang hydrophobic capped structures giving a high re-entrant curvature on wood. A more than planned amount of work was also dedicated to UV- and Weatherometer tests and antifungal work. In addition, the postdoc-project included joint publications with Maziar Sedighi, Golrokh Heydari Hamedani and Lina Ejenstam, see publication list, which were not included in the original plans.

3 Introduction

Wood plays an important role in society, in terms of heat source, raw material for paper and as a construction material. Due to its superior mechanical properties, light weight, easy converting and aesthetic appearance it is extensively used in buildings, bridges, furniture and so forth [1, 2]. However, a drawback in exterior building material applications wood has often poor weathering properties. Weathering is a surface phenomenon caused mainly by solar radiation, moisture and microbial degradation [1, 2]. Wood, as a hydrophilic, hygroscopic, porous and fibrous material, is especially vulnerable to water sorption because of the rapid penetration into the structure of wood causing swelling and eventual decrease of mechanical properties as well as providing conditions for biological degradation. Water repellency is one of the main reasons why exterior wood products are coated [3, 4, 5, 6].

In recent years, liquid repellent/superhydrophobic surfaces inspired by nature, e.g. the lotus leaf have attracted much attention in fundamental and applied research. There are numerous studies on how to improve water repellency of wooden surfaces using novel surface modification techniques. The function of the oxide particles is to increase surface roughness, which together with a low surface energy coating can give a superhydrophobic surface. Roughness combined with hydrophobicity results in air/vapor pockets trapped between the solid and liquid (composite interface) described by Cassie-Baxter [7] thus leading to a significant decrease in the solid–liquid adhesion and an increase of the contact angle [8]. It can also result in a solid-liquid interface with very high apparent water contact angles but which is wetted at the roughness interstices as described by Wenzel [9]. Superhydrophobic surfaces are defined by a water contact angle of 150° or above and a sliding or roll-off angle below 10° [10, 11, 12]. Not only water, but also other liquids are known to affect wood [3]. In spite of numerous natural superhydrophobic surfaces, there are no known naturally occurring surfaces that can show high contact angles (>150°) and low roll-off angles (<10°) with sessile drops of oils and non-polar liquids.

The target of the postdoc-project was to create a liquid repellent/superamphiphobic surface on wood using a two-step approach and study its repellence against severe climate conditions, i.e. rain and UV-exposure cycles and different kind of fungal, i.e. mold, blue stain, etc. The specific sub-micron- and nanostructure onto wood surfaces was generated by liquid flame spray (LFS) technique. LFS is a thermal aerosol-based process utilized for depositing nano-sized metal and metal oxide particles. A limitation of a LFS-based superhydrophobic TiO_2 coating has been the poor repellency against low surface tension liquids [13]. We use plasma deposition to provide a hydrophobic capping of the TiO_2 nanoparticle coating by a low surface energy fluorine plasma polymer coating. To our knowledge, this is the first time superamphiphobicity based on overhang structures is shown for a renewable bio-based material. An aim of the plasma polymer layer was also to improve the durability of the TiO_2 coating, since commercial application of superamphiphobic surfaces largely relies on their mechanical and forced wetting durability [12, 14, 15]. Despite the importance of durability, this aspect has received relatively little attention, especially in wood applications [3, 16, 17]. The resulting coatings show extreme water and oil repellency and offer a novel and scalable surface modification technique to a variety of substrates, here exemplified on wood surfaces. However, the durability against forced wetting, moisture and UV-illumination must be enhanced before the coatings can be applied in severe outdoor applications. Evidently, a link between lab-scale wetting test and real life wetting (Weathero-meter) test is needed.

4 Results

4.1 Repellence against liquids

Wood can have a rather geometrically homogeneous multi-scale structure. The fibrous structure of wood gives a micro-scale roughness, whereas uniformly distributed TiO_2 nanoparticle coating containing both particles and agglomerates, provides sub micrometer- and nano-scale roughness. Such a multi-scale surface roughness together with the right surface chemistry can provide an air/vapor layer at the interface between the surface and drops preventing the liquid to wet the surface and penetrate through the thin coating into the wood. The wettability of TiO_2 and PFH coated wood surfaces was evaluated by measuring static contact angles and roll-off angles of water, ethylene glycol, diiodomethane, olive oil and hexadecane with surface tensions of 72.8, 48.3, 50.8, 32.1, 27.6 mNm^{-1}, respectively. Figure 1 shows the static contact angle (CA).

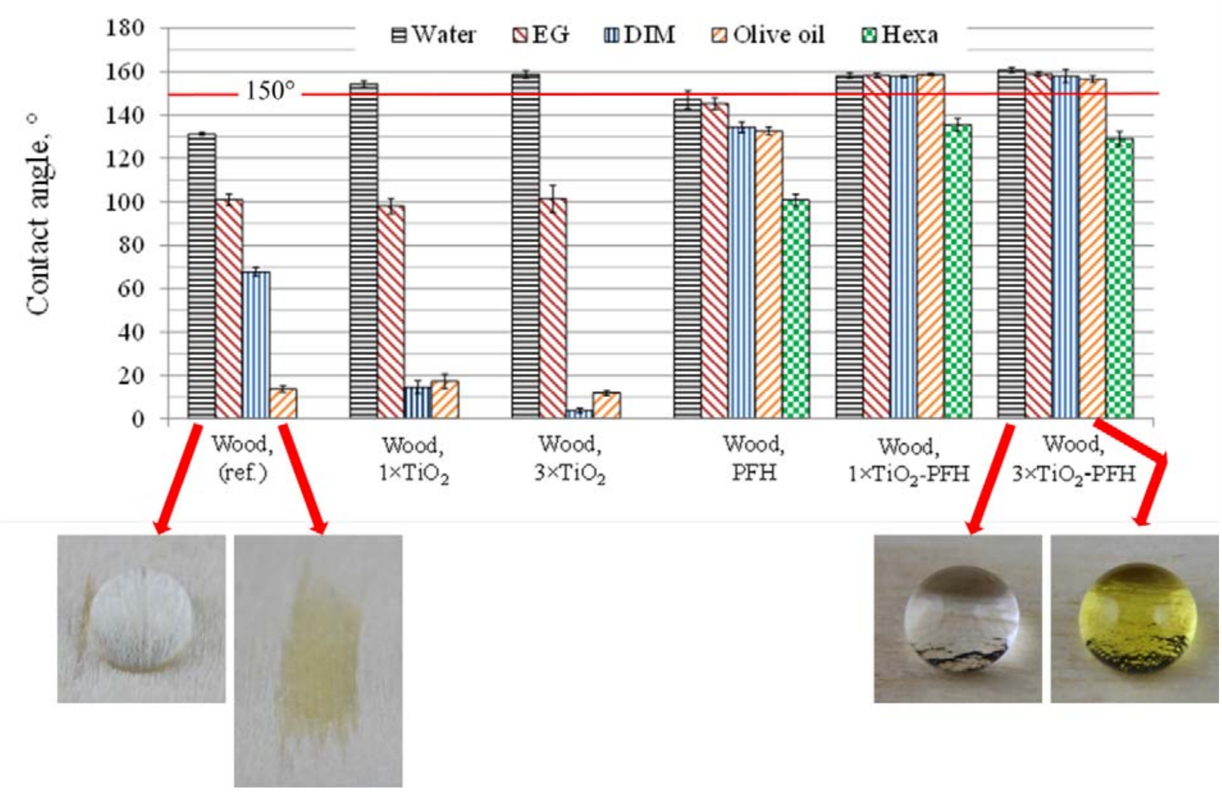

Figure 1. *Static contact angles of water, ethylene glycol (EG), diiodomethane (DIM), olive oil and hexadecane (Hexa) on (1× and 3×) TiO_2-PFH coated wood. Static CA of hexadecane on wood, 1× and 3×TiO_2 coated wood is <2°. Inset showing ~10 mL drops of water and olive oil on uncoated and fully coated wood.*

As shown in Figure 1, the TiO_2 coating alone increases the static CA of water above 150°, but not for the other liquids. On the other hand, the PFH layer enhances the repellency of wood against all liquids, but with no values above 150°. Combining TiO_2 and PFH coatings into a composite coating increases the CA values of all liquids, except for hexadecane, above 150°. A static contact angle >150° is, however, not enough to be defined as a super repellent surface, since the contact angle hysteresis or roll-off angle has to be below 10° as well. Table 2 shows that the roll-off angles of water, ethylene glycol, diiodomethane and olive oil of TiO_2 and PFH coated surfaces are indeed below 10°.

Table 2. *Roll-off angles of water, ethylene glycol (EG), diiodomethane (DIM), olive oil and hexadecane (Hexa) on TiO_2 (1× and 3×) and PFH coated wood.*

Sample	**Roll-off angle, °**				
	Water	**EG**	**DIM**	**Olive oil**	**Hexa**
Wood, 1×TiO_2	L: 7 ± 1 T: 9 ± 2	n.d.	n.d.	n.d.	n.d.
Wood, 3×TiO_2	L: 5 ± 1 T: 6 ± 1	n.d.	n.d.	n.d.	n.d.
Wood, 1×TiO_2-PFH	< 2 *)	L: 2 ± 0.5 T: 3 ± 0.5	L: 2° ± 0.5° T: 3° ± 0.5°	L: 4 ± 1 T: 7 ± 2	n.d.
Wood, 3×TiO_2-PFH	< 2 *)	L: 2 ± 0.5 T: 2 ± 0.5	L: 2 ± 0.5 T: 2 ± 0.5	L: 3 ± 0.5 T: 5 ± 1	n.d.

**) Water droplets run away when first placed on the surface. When the droplet gets pinned it then rolls off below 2° tilting. The roll-off angles were measured in both longitudinal (L) (fiber orientation of wood) and tangential (T) tilting directions. n.d. means not determined, since the static CA was below 150°.*

The TiO_2-PFH coated wood surfaces are superhydrophobic and superoleophobic, since the static CAs of water and oil are above 150° and roll-off angles below 10°. Surfaces that are both superhydrophobic and superoleophobic have been generally classified as superamphiphobic, even though in some cases this definition has been extended to include also even lower surface tension liquids than oil, like alkanes or fluorinated liquids [10, 18]. For hexadecane of even lower surface tension than the olive oil, we note a very high CA of 130–135°.

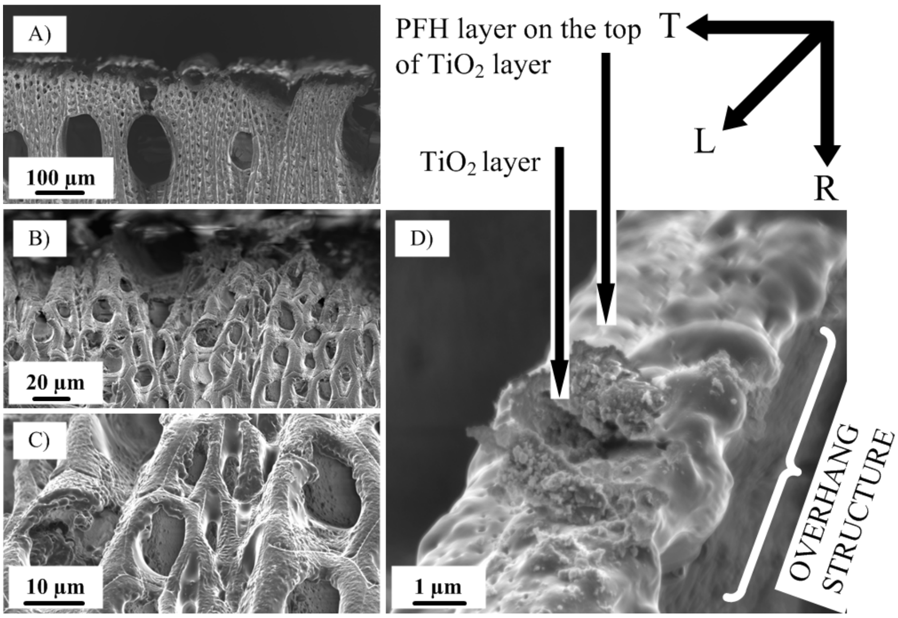

Figure 2. *FEG-SEM images of the cross section of the coated wood samples at successive magnifications of 3×TiO_2-PFH coated wood. The overhang structure is seen in D). In addition, the individual TiO_2 and PFH layers are clearly seen in a small area where the PFH-TiO_2 coating has been damaged. T: tangential direction, L: longitudinal (fiber orientation of wood) direction and R: radial direction.*

The extremely low wettability, also hexadecane is non-wetting although not super-repellent, is suggested to be due to these overhang hydrophobic capped structures giving a high re-entrant curvature for wetting liquids, see Figure 2. This mechanism was suggested in earlier studies [18, 19] and experimentally shown for fabricated silicone substrates and for electrospun fluorine polymers but has so far not been reported for natural biobased materials using thin coatings. The parameters describing overhang structures have been explored in detail [10]. A requirement for overhang on wood seems to be to prepare the coating on the right wood specie and on the right direction of that particular wood in order to fulfill the geometrical requirement of superoleophobicity.

To our knowledge, this is the first time superamphiphobic properties based on capped overhang structures have been accomplished on a natural biobased material such as wood. Equally, we suggest that other biobased materials can be surface modified in the same way as long as the geometry and hydrophobicity criteria are fulfilled. The fundamental understanding of super liquid repellency and the detailed results supporting it are discussed in manuscript 1.

4.1.1 Self-cleaning effect

Self-cleaning of a surface is a very interesting feature in many practical applications and was investigated by spreading sand particles as contaminant on the surface of the TiO_2-PFH coated wood samples. It was observed that the rolling water and oil droplets were able to take away the sand from the surface demonstrating a self-cleaning capability of the surfaces (see Figure 3 I-P).

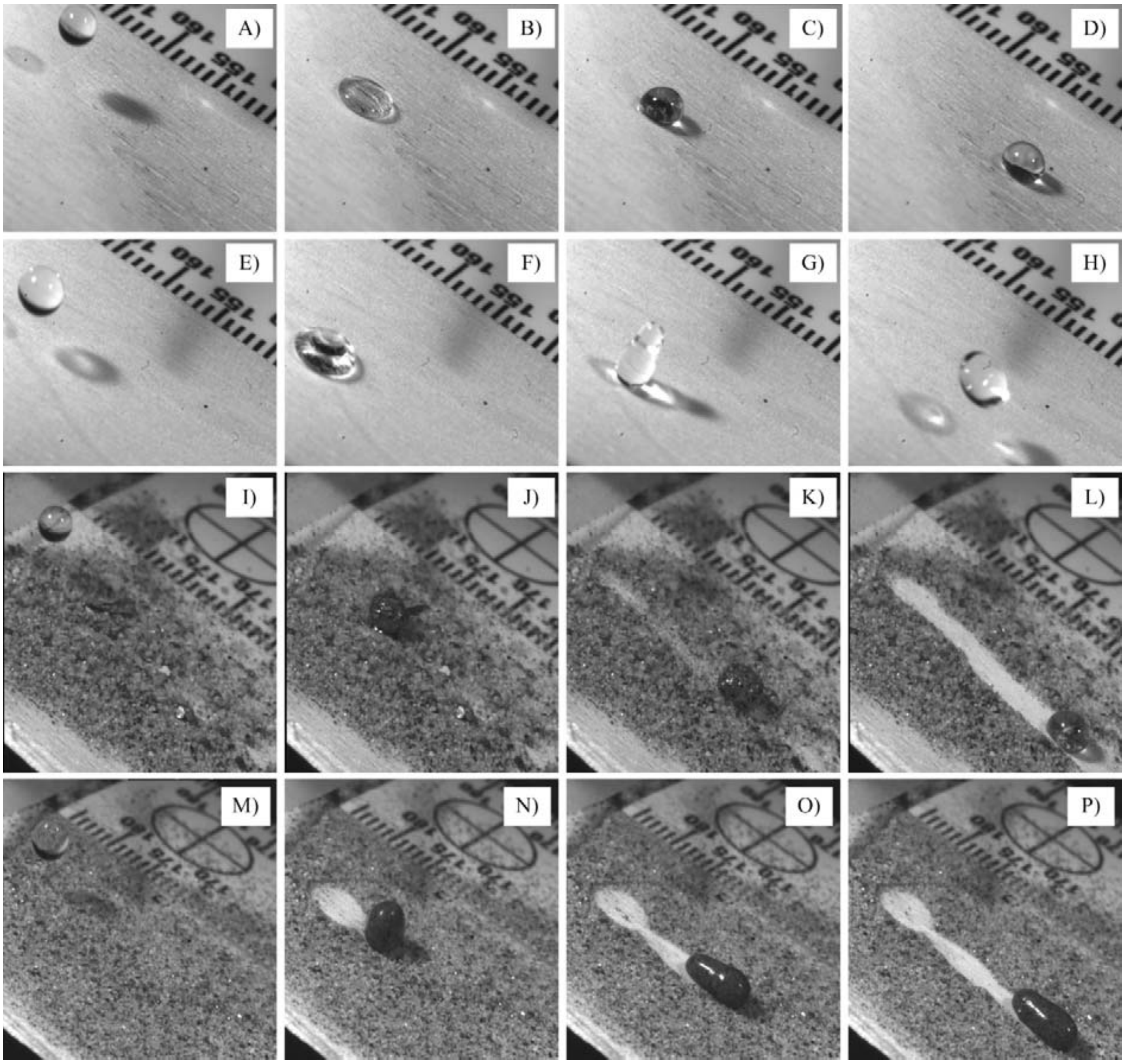

Figure 3. *Snapshots from movies (supporting information): A-D: oil droplet on 3×TiO_2-PFH coated wood, E-H: water droplet on 3×TiO_2-PFH coated wood surface, I-L: self-cleaning using oil droplet on 3×TiO_2-PFH coated wood (I and J: 1st droplet, K: 2nd droplet, L: 5th droplet) and M-P: self-cleaning using water droplet on longitudinal direction on 3×TiO_2-PFH coated wood.*

Although the roll-off angles of water and oil are well below 10°, a clear difference in their wetting dynamics can be observed, especially when the droplets are dispensed on the surface from a height (forced wetting) instead of sessile (spontaneous wetting) as in the roll-off angle measurement. As seen in the images in Figure 3 A-H, the water droplet bounces off from the surface in fractions of a second whereas the oil droplet rests on the surface a short while and then starts to slowly roll along on the surface. An interesting observation caused by the wetting state transition is seen when oil is dropped on the single and three times TiO_2-PFH coated samples from different heights. The single coated surface can keep the repellency against oil when the dropping height is 20 mm, but if the dropping height is increased to 50 mm the oil droplet sticks to the surface. The situation is the same with the three times coated surface, but instead of 50 mm dropping height the oil droplet sticks to the surface when the dropping height is 100 mm. In the case of a dispensed droplet there is forced wetting, in this case leading to a partial transition from Cassie-Baxter to Wenzel wetting state. The wetting transition and related droplet pinning are discussed in manuscript 1.

4.2 Repellence against severe climate conditions

A natural look of wood is desired and is therefore sometimes protected by lacquer coatings in many end applications, such as buildings, boats and furniture. It is thus vital to assess if the coatings affect the visual properties of wood. Poor durability of coatings is a major limitation for successful utilization in applications where self-cleaning and liquid repellence is required. In the present study, a water drop impact, UV illumination and Weathero-meter tests were used to evaluate the wetting durability of the TiO_2, SiO_2, CeO_2 and PFH coated wood surfaces.

4.2.1 Lab-scale tests

Wetting durability

The surface sensitivity of water droplet test makes it very suitable for studying the wetting dynamics and drop impact resistance of superamphiphobic surfaces. In the test, water droplets were repeatedly dropped on the same spot on the coated sample and the change in wetting dynamics was followed.

Table 3. *Water droplet impact resistance. 5 µL water drops were dispensed from a height h of 10 cm (impact velocity U of 1.4 m/s). The tilting angle of sample was 45° and the sequence was one drop every third second.*

Sample	**The amount of water droplets**
Wood (ref.)-PFH	~ 50
Wood-1×TiO_2	~ 500
Wood-3×CeO_2-PFH	~ 355 000
Wood-1×CeO_2-PFH	~ 240 000
Wood-3×SiO_2-PFH	> 500 000
Wood-1×SiO_2-PFH	> 500 000
Wood-3×TiO_2-PFH	> 500 000
Wood-1×TiO_2-PFH	> 500 000

No changes in the wetting properties of TiO_2-, SiO_2-PFH coated surfaces were observed even after 500 000 drop impacts, whereas the wetting of CeO_2-PFH coated surfaces changed after ~240 000 and ~355 000 water droplets, as seen in Table 3. The wetting of TiO_2 coated surfaces without the PFH coating changed already after 500 drops. The wetting durability results and forced wetting phenomenon are discussed more detailed in the manuscript 1.

UV-repellence

The UV-repellence of CeO_2, TiO_2 and SiO_2 + PFH coatings was evaluated at lab-scale by using UV-lamp (wavelength: 254 nm, intensity: 2.25 mW/cm^2) and the changes on wetting and color was followed. Table 4 shows how the wetting (CA) of different LFS-coatings change under UV-light.

Table 4. *CA values of LFS/CeO_2, TiO_2 and SiO_2 +PFH under UV-exposure.*

	UV (0)	UV (12h)	UV (24h)	UV (48h)	UV (96h)	Weatherometer (72h)
Wood (ref.) + PFH	145.4 ± 0.1	142.2 ± 0.5	124.8 ± 3.8	110.8 ± 1.7	102.3 ± 6.3	115.9 ± 0.6
Wood/1×TiO_2+ PFH	*)	118.7 ± 3.8	95.3 ± 1.4	32.4 ± 2.6	< 5°	31.5 ± 0.5
Wood/3×TiO_2 + PFH	*)	128.4 ± 1.8	105.1 ± 2.8	65.1 ± 1.8	< 5°	101.0 ± 1.0
Wood/1×SiO_2 + PFH	*)	*)	*)	136.7 ± 0.3	132.0 ± 4.2	96.6 ± 0.5
Wood/3×SiO_2 + PFH	*)	*)	*)	133.6 ± 2.6	90.1 ± 4.2	< 5
Wood/1×CeO_2 + PFH	*)	127.0 ± 2.2	123.0 ± 0.6	123.6 ± 2.0	113.6 ± 3.6	107.9 ± 1.5
Wood/3×CeO_2 + PFH	*)	136.3 ± 0.3	134.1 ± 1.1	133.2 ± 2.2	129.3 ± 0.4	121.6 ± 0.6

*) Droplet runs away (CAW > 150°), finds a place to pin and rolls-off before 2° tilting !

UV-repellence of the coatings depends on the used nanoparticle. By comparing CAW in the Tables 4 and 5 (Appendix 2), we can see that the additional PFH-layer increases UV-repellence significantly. However, the superhydrophobicity of SiO_2 and PFH coating, which was the most UV-repellent coating is lost after 24 hours exposure. In addition, a major color changes, i.e. yellowing of wood, are observed after 96 hours UV-exposure, see Tables 6 and 7 (Appendix 2).

4.2.2 Weatherometer tests

Weatherometer tests were used to simulate severe climate conditions, i.e. UV-exposure and rain cycles. The Weatherometer settings for 72 hours exposure were set based on the EN ISO 4892-2:2006 - Plastics – Methods of exposure to laboratory, light sources – Part 2: Xenon-arc lamps (ISO 4892-2:2006). The color and CAW values after the Weatherometer test are presented in Tables 4 and 7 (Appendix 2). Evidently, the repellence of the CeO_2, TiO_2 and SiO_2 + PFH coatings is poor. The color change is significant and liquid repellence is lost. Figure 4 shows pictures of the uncoated and 3×CeO_2 and PFH coated wood samples before and after Weatherometer test and the Figure 6 in Appendix 2 the rest of the coated wood samples.

Figure 4. *The uncoated (above) and 3×CeO_2 and PFH (below) wood samples before (left) and after (right) Weatherometer test.*

Clear dimensional changes can be observed on uncoated wood sample, but not on any nanoparticle and plasma coated sample, see Figures 4 and 6 (Appendix 2). The main reason for the loss of water repellence is the cracking of coated wood. As discussed before, the right surface structure and chemistry are leading high repellence against water and oil, but the repellence against water vapor is not surface related phenomenon. The conditions in Weatherometer changes from rain (moisture content 100%) to UV-exposure (moisture content 0%) cycles, so the wood samples uptake moisture and dry-up several times during the test. The thin plasma layer (30-50 nm) and porous nanoparticle coating (< 90%) are not able prevent the diffusion of water vapor or UV-light, which eventually leads to color change and loss of water repellence because of the cracking of coated wood surface.

4.3 Antifungal properties

Disinfection or inactivation of biological species such as bacteria is of strong interest for many applications. Different type of biological species, like bacteria, mould, fungus, etc, can cause severe problems in wood constructions. Silver is known for its antimicrobial properties and has been used for years in the medical field for antimicrobial applications. Silver nanoparticles have the ability to rapidly kill bacteria and fungi. However, in some applications the use of silver has raised questions of safety, and therefore the use of silver was decided not be used in this study, but other potential candidates, i.e. TiO_2, SiO_2, CeO_2 and ZnO were studied. The resistance of coated wood against different discoloring fungi (moulds and staining fungi) were studied in mold chamber. The TiO_2, SiO_2, CeO_2 and ZnO coatings were also applied on filter paper and the antifungal properties were evaluated according to ASTM D5590, Fungal defacement: accelerated four-week agar plate assay. The following fungal/fungi were tested: Aspergillus niger: CBS 113.50, Penicillium funiculosum: CBS 235.94, Aureobasidium pullulans: DSM 3497, DSMZ-Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Braunschweig, Germany and Identical to strain no. IMI 269 216 of culture deposited at CABI Bioscience, Egham. Figure 5 shows pictures of uncoated, ZnO coated and SiO_2-PFH coated wood samples on mold chamber (ASTM D3273) after 1 and 3 week exposure.

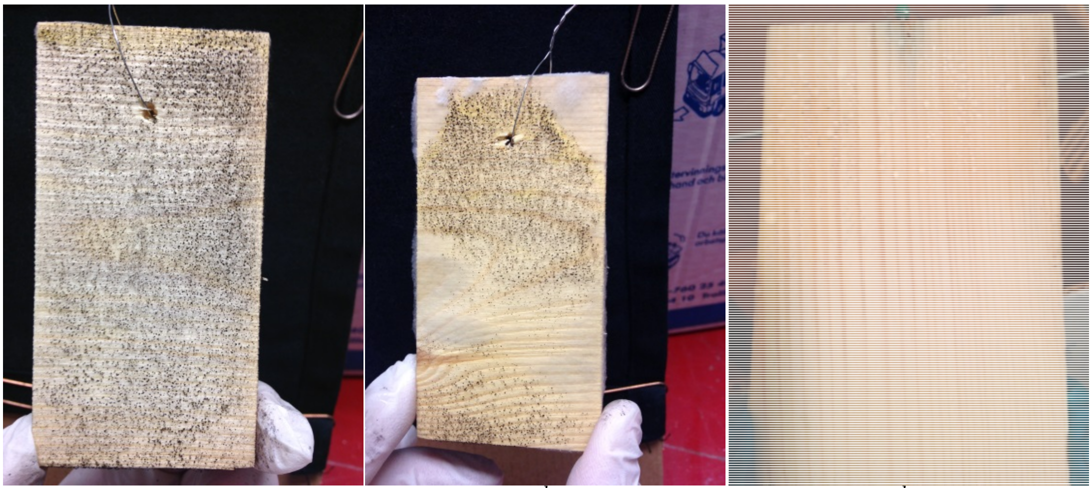

Figure 5. *Uncoated (1st), ZnO coated (2nd) and SiO_2-PFH coated (3rd) wood samples on mold chamber (ASTM D3273) after 3 week exposure.*

Generally, only minor improvements in fungal resistance of TiO_2, SiO_2, CeO_2 and ZnO coated wood samples can be seen. On the other hand, additional plasma layer improves the fungal resistance significantly, as seen in Figure 5. Similar results were seen in the fungal tests made on coated filter papers. Most likely reason for poor performance of coatings without PFH layer is the moisture uptake and the absence of UV-light, i.e. no photocatalytic reactions. The samples were stored dark at high humidity conditions where water droplets condensate on the surface. The water repellence of SiO_2-PFH coated wood sample is the likely reason why only minor fungal growth was seen after 3 weeks of exposure for mold.

5 Conclusions and future work

The multifunctional coatings on wood were created using two state of the art techniques, i.e. liquid flame spray (LFS) and plasma deposition. The fibrous structure of wood gives a micro-scale roughness, whereas uniformly distributed LFS coated nanoparticles and agglomerates, provided sub micrometer- and nano-scale roughness. Such a multi-scale surface roughness together with the right surface chemistry, i.e. plasma deposited PFH-coating can provide an air/vapor layer at the interface between the surface and liquid drops preventing liquids to wet the surface and penetrate through the thin coating into the wood. To our knowledge, this was the first time superamphiphobicity (water and oil repellence) based on overhang structures is shown for renewable bio-based material, such as a wood.

The coating had high transparency and it did not change color of wood. The self-cleaning on coated wood surfaces was demonstrated by using water and oil droplets. The plasma layer improved the durability of the nanoparticle coatings in water droplet impact tests, which is important since commercial applications of liquid repellent surfaces largely rely on their durability. However, the coatings had limited durability against severe climate conditions in Weatherometer-test where surfaces were exposed to rain and UV-illumination cycles. The combination of thin top coating and porous bulk coatings is an ideal for liquid repellence, but do not function against moisture and UV-illumination. Most likely reason for the loss of liquid repellence of the coating is the repeatable wetting and drying of wood, which causes mechanical deformation and eventually leads to cracking of coated wood surface. The SiO_2-PFH coating improved fungal resistance of wood as long as the wood surface did not get wet.

From the industrial point of view the key question is the durability of the coatings. In outdoor application, the coated wood have to perform against several deteriorating factors, such as UV, moisture, fungal and water simultaneously. One of the main observation in the research was the poor correlation between lab-scale spontaneous wetting tests (e.g. contact angle measurements) and forced wetting test (e.g. Weatherometer test). There is an evident need to develop lab-scale measurement technique for forced wetting, which can predict the performance of coating in severe climate conditions.

6 Publications

Tuominen, M. *Functional multilayer coatings to improve properties of wood. Elevator Pitch, "Post-graduate session" at SPCI Convention 25th of September, Stockholm, Sweden, 2013.*

Tuominen, M.*; Teisala, H.; Haapanen, J.; Aromaa, M.; Mäkelä, J.M.; Stepien, M.; Saarinen, J.J.; Toivakka, M.; Kuusipalo, J. Adjustable wetting of Liquid Flame Spray (LFS) TiO_2-nanoparticle coated board: Batch-type versus roll-to-roll stimulation methods. Nordic Pulp and Paper Research Journal. 2014. 29(2): p. 271-279.*

Tuominen, M.*, Multifunctional Nanoparticle Coatings on Cellulose Based Substrates Using Liquid Flame Spray (LFS) Technique, in PPS 2014 (Polymer Processing Society) Europe-Africa PPS Conference, 2014: Tel Aviv, Israel. (INVITED SPEAKER)*

Tuominen, M.*, Multifunctional Nanoparticle Coating Using Liquid Flame Spray (LFS)-Technique, in "Eco-sustainable Food Packaging Based on Polymer Nanomaterials", COST ACTION FA0904. 2014: Rome, Italy. (INVITED SPEAKER)*

Tuominen, M.*; Teisala, H.; Haapanen, J.; Aromaa, M.; Stepien, M.; Mäkelä, J.; Saarinen, J.; Toivakka, M.; Kuusipalo, J. Multifunctional Nanoparticle Coatings on Cellulose Based Substrates Using Liquid Flame Spray (LFS) Technique. TAPPI International Conference on Nanotechnology for Renewable Materials, 24-27 June, 2013, Stockholm, Sweden.*

Teisala, H.; ***Tuominen, M.****; Kuusipalo, J. Superhydrophobic Coatings on Cellulose-Based Materials: Fabrication, Properties, and Applications. Advanced Materials Interfaces. 2014. 1(1), p.1-20.*

Songok, J.; ***Tuominen, M***.*; Teisala, H.; Haapanen, J.; Mäkelä, J.; Kuusipalo, J.; Toivakka, M., Paper-based micro fluidics: Fabrication technique and dynamics of capillary-driven surface flow. ACS Appl. Mater. Interfaces* ***2014,*** *6 (22), 20060-20066.*

Haapanen, J.; Aromaa, M.; Teisala, H.; ***Tuominen, M***.*; Stepien, M.; Saarinen, J. J.; Heikkilä, M.; Toivakka, M.; Kuusipalo, J.; Mäkelä, J. M., Binary TiO2/SiO2 nanoparticle coating for controlling the wetting properties of paperboard. Mater Chem Phys* ***2015,*** *149, 230-237.*

Ejenstam, L.; ***Tuominen, M***.*; Haapanen, J.; Mäkelä, J. M.; Pan, J.; Swerin, A.; Claesson, P. M., Long-term corrosion protection by a thin nano-composite coating. Appl Surf Sci* ***2015,*** *357, Part B, 2333-2342.*

Moghaddam Maziar, S.; Heydari, G.; ***Tuominen, M***.*; Fielden, M.; Haapanen, J.; Mäkelä Jyrki, M.; Wålinder Magnus, E. P.; Claesson Per, M.; Swerin, A., Hydrophobisation of wood surfaces by combining liquid flame spray (LFS) and plasma treatment: dynamic wetting properties. In Holzforschung, 2015; Vol. 0.*

Golrokh Heydari; Maziar Sedighi Moghaddam; ***Mikko Tuominen****; Matthew Fielden; Janne Haapanen; Jyrki M Mäkelä; Per M ClaessonTemperature-Induced Supercooled Water Wetting*

Hysteresis on Stochastically Rough Hydrophobic Surfaces. Submitted to Journal of Colloid and Interface Science.

Golrokh Heydari, Eric Tyrode, Heli Koivuluoto, Christian Stenroos, ***Mikko Tuominen****, and Per M. Claesson. Ice-release Properties of Hydrophilic Mica Surfaces. Submitted to Journal of Physical Chemistry letters.*

Dimitar Valtakari, Milena Stepien, Janne Haapanen, Hannu Teisala, ***Mikko Tuominen****, Jurkka Kuusipalo, Jyrki M. Mäkelä, Martti Toivakka, and Jarkko J. Saarinen. Planar fluidic channels on TiO2 nanoparticle coated paperboard, Submitted to Nordic Pulp and Paper Research Journal.*

Mikko Tuominen*, Hannu Teisala, Janne Haapanen, Jyrki M. Mäkelä, Mari Honkanen, Minnamari Vippola , Stig Bardage, Magnus E.P. Wålinder and Agne Swerin, Functional multilayer coatings to improve properties of wood, Tappi Nanotechnology of Renewable Materials, to be held in Grenoble, June 13-16, 2016 (submitted)*

7 References

1. Olsson, S., Enhancing UV protection of clear coated exterior wood by reactive UV absorber and epoxy functional vegetable oil. **2014**.
2. Lu, Y.; Xiao, S.; Gao, R.; Li, J.; Sun, Q., Improved weathering performance and wettability of wood protected by CeO2 coating deposited onto the surface. *Holzforschung* **2014,** *68* (3), 345-351.
3. Hsieh, C. T.; Chang, B. S.; Lin, J. Y., Improvement of water and oil repellency on wood substrates by using fluorinated silica nanocoating. *Appl Surf Sci* **2011,** *257* (18), 7997-8002.
4. Wang, C.; Piao, C.; Lucas, C., Synthesis and characterization of superhydrophobic wood surfaces. *J. Appl. Polym. Sci.* **2011,** *119* (3), 1667-1672.
5. Wang, S.; Wang, C.; Liu, C.; Zhang, M.; Ma, H.; Li, J., Fabrication of superhydrophobic spherical-like α-FeOOH films on the wood surface by a hydrothermal method. *Colloids Surf. A Physicochem. Eng. Asp.* **2012,** *403*, 29-34.
6. Fu, Y.; Yu, H.; Sun, Q.; Li, G.; Liu, Y., Testing of the superhydrophobicity of a zinc oxide nanorod array coating on wood surface prepared by hydrothermal treatment. *Holzforschung* **2012,** *66* (6), 739-744.
7. Cassie, A. B. D.; Baxter, S., Wettability of porous surfaces. *Transactions of the Faraday Society* **1944,** *40*, 546-551.
8. Nosonovsky, M.; Bhushan, B., Superhydrophobic surfaces and emerging applications: Non-adhesion, energy, green engineering. *Curr. Opin. Colloid Interface Sci.* **2009,** *14* (4), 270-280.
9. R.N, W., Resistance of solid surfaces to wetting by water. *Industrial & Engineering Chemistry* **1936,** *28* (8), 988-994.
10. Butt, H. J.; Semprebon, C.; Papadopoulos, P.; Vollmer, D.; Brinkmann, M.; Ciccotti, M., Design principles for superamphiphobic surfaces. *Soft Matter* **2013,** *9* (2), 418-428.
11. Deng, X.; Mammen, L.; Butt, H. J.; Vollmer, D., Candle soot as a template for a transparent robust superamphiphobic coating. *Science* **2012,** *335* (6064), 67-70.
12. Kota, A. K.; Choi, W.; Tuteja, A., Superomniphobic surfaces: Design and durability. *MRS Bull* **2013,** *38* (5), 383-390.
13. Teisala, H.; Tuominen, M.; Aromaa, M.; Stepien, M.; Mäkelä, J. M.; Saarinen, J. J.; Toivakka, M.; Kuusipalo, J., High- and low-adhesive superhydrophobicity on the liquid flame spray-coated board and paper: Structural effects on surface wetting and transition between the low- and high-adhesive states. *Colloid Polym. Sci.* **2013,** *291* (2), 447-455.
14. Xue, Z.; Liu, M.; Jiang, L., Recent developments in polymeric superoleophobic surfaces. *J Polym Sci Part B* **2012,** *50* (17), 1209-1224.
15. Verho, T.; Bower, C.; Andrew, P.; Franssila, S.; Ikkala, O.; Ras, R. H. A., Mechanically Durable Superhydrophobic Surfaces. *Adv Mater* **2011,** *23* (5), 673-678.
16. Wang, S.; Shi, J.; Liu, C.; Xie, C.; Wang, C., Fabrication of a superhydrophobic surface on a wood substrate. *Appl Surf Sci* **2011,** *257* (22), 9362-9365.
17. Liu, F.; Wang, S.; Zhang, M.; Ma, M.; Wang, C.; Li, J., Improvement of mechanical robustness of the superhydrophobic wood surface by coating PVA/SiO2 composite polymer. *Appl Surf Sci* **2013,** *280*, 686-692.
18. Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., Designing superoleophobic surfaces. *Science* **2007,** *318* (5856), 1618-1622.

19. Tuteja, A.; Choi, W.; McKinley, G. H.; Cohen, R. E.; Rubner, M. F., Design parameters for superhydrophobicity and superoleophobicity. *MRS Bull* **2008,** *33* (8), 752-758.

8 Appendix

8.1 Manuscript 1: Superamphiphobic capped overhang coating on a biobased material

Superamphiphobic capped overhang coating on a biobased material

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8.2 Results for manuscript 2: Climate protective coating for wood

Climate protective coating for wood

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Table 5. *CA values of LFS/CeO_2, TiO_2 and SiO_2 under UV-exposure.*

	UV (0)	+ UV (3h)	+ UV (12h)
Wood (ref.)	87.1 ± 1.7	85.8 ± 1.0	88.0 ± 0.8
Wood/1×TiO_2	150.6 ± 0.6	32.6 ± 6.4	< 5°
Wood/3×TiO_2	151.1 ± 0.5	45.3 ± 2.4	< 5°
Wood/1×SiO_2	8.3 ± 1.9	< 5°	< 5°
Wood/3×SiO_2	6.7 ± 1.6	< 5°	< 5°
Wood/1×CeO_2	137.5 ± 1.8	110.2 ± 3.6	102.5 ± 3.6
Wood/3×CeO_2	145.4 ± 1.2	121.2 ± 3.0	101.4 ± 0.8

Table 6. The CIE $L^*a^*b^*$ color values and color change of TiO_2, SiO_2, CeO_2 and PFH coated wood (compared to uncoated wood).

				Color change (compared to wood)			
	L*(D65)	a*(D65)	b*(D65)	ΔE*	ΔL*	Δa*	Δb*
Wood	82,1	5,0	19,2				
+PFH	83,4	4,8	19,3	1,3	1,3	-0,2	0,1
/3×CeO_2+PFH	83,2	4,1	20,2	1,7	1,1	-0,8	1,0
/1×CeO_2+PFH	84,0	3,6	19,3	2,4	1,9	-1,4	0,1
/3×SiO_2+PFH	83,6	3,9	19,6	1,9	1,5	-1,1	0,4
/1×SiO_2+PFH	84,6	4,1	20,1	2,8	2,5	-0,9	0,8
/3×TiO_2+PFH	82,6	4,3	21,3	2,3	0,5	-0,6	2,1
/1×TiO_2+PFH	83,2	4,1	20,9	2,2	1,1	-0,8	1,7

Table 7. The CIE $L^*a^*b^*$ color values and color change of TiO_2, SiO_2, CeO_2 and PFH coated wood after 96 hours exposure to UV.

	Before			After 96h UV-exposure			Color change			
	L*(D65)	a*(D65)	b*(D65)	L*(D65)	a*(D65)	b*(D65)	ΔE*	ΔL*	Δa*	Δb*
Wood	82,1	5,0	19,2	78,8	6,5	31,5	12,8	-3,3	1,6	12,3
+PFH	83,4	4,8	19,3	77,1	7,8	32,2	14,7	-6,3	3,0	12,9
/3×CeO_2+PFH	83,2	4,1	20,2	78,5	6,7	33,1	13,9	-4,7	2,5	12,8
/1×CeO_2+PFH	84,0	3,6	19,3	77,3	6,8	32,1	14,8	-6,7	3,2	12,8
/3×SiO_2+PFH	83,6	3,9	19,6	78,3	7,0	32,5	14,3	-5,3	3,1	12,9
/1×SiO_2+PFH	84,6	4,1	20,1	79,5	6,2	32,0	13,1	-5,1	2,1	11,9
/3×TiO_2+PFH	82,6	4,3	21,3	77,1	7,5	31,1	11,7	-5,5	3,1	9,8
/1×TiO_2+PFH	83,2	4,1	20,9	78,3	7,0	33,5	13,8	-4,9	2,9	12,6

Table 8. The CIE $L^*a^*b^*$ color values and color change of TiO_2, SiO_2, CeO_2 and PFH coated wood after 72 hours Weathero-meter test.

	Before weatherometer			After 72h of weatherometer			Color change (compared to wood)							
	L* (D65)	a* (D65)	b* (D65)	L* (D65)	a* (D65)	b* (D65)	ΔE*	ΔL*	Δa*	Δb*	ΔE*	ΔL*	Δa*	Δb*
Wood	82,1	5,0	19,2	78,3	6,9	22,0	5,0	-3,7	2,0	2,8				
+PFH	83,4	4,8	19,3	79,4	6,7	23,4	6,0	-3,9	2,0	4,1	1,30	1,28	-0,22	0,09
/3×CeO_2+PFH	83,2	4,1	20,2	80,4	6,8	24,0	5,4	-2,8	2,6	3,8	1,73	1,13	-0,84	1,01
/1×CeO_2+PFH	84,0	3,6	19,3	79,1	7,7	25,2	8,7	-4,9	4,1	5,9	2,36	1,91	-1,38	0,06
/3×SiO_2+PFH	83,6	3,9	19,6	79,6	7,3	22,7	6,1	-4,0	3,4	3,1	1,91	1,54	-1,06	0,39
/1×SiO_2+PFH	84,6	4,1	20,1	80,6	6,9	21,9	5,3	-4,1	2,8	1,8	2,80	2,53	-0,85	0,85
/3×TiO_2+PFH	82,6	4,3	21,3	78,1	7,5	23,6	5,9	-4,5	3,2	2,2	2,27	0,48	-0,64	2,13
/1×TiO_2+PFH	83,2	4,1	20,9	79,0	7,8	23,0	5,9	-4,2	3,6	2,1	2,20	1,12	-0,84	1,69

Table 9. *CA values of LFS/CeO_2, TiO_2 and SiO_2 under UV-exposure*

	UV (0)	+ UV (3h)	+ UV (12h)
Wood (ref.)	87.1 ± 1.7	85.8 ± 1.0	88.0 ± 0.8
Wood/1×TiO_2	150.6 ± 0.6	32.6 ± 6.4	< 5°
Wood/3×TiO_2	151.1 ± 0.5	45.3 ± 2.4	< 5°
Wood/1×SiO_2	8.3 ± 1.9	< 5°	< 5°
Wood/3×SiO_2	6.7 ± 1.6	< 5°	< 5°
Wood/1×CeO_2	137.5 ± 1.8	110.2 ± 3.6	102.5 ± 3.6
Wood/3×CeO_2	145.4 ± 1.2	121.2 ± 3.0	101.4 ± 0.8

Figure 6. *The PFH coated wood samples before (1st) and after (2nd), 1×CeO_2-PFH before (3rd) and after (4th), 1×SiO_2 + PFH before(5th) and after (6th), 3×SiO_2 + PFH before(7th) and after (8th), 1×TiO_2 + PFH before(9th) and after (10th) and 3×TiO_2 + PFH before(11th) and after (12th) Weatherometer test.*

8.3 Results for manuscript 3: Antifungal coating for wood

Antifungal coating for wood

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Figure 7. *Uncoated (1st), SiO_2 (2nd), TiO_2 (3rd), CeO_2 (4th), ZnO(5th) and 1×SiO_2 + PFH(6th) coated wood samples after 3 weeks in mold chamber.*