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Abstract

Eco-friendly, sustainable products as well as energy efficient building have gained more and more interest in recent years. Porous, natural materials, e.g. wood and natural textiles, have the ability to buffer moisture, evening out the extremes in relative humidity thus providing a more convenient indoor climate. For some applications the hydrophilic nature of natural textiles is, however, considered a drawback. The goal of this work was to develop a coating that provides hydrophobic properties to textiles, as well as other cellulosic substrates, yet preserving their ability to adsorb and release moisture. Antibacterial properties are an additional benefit. Only natural and non-toxic materials were used.

The coatings were fabricated according to the layer-by-layer method. Poly-L-lysine, a dispersion of carnauba wax and colloidal lignin particles were used. Poly-L-lysine acted as a cation, and antibacterial agent and the colloidal lignin particles acted as antibacterial agents as well. The wax dispersion provided hydrophobicity without inhibiting breathability, thanks to an uneven structure of wax droplets with enough space in between for air and water vapour to pass through. The adsorption behaviour was studied with QCM-D, contact angle measurements gave information about wetting properties classified the hydrophobicity and AFM imaging gave information about surface morphology. Contact angle, surface roughness and oxygen permeability were measured on coated freestanding CNF films, providing more information about the surface properties of the coatings. Contact angle and moisture buffer value were determined for textiles samples.

The results showed that the coatings were hydrophobic, and with textiles, even superhydrophobicity was achieved. The hydrophobicity mostly depended on the amount of wax in the top layer of the coating. With the thickest wax coatings, the moisture buffering slightly decreased, the extent of the decrease depending on the textile substrate.

These coatings have a great potential to be used in textile technology, both in domestic and wearable textiles. Unlike many common textile coatings today, these coatings are non-toxic, natural and suitable for a sustainable society.

Keywords Textile, hydrophobicity, moisture buffering, CNF film, polylysine, wax dispersion

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Sammandrag

Ekologiska, hållbara produkter liksom också energieffektivt byggande har vunnit mer och mer intresse de senaste åren. Porösa, naturliga material, som trä och naturtextilier, har förmågan att fungera som fuktighetsbuffert, och genom att jämna ut ytterligheterna i den relativa luftfuktigheten erbjuda ett behagligare inomhusklimat. För vissa tillämpningar anses naturtextiliers hydrofila natur emellertid vara en nackdel. Syftet med detta arbete var att utveckla en ytbeläggning som gör textilier och andra cellulosasubstrat hydrofoba, men ändå bevarar deras förmåga att uppta och avge fukt. Antibakteriella egenskaper är ytterligare en fördel. Endast naturliga och ogiftiga material användes.

Ytbeläggningarna framställdes enligt lager-på-lager-metoden. Poly-L-lysin, en dispersion av carnauba vax och kolloidala ligninpartiklar användes. Poly-L-lysin fungerade som en katjon och antibakteriellt medel, och de kolloidala ligninpartiklarna fungerade också som antibakteriellt medel. Vaxdispersionen gav hydrofobitet utan att hindra andningsförmågan, tack vare en ojämn struktur av vaxdroppar med tillräckligt med utrymme mellan dropparna för att luft och vattenånga skulle kunna passera genom. Adsorptionen studerades med QCM-D, kontaktvinkelmätningar gav information om vätningssegenskaper och AFM mätning gav information om ytan. Kontaktvinkel, ytråhet och syrepermeabilitet mättes på ytbelagda fristående CNF filmer, och gav information om beläggningens ytegenskaper. Kontaktvinkel och förmåga att uppta och avge fukt mättes på textilprover.

Resultaten visade att ytbeläggningarna var hydrofoba, och på textilier även superhydrofoba. Hydrofobin berodde mest på mängden vax i det översta lagret på beläggningen. Med de tjockaste vaxbeläggningarna minskade fuktighetsbufferten något, omfattningen av minskningen berodde på textiliesubstratet.

Dessa ytbeläggningar har stor användningspotential inom textilieteknologin, både som hushålls- och bärbara textilier. Till skillnad från många vanliga ytbeläggningar för textilier som används idag är dessa beläggningar ogiftiga, naturliga och passar ett hållbart samhälle.

Nyckelord Textil, hydrofobi, fuktighetsbuffert, CNF film, polylysin, vaxdispersion

Preface

This work has been done within the WoodLife project, and I'd like to thank the people working with this project for letting me be a part of it. It is a privilege to write a funded Master's Thesis about an interesting topic, and I am grateful for this opportunity. This project has definitely broadened my horizons regarding indoor environments. I'd also like to thank my colleagues at Puu, especially Monika's group, for a positive atmosphere. It has been nice working with you, and the best part is that our collaboration doesn't end here!

My biggest thanks go to my supervisor and instructors, Monika, Alina and Mark. Thank you for your support, patience and interest! Without your help this work would have been what it is today. The timetable got tight at the end (as always), and I thank you for keeping up with that.

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Espoo, 5.9.2016

Nina Forsman

Table of contents

1	Introduction	1
2	Literature review.....	3
2.1	Moisture and temperature effect on air quality.....	3
2.1.1	Passive climate control and natural materials.....	4
2.2	Textiles and their desired properties.....	5
2.3	Surface modification of (natural) textiles.....	7
2.3.1	Hydrophobic, breathable textiles.....	7
2.3.2	Antibacterial textiles.....	9
2.4	Layer-by-layer adsorption (L-b-L).....	10
2.4.1	Properties of the coating components used.....	11
3	Experimental.....	14
3.1	Materials.....	14
3.1.1	Poly-L-lysine.....	14
3.1.2	Wax dispersion.....	14
3.1.3	Colloidal lignin particles.....	14
3.1.4	Freestanding cellulosic films.....	15
3.1.5	Textile samples.....	15
3.2	Methods.....	15
3.2.1	QCM-D.....	15
3.2.2	Contact angle.....	16
3.2.3	Zeta-potential.....	17
3.2.4	AFM.....	18
3.2.5	Coating of CNF freestanding films and fabrics.....	18
3.2.6	Roughness.....	18
3.2.7	Moisture buffering capacity.....	19
3.2.8	Oxygen Transfer Rate.....	19
4	Results and discussion.....	20
4.1	Thin film studies to understand the layer build-up.....	20
4.1.1	QCM-D.....	20
4.1.2	Contact angle.....	25
4.1.3	AFM.....	27
4.2	Surface modification of macroscopic samples.....	31

4.2.1	The samples	31
4.2.2	Wetting and Roughness	32
4.2.3	Moisture buffering.....	36
4.2.4	Oxygen Transmission Rate	40
5	Conclusions	42
6	Bibliography	45

1 Introduction

Energy efficient building have gained more and more interest in recent years. An important part in energy efficient building is the use of passive climate control, where hygroscopic materials play a major role. Hygroscopic materials can buffer moisture and therefore regulate the indoor climate and make the environment more convenient for the residents. Porous natural materials, e.g. natural textiles, wood, etc., have hygroscopic properties. While moisture buffering of household textiles is important for comfort of the inhabitants, breathability in combination with protection from water is major issue in the clothing industry. By studying moisture buffering and breathability, especially of natural textiles, new insights into how to obtain these properties can be gained. In this work, special emphasis was put on how different coatings affect these properties.

In addition to increasing interest in energy efficient building, there is a growing demand for natural, eco-friendly, sustainable products and natural breathable, hygroscopic textiles fit this demand well. However, a main drawback of natural textiles, and many synthetic textiles, is their hydrophilicity. To add a coating that makes the textiles hydrophobic but still preserve the breathable, moisture buffering properties was therefore the goal in this study. In a recent study, zinc oxide and wax particles deposited onto wood using the layer-by-layer (L-b-L) technique showed very promising results with very high water contact angles in combination with excellent moisture buffering ability (Lozhechnikova 2016). For this work, the idea was to mimic this coating on textiles but instead of ZnO use a more environmentally friendly cationic component, polylysine. Even though breathability, hygroscopicity and hydrophobicity were the most important properties aimed at, antibacterial properties were also of interest, but not the main focus. Colloidal lignin particles can introduce antibacterial properties, but it was beyond the scope of this work to test the antibacterial properties.

Various cellulose substrates were used to gain as detailed as possible understanding of the layer build-up. The quartz crystal microbalance with dissipation (QCM-D) and ultrathin films of cellulose nanofibrils were employed to fully understand the adsorption process, with special emphasis on the effect of pH on the behaviour of polylysine. The water

contact angle, hereafter simply referred to as contact angle, was measured to evaluate the hydrophobicity and atomic force microscopy (AFM) was used to study the coating in more detail. After that, L-b-L was also performed on freestanding cellulose nanofibril (CNF) films to learn how wax concentration and number of bilayers affected the wetting properties. Contact angle, roughness and antibacterial properties were all measured. Lastly, L-b-L deposition was performed on real fabrics and contact angle and moisture buffering were measured, to learn about the hygroscopic properties and the performance of the coatings in real life. The fabrics were all-natural and came from plants fibres (e.g. cotton, linen), no animal-based fabrics (e.g. wool, silk) were used.

The hypothesis was that these coatings of polylysine, wax particles and lignin nanoparticles would perform similarly to Lozhechikova's (2016) coatings on wood with ZnO and wax particles. Moisture buffering will not become poorer due to the coatings, but the material will be hydrophobic, possibly even superhydrophobic. The more bilayers that are deposited, the higher the hydrophobicity will be.

2 Literature review

2.1 Moisture and temperature effect on air quality

The indoor climate and air quality are factors that have a major impact on people's health and wellbeing, due to the extensive time spent indoors. Indoor climate and air quality are affected by many different factors, such as chemicals, microbes, particles, humidity, ventilation, temperature etc. (SCHER 2007). Nevertheless, for the perceived air quality not all factors are equally important. Perceived indoor air quality can be quantified as humidity and temperature, since these two factors have the greatest impact on how we perceive the indoor air (Fang 2000). Temperature is easily measured and perceived and will mostly be left out of this thesis. The relative humidity is subtler, but has a large impact on the air quality and wellbeing of the residents. Extremes in humidity are to be avoided. Too low humidity has been linked with health problems such as respiratory illness, dry eyes and dry skin (Berglund 1998). Too high humidity causes physical discomfort increase microbial growth, which can be harmful both for the health of the residents and the building itself (Arundel 1986). Rapid variations are also to be avoided. The best relative humidity in terms of health and comfort for the residents is 40-60% (Arundel 1986).

There are plenty of factors that affect the humidity in a room and buildings at large. Any bodies of water will eventually evaporate, but large open bodies of water usually only occur in wet areas such as bathrooms, saunas and kitchens. Wet materials, e.g. newly washed or rain soaked clothes or other materials, bring a lot of moisture to the room and building. The extent to which this water affects the indoor climate depends on how freely the moisture can move (e.g. through open doors). Every living organism, human, plant or pet, also affects both the moisture and heat levels in a room, and too many humans in the same place often lead to too much moisture and heat which is perceived as poor air quality. Hygroscopic materials like wood, fabrics and paper can take up and release moisture and heat, but this ability depends on their treatment and traditional paints tend to decrease the hygroscopic behaviour of wood (Hameury 2008) (Lozhechnikova 2015), even though there are some coatings that actually improve the moisture buffering (Lozhechnikova 2015) (Hameury 2008). However, the overall greatest impact regarding indoor humidity comes from air conditioning (Fang 2000). Air conditioning can efficiently

remove moisture from the air, and often air conditioning is too effective, leaving the room too dry. Air condition also requires energy and the renewal of air can count for as much as half of the total heat loss in a building (Woloszyn 2009), so keeping the air conditioning to a minimum reduces energy consumption and costs.

2.1.1 Passive climate control and natural materials

The relative indoor humidity is not constant, but changes during the day due to changes in outside air, activity of residents etc. Due to the variations, air conditioning is more useful when it is not set at a specific rate all the time, but is adapted to the indoor climate. Ventilation systems that change the ventilation rate according to relative humidity, have shown potential to efficiently renew the air only when needed (Woloszyn 2009). Another way to reduce ventilation need and keep the relative humidity suitable is to use hygroscopic materials, or in other words use a passive system. Many porous materials can buffer moisture and capture and release humidity depending on the surroundings, evening out the extremes. In addition to porosity, i.e. free volume, materials also need to be hydrophilic and have a high exchange surface in order to buffer moisture. Some part of the material needs to adsorb and release water, hence the hydrophilicity, and this adsorption/release need to take place somewhere. If the exchange surface is small the moisture exchange will be small, and the change in relative humidity will be negligible, i.e. no buffering. A high exchange surface allows a lot of moisture exchange, and thus observable changes in the humidity, i.e. buffering. In a moisture buffering material, the water vapour enters the free volume, but are not trapped there and move in and out from the material depending on the surrounding relative humidity (Céline 2013). For breathability only porosity is enough. Nevertheless, even though passive climate control and moisture buffering reduce the need of ventilation, they do not eliminate it. Humans produce CO₂ and the building materials might release unpleasant or even harmful gases (i.e. VOC, volatile organic compounds), so some air renewal will always be needed.

Materials of natural origin with porosity, like wood and textiles, are known for their hygroscopic behavior. Besides good moisture buffering, wood and natural textiles have many other favorable properties, such as renewability, non-toxicity and availability. Both materials are also in lines with the growing interest in eco-friendly building. The

hygroscopic behavior of wood has been widely studied, but for textiles mainly moisture vapour transport studies have been done with clothing applications in mind. However, all hygroscopic materials play a part in the indoor climate and need therefore to be taken into account, and the effect of textiles is mainly to even out the extremes in relative humidity (Derluyn 2007).

2.2 Textiles and their desired properties

Textiles have been used in our everyday life for thousands of years. The most obvious use is in clothing, but domestic textiles (e.g. carpets, table cloths, curtains, furnish coverings and bedsheets) are also a huge application area for textiles. Even though textiles have plenty of good properties, they also have some less desirable properties. To improve the properties different techniques to modify the textiles have been invented, as well as new raw materials and fabrication methods for textile production, as is the case with most synthetic textiles. Waterproofness (hydrophobicity) combined with breathability are two properties that are often desired. Examples of modification/manufacturing methods that produce breathable yet hydrophobic textiles include microporous and hydrophilic membranes and coatings or a combination of both, as well as the use of retroreflective microbeads, closely woven fabrics and textiles based on biomimetic approaches (Mukhopadhyay and Midha 2008).

The largest part of textiles used today are synthetic (Carmichel 2015). Figure 2.1 shows the total fibre demand of the world from 1990 and estimated to 2030. Polyester is the most used fibre with a demand of 46.1 million tons in 2014, followed by cotton as the most used natural fibre (Carmichel 2015). The demand for natural fibres, cotton and wool, was 25.4 million tons in 2014, and cotton makes by far up for the largest part of it (Carmichel 2015). In the figure cellulosic fibres refers to fabricated textiles based on dissolved plant cellulose (e.g. viscose, rayon), not fibres that contain cellulose (cotton), and the demand for these cellulosic fibres is estimated to grow in the future.

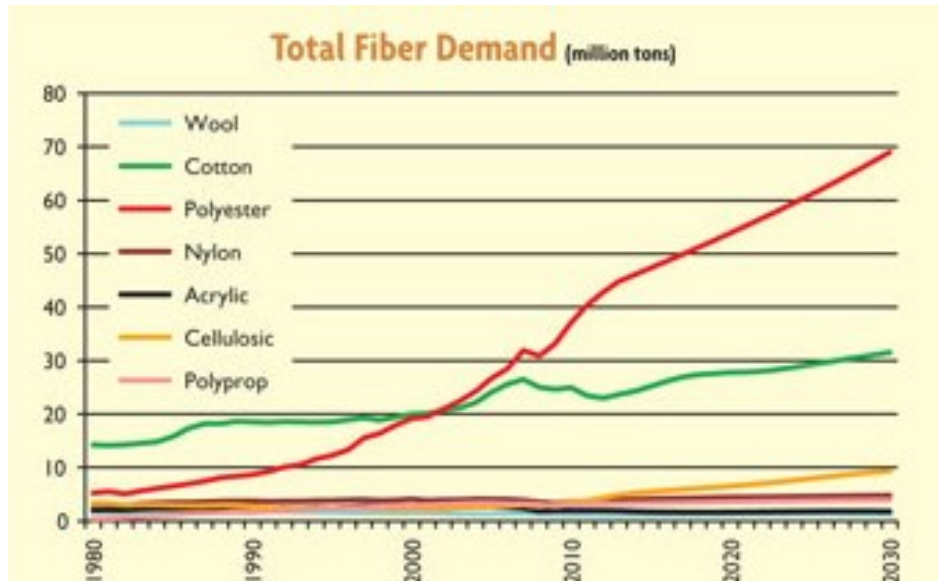


Figure 2.1. Total fibre demand globally from 1990 to 2015, and estimated until 2030 (Carmichel 2015).

Functional textiles are usually synthetic and/or modified with synthetic polymers. A famous example is Gore-Tex, a textile made out of a thin film of expanded polytetrafluoroethylene (PTFE), and other common coatings are polyurethane, poly (ethyl acrylate) and polyvinylchloride (Mukhopadhyay and Midha 2008), all synthetic polymers. Gore-Tex is specifically designed to be breathable but waterproof at the same time, due to pores smaller than water droplets but larger than water vapour, which is a common way to make breathable hydrophobic textiles. The polymer fibres themselves are usually neither hygroscopic nor porous, but the structure of the textile gives the desired properties.

Natural (cellulosic) textiles on the other hand are hydrophilic and porous. Thus the approach of controlled porosity of the fabric outlined above will not work. The hydrophilic, porous cellulose fibres would quickly absorb the water. On the other hand, the porosity and hydrophilicity of the cellulose fibres gives the textiles naturally breathability and moisture buffering properties.

2.3 Surface modification of (natural) textiles

The surface properties of any material are of great importance. The surface is the contact to the outside world, and the properties of the surface determine how the material interacts with its surroundings. The bulk properties (e.g. density, mechanical strength etc.) are usually unaffected by the surface modification. Common reasons to modify the surface are to make the textile waterproof, improve softness, improve adhesion and make the textile antibacterial and less prone to adsorb dirt.

Different surface modification techniques for altering the surfaces of textiles have been developed. These methods will be discussed below grouped based on the properties aimed at. The methods presented should not be seen as a complete list.

2.3.1 Hydrophobic, breathable textiles

Since waterproofness is an often desired property of textiles there are also many surface modifications methods developed to increase the hydrophobicity of textiles, but there are not as many methods that give both hydrophobic and breathable properties. Common techniques to add both these properties is to use polymers to fabricate a coating, or the whole textile, that has pores small enough for water vapour to pass but not water droplets (Mukhopadhyay and Midha 2008). Another way to proceed is to only coat the fibers of the textiles with a hydrophobic coating, and leave the pores uncoated, which would still allow water vapour to pass through.

To fabricate a polymeric coating grafting can be used. Grafting is a surface modification method where a polymer is bound to the substrate, and used in various applications. Depending on the polymer that is grafted onto the substrate, different properties can be obtained, which makes grafting a highly versatile method. For introducing hydrophobic properties on cotton fabrics polyethylene glycol (Badanova 2014), 1,1,2,2-tetrahydroperfluorodecylacrylate (Tsafack 2007) and 1*H*,1*H*,2*H*,2*H*-nonafluorohexyl-1-acrylate (Deng 2010) among others have proved to be successful. Badanova et al. reported that the air permeability was unchanged (Badanova 2014), but in the other papers no results for breathability/moisture buffering were reported. Since the polymers are bound to the cellulosic fibers in the cotton one could imagine that the pores in the

fabric are unaffected, and let water vapour through after grafting, but no results were reported. Grafting on textiles is of course not limited to cotton. Qi et al. successfully coated a poly(ethylene terephthalate) substrate with fluorocarbon using ion beam sputtering (Qi 2002). The coated fabric had good hydrophobicity and the original moisture permeability remained, due to the fluorocarbon only coating the fiber surfaces and not the pores in the fabric (Qi 2002). This supports the hypothesis that grafting does not affect the breathability.

The grafting can happen chemically with a catalyst, using a high-energy source (ultraviolet radiation) or plasma-induced (Wei 2009). Each of these grafting methods have their strengths and weaknesses, and some polymers are better suited for one method than for the other. In terms of environmentally friendly methods, only plasma grafting is seen as a green grafting method (Kalia 2013). The polymer itself also contributes to how green the grafting is, many man-made polymers, not all though, are not biodegradable or eco-friendly.

Biomimetic inspiration has gained interest in recent years. The nature has had millions of years to create and improve different kinds of surfaces, and many plant leaves (including the lotus leaf) and insects have developed superhydrophobic structures (Hoefnagels 2003). These surfaces are superhydrophobic due to a combination of low surface energy and a rough nanostructure (Hoefnagels 2003) (Liu 2007) (Sun 2004). The same principle was also used in this work to obtain a hydrophobic surface. This superhydrophobic behaviour is combined with another great property, self-cleaning (Sun 2004) (Xu 2008). The common way to prepare superhydrophobic structures is to use nanoparticles, often silica nanoparticles (Gao 2009) (Xu 2010) (Xue 2009) (Yu 2007) but also ZnO nanorods (Xu 2010) (Xu 2008) and carbon nanotubes (Liu 2007) are used. Gao et al. reported negligible changes in air permeability (Gao 2009), otherwise breathability/moisture buffering properties have not been reported for superhydrophobic substrates. However, these are non-continuous nanoparticle coatings, which indicates pores large enough for water vapour to pass. From a health and safety point of view, the use of nanoparticles is problematic. Nanoparticles from surfaces leach and enter the human body and affect the biological processes, but there is currently insufficient information available on the effects and furthermore different nanoparticles behave differently (Hoet 2004).

Conventional chemical methods to increase hydrophobicity in plant fibres (and further on textiles) include acetylation and benzylation (Kalia 2013). The problem with chemical treatments is that they require large amounts of hazardous solvents and produce equally hazardous waste (Kalia 2013). Acetylation also greatly reduces the hygroscopic behaviour of natural fibres (Mohanty 2012).

2.3.2 Antibacterial textiles

Textiles are a good medium for bacterial growth (Sun 2002), and antibacterial textiles have therefore gained a lot of interest, especially in biomedical applications. There are many methods to introduce antibacterial properties in textiles, and not all can be presented here. Certain chemical agents have good antibacterial properties, but used on textiles there is a risk of harmful or toxic effect on humans (Dastjerdi 2010).

As well as for superhydrophobic properties, nanoparticles are also used for antibacterial properties, but instead of using silica nanoparticles, silver nanoparticles (Dubas 2006) (Paladini 2015) (Hebeish 2011) and other inorganic (TiO₂, ZnO, Au, etc.) nanoparticles (Dastjerdi 2010) (Montazer 2011) are used. To apply the nanoparticles to the textile surfaces there are many different methods, as for how to produce the nanoparticles, and they include in-situ photo-reduction (Paladini 2015), immersing, pressing and drying (Hebeish 2011), enzymatic activation and ultrasound bath with crosslinking agent (Montazer 2011) and layer-by-layer (Dubas 2006). Layer-by-layer (L-b-L) is a versatile method, where alternating layers of cationic and anionic compounds are built up (Decher 1992), and depending on which compounds are used different properties are achieved. L-b-L will be presented further in section 2.4. Which coating method to use depends on the nanoparticle and the textile substrate is in question. However, the effectiveness of the coatings differs, from around an antibacterial rate at 50% (nano-Ag on silk, *Staphylococcus aureus* tested) (Dubas 2006) to up to 100% (nano-TiO₂ on polyester/wool, *Escherichia coli* tested) (Montazer 2011). But since not the same bacteria or even the same textile substrate was tested, it is impossible to definitely say which method works better.

The use of nanoparticles may be seen as a green textile coating method (Hebeish 2011), but there is also criticism (Dastjerdi 2010). As discussed in section 2.3.1, there is currently not enough information available on how nanoparticles behave in the human body and on the biological processes (Hoet 2004) (Dastjerdi 2010).

Another method to fabricate antibacterial textiles is to use poly-L-lysine (PLL). PLL is a cationic polyelectrolyte based on an amino acid, and will be discussed further in section 2.4.1. PLL can be added to the textile surface, but one method is to enzymatically pre-treat the textile and then graft PLL onto the surface (Xing 2015) (Jin 2009) (Guo 2013). PLL can also be added using charge (Chang 2012), and then the adsorption is affected by the solution environment (pH) and the higher the pH the more PLL was adsorbed. The antibacterial performance of the PLL-coated fabrics was more similar than the fabrics coated with nanoparticles. Grafted PLL on silk showed an antibacterial rate of 90% on *S. aureus* and *E. coli*, whereas PLL adsorbed by charge onto wool had antibacterial rates over 96% when *E. coli* and *Micrococcous luteus*.

2.4 Layer-by-layer adsorption (L-b-L)

In this work, surface modification was done using the layer-by-layer method (Decher 1992). The adsorption is driven by the entropy gain due to the release of counter ions upon adsorption of oppositely charged component on oppositely charged substrates. Two oppositely charged layers form a bilayer. The method was originally developed to build up polyelectrolyte multilayers but recently also nanoparticles have been used in the multilayers (Kotov 1995) (Dubas 2006). Cellulose is negatively charged, meaning that the next layer has to be cationic, followed by the anionic component. The procedure is very simple; the substrate is alternately immersed in cationic and anionic solutions (Figure 2.2). These steps are repeated until the desired amount of layers is obtained, which can be up to 100 bilayers. (Decher 1992).

The L-b-L method has many advantages, such as being simple, low-cost, controllable and versatile. L-b-L can also be done on most substrates, regardless size and shape (Decher 1992). In conventional L-b-L the substrate and layer compounds must be charged, since the charge holds the system together, but recently methods for the use of uncharged

components have been investigated (Zhang 2007) (Kharlampieva 2009). A system held together by charge may give defined layers, but has a disadvantage when it comes to washing, the electrostatic interactions could be destroyed during the laundry process and the layers coming off (Wei 2009).

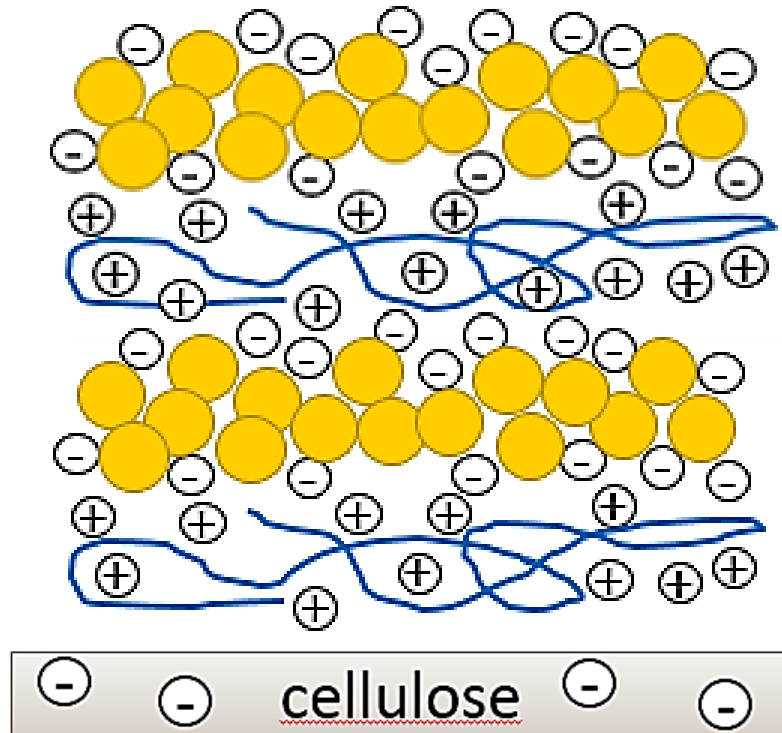


Figure 2.2. The L-b-L build-up. In this figure, the bilayers consist of layer of positively charged polymer and a layer of negatively charged particles.

2.4.1 Properties of the coating components used

Lysine is an amino acid that has one hydroxyl group and two amino groups, one next to the α -carbon and one next to the ϵ -carbon. Polymerized lysine is called polylysine, and depending on whether the α -carbon or the ϵ -carbon is polymerized, either α -polylysine or ϵ -polylysine is obtained. α PL is synthetically produced and ϵ PL is produced by bacteria. Further on there are both L- and D-lysine, and the L-form (Figure 2.3) is naturally occurring while the D-form is artificial (Sitterley 2008). Poly-L-lysine (PLL) is a highly charged polycation (Zou 2010) and enhances electrostatic interactions between positively and negatively charged ions and increases the amount of positively charged sites to bind to (Sitterley 2008) (Alamanda Polymers 2016). Due to this role as an attachment factor PLL is used in surface modifications and tissue cultures (Sitterley 2008). The isoelectric point,

the pH at which a molecule carries no net charge, is 9.7 for lysine and 9.0 for ϵ -PLL (Curylo 2008). As PLL is based on an amino acid, it is environmentally friendly and completely non-toxic.

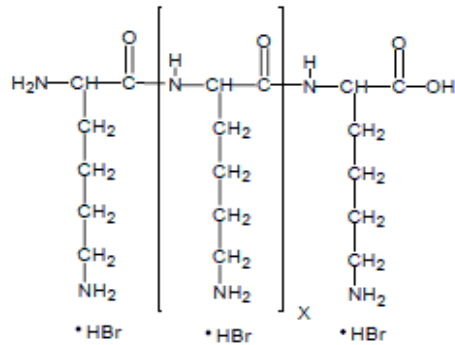


Figure 2.3. Poly-L-lysine (Sitterley 2008).

Wax is a natural water repellent, but the use of wax to waterproof textiles has been combined with problem such as insufficient stability of the wax emulsion/dispersion used and the durability of the coating (Fluck 1956). However, as discussed in section 2.3.1, it is not only surface energy, but also surface roughness, that contributes to the hydrophobicity of a material (Quéré 2002). For creating a hydrophobic surface, a wax dispersion has proved to be successful on wood (Lozhechnikova 2015), and the dispersion is stable. Additionally, a wax dispersion has higher possibility to be breathable than a continuous film of wax, since there are small holes in the structure allowing the water vapour to pass through.

Lignin is the second most abundant natural polymer after cellulose, and is an amorphous macromolecule. The exact composition of lignin varies a bit from plant to plant. In the plants, lignin helps to protect against pathogens (Boerjan 2003). However, the insolubility of lignin in water has been a problem for large-scale use (Lievonon 2015), but a dispersion of colloidal lignin particles in water overcome this issue. The use of colloidal lignin particles is a green alternative for improving the antibacterial properties of natural textiles, as well as giving antistatic properties and protecting against UV radiation (Kozlowski 2008).

In this work the L-b-L technique was used on CNF films and natural plant textiles (cotton and linen). PLL is working as the only cation in the L-b-L adsorption, and possibly contributes to the antibacterial properties. The colloidal lignin particles were added to

give even more antibacterial properties. The wax dispersion was added to provide hydrophobicity, as a combination of low surface energy and surface roughness. This structure will hopefully also be self-cleaning, and further contribute to the antibacterial properties. Particles were chosen as an alternative to continuous film-forming coating to not decrease the moisture buffering and breathability of the natural textiles.

3 Experimental

3.1 Materials

3.1.1 Poly-L-lysine

0.1 % (w/v) PLL with a molecular weight of 150,000-300,000 was purchased from Sigma-Aldrich. The pH of the PLL was altered using buffer solutions, 0.1 M HCl and 0.1 M NaOH. PLL was with its original concentration.

3.1.2 Wax dispersion

Refined carnauba wax was purchased from Sigma-Aldrich. The wax dispersion was prepared by heating water to 90 °C and adding wax to the heated water for the wax to melt. Carnauba wax has a melting point of 86 °C. The solution was sonicated for 5 min using a Branson Digital Sonifier® in order to make it as uniform as possible. After sonication, the dispersion was cooled down in ice bath for stabilizing it. Lastly, the dispersion was filtered using a pore 1 filter (100-160 µm).

3.1.3 Colloidal lignin particles

An aqueous dispersion of colloidal lignin particles was prepared according to the method described by Lievonen et al. (2015). Kraft process extracted lignin, further purified using Lignoboost concept, was dissolved in tetrahydrofuran (THF) and filtered through a 0.7 µm filter. After that the solutions was put into a dialysis bag, which was immersed in an excess of deionized water (periodically replaced). The dialysis took place for at least 24 h under slow stirring, and during this process the nanoparticles were formed. After particle formation, water was replaced to remove THF solvent, and the dispersion was centrifuged at 2000 rpm and 5000 rpm for 20 min. The dry matter content determination was determined to be 300 mg/L.

3.1.4 Freestanding cellulosic films

CNF films were used as a substrate to see how the coatings would perform. To prepare a film 100 ml 85% CNF was filtered for 20 min using 2.5 bar pressure. The film was hot-pressed for two hours at 100 °C and with a pressure of 1800 kg/cm². The prepared films were stored in standard conditions, 23 °C and relative humidity of 50%.

3.1.5 Textile samples

Three different textiles were purchased from Eurokangas, one was 100% linen and two were 100% cotton. Of the cotton samples, one was a lightweight bedsheet fabric, and the other was a thicker fabric. All fabrics were white, so that possible discoloration would be easily detected (Figure 3.1).

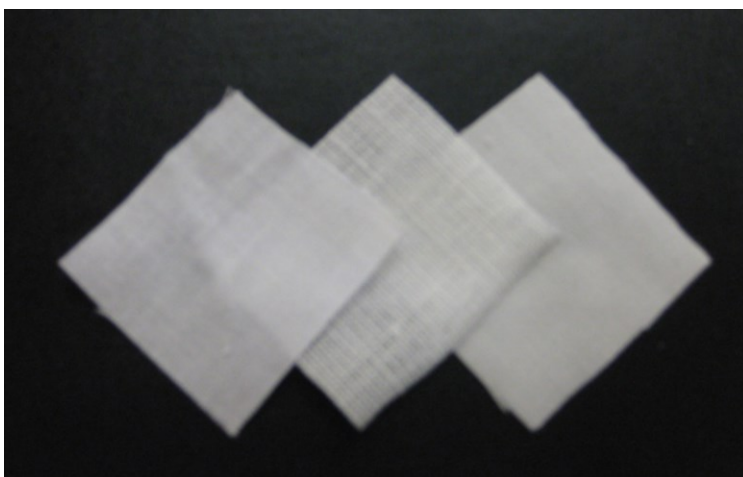


Figure 3.1. The textile samples. From left to right light cotton, linen and heavy cotton.

3.2 Methods

3.2.1 QCM-D

In QCM-D, a small quartz crystal is oscillating at its resonance frequency. When something is adsorbed onto the crystal, the oscillation frequency decreases, and the adsorbed mass can be calculated from this change in frequency. Similarly, when something is desorbed, the frequency increases. Thus, the adsorption (or desorption) process can be monitored in real-time. The dissipation, energy losses due to friction, are also monitored. This gives information about the viscoelastic properties of the adsorbed layer. (Rodahl 1995).

Prior to QCM-D, the QCM-D gold crystals were coated with cellulose, since the adsorption on cellulose, not gold, was of interest. To fabricate a cellulose coating spin coating was used, a method where the coating material (liquid) is put onto the substrate, which is rotated at high speed spreading the coating thanks to the centrifugal force. The crystals were spin coated with supernatant CNF. To get the CNF to attach to the gold surface 3.4 g/L polyethylene-imine (PEI) was used. To clean the crystals, they were rinsed in MilliQ water and dried with N₂ gas, and after that they were soaked in PEI for 15 min, and rinsed to remove excess PEI. Supernatant CNF was spin coated for 1 min at 3000 rpm in vacuum onto the PEI coated crystals, which were then stored in desiccators until QCM-D. PEI is not needed in surface modification of freestanding CNF films or fabrics; it is only needed to bind the CNF to the gold crystal.

QCM-D experiments were carried out with the E4 instrument (Q-sense AB, Västra Frölunda, Sweden). Samples were pre filtered with a 0.45 µm filter, except for the wax dispersion, which was filtered with a 1 µm filter. All samples were sonicated for a few minutes before use. The concentration of PLL was 10 mg/L and of the wax dispersion and colloidal lignin particles 100 mg/L. Material was adsorbed until a stable plateau in frequency was acquired. Consecutive layer was adsorbed only after a stable plateau was acquired during rinsing. The pumping rate was constantly 0.1 ml/min. Mass changes were calculated according to the Johannsmann equation (1) (Johannsmann 1992).

$$m_0 = \frac{\sqrt{\rho_q \mu_q} \Delta f}{2f_0 f} \quad (1)$$

3.2.2 Contact angle

Contact angle (CA) measurement is a commonly used method to quantify the wettability of a solid surface. The idea is simple, a droplet of water is discharged onto the surface and the image is recorded with a camera, the contact angle between the droplet and the surface is then determined with a computer program. A surface with a CA > 90° is classified as hydrophobic, and with a CA > 150° the surface is superhydrophobic. With a CA < 90° the surface is hydrophilic. The static contact angle was measured for 60 seconds, but due to bending of the CNF films, the contact angle at 5 seconds was analysed. Due to

consistency and comparison reasons, the contact angles for QCM-crystals and textiles were also analysed at 5 seconds. The contact angle was measured with a CAM 2000 (KSV Instruments LTD).

3.2.3 Zeta-potential

In an aqueous solution, a charged particle will attract ions of the opposite charge to itself. The particle is often negatively charged (as is cellulose in this work), meaning that the attracted ions are positively charged. Part of the cations are adsorbed onto the negatively charged particle forming a layer called the Stern layer. Outside the Stern layer lays the diffusion layer, where cations outnumber anions. The zeta potential is the drop in potential in this diffusion layer (Figure 3.2). (Chen 2016). The zeta-potential is also called electrokinetic potential (McNaught 1997), and gives information about the stability of a suspension (Chen 2016). Indirectly the zeta-potential is also a measurement of the charge of the particle. The higher the charge the more counter ions are attracted, which is observed as a higher the zeta-potential. The zeta-potential was measured with a Zetasizer Nano-ZS90 (Malvern, UK).

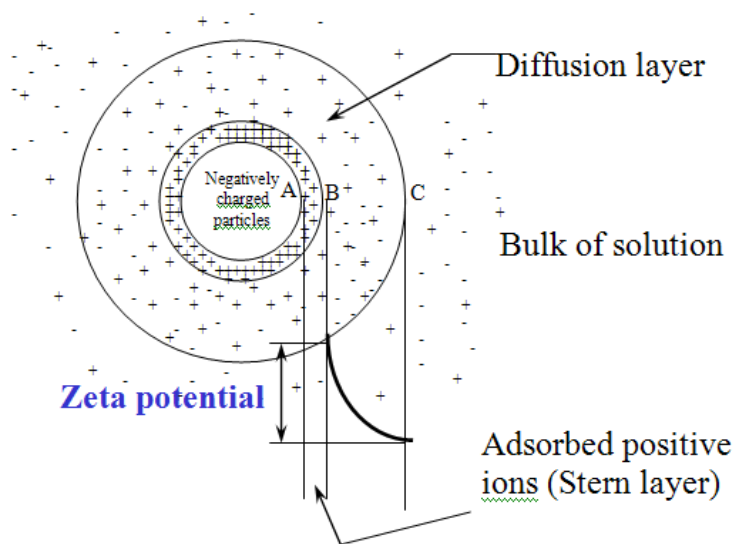


Figure 3.2. The zeta-potential of a particle in an aqueous solution (Chen 2016).

3.2.4 AFM

AFM, or Atomic Force Microscopy, is a scanning probe microscopy technique and gives topographical information. At the end of a cantilever is a sharp tip that scans over the surface. The cantilever bends due to interactions between the tip and the surface, and by recording the changes, an image of the surface is acquired. There are two common imaging modes, tapping mode and contact mode. Only tapping mode was used in this work, since it is better suited for soft samples. In tapping mode, the tip is oscillating at its resonance frequency and three images are acquired, one height image, one amplitude image and one phase image. The height image gives clear topographical information, but sometimes the phase contrast image can be more informative (Eronen 2011). In this work AFM was done on QCM crystals, since CNF films and textiles are less suitable for AFM.

3.2.5 Coating of CNF freestanding films and fabrics

Layer-by-Layer deposition was done on both CNF films and textiles. Prior to L-b-L the substrates were soaked in water for a few minutes. After one layer was adsorbed the substrate was rinsed with water three times, in different beakers, to get rid of non-adsorbed material. Then the next layer was adsorbed. The immersion time was always 5 minutes. The samples were dried and stored between blotting sheets, under a light pressure, in standard conditions. A few samples were dried at 103 °C for 1h, and then stored in standard condition.

3.2.6 Roughness

The surface roughness was measured at MIKES, VTT, using a scanning white light interference microscope (ContourGT-K, Bruker). The arithmetical mean height of the scale limited surface, S_a , was analyzed. S_a is calculated according to equation (2) (ISO-25178 2012).

$$S_a = \frac{1}{A} \iint_A |z(x,y)| dx dy \quad (2)$$

The area scanned was 423 μm x 564 μm , the focus was 20x0.55x, and each sample was measured three times.

3.2.7 Moisture buffering capacity

The hygroscopic behavior of the textiles was tested in a climate chamber at 23 °C with cycles of 16 h 33% RH and 8h 75% RH, to resemble the NORDTEST standard (Rode 2005). Two coatings, PLL-wax-PLL-wax, $c_{wax} = 10$ g/l, and the same coating that had been dried at 103 °C for 1 h, and no coatings as reference were tested on all three fabrics, with three samples of each. The sample size was 5x5 cm. Prior to testing the samples were stabilized in the chamber for two cycles.

3.2.8 Oxygen Transfer Rate

The oxygen transfer rate (OTR) tells how fast oxygen flows through a material and gives information about breathability. OTR was measured at VTT using a Systec M8001 and M8011. The surface area measured was 5 cm², temperature 23 °C and RH 50% and 80%.

4 Results and discussion

4.1 Thin film studies to understand the layer build-up

4.1.1 QCM-D

With QCM-D the adsorption was studied in detail, and the first thing looked at was how the pH of PLL affects the adsorption. The results are shown in Figure 4.1.

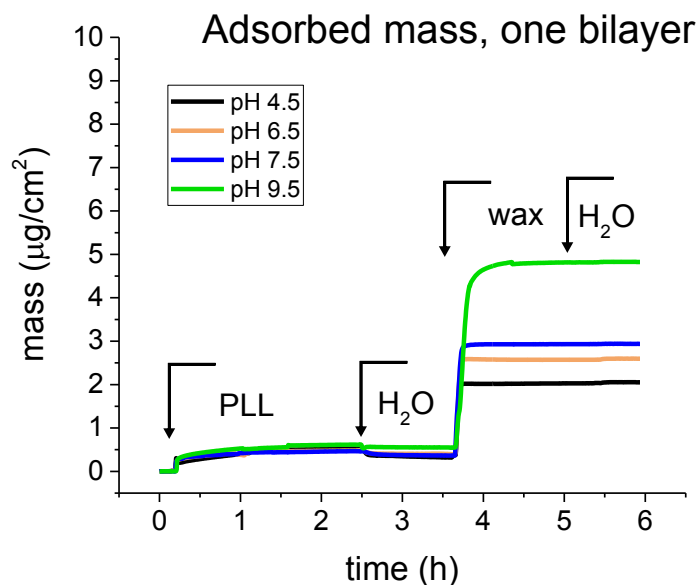


Figure 4.1. The adsorbed mass calculating using Johannsmanns equation (1) for one bilayer of PLL and wax. The pH of PLL was altered and the pH of the wax dispersion remained unchanged.

From the results it can clearly be seen that the adsorption of both PLL and wax increases with increasing pH of PLL. The difference is seen clearest when the pH is 9.5, when the pH is 4.5-7.5 the difference is less significant. Overall the adsorption of wax is much higher than PLL, but the wax concentration was also 10 times greater than PLL. The wax adsorbed quickly, whereas it took a little bit longer for PLL to reach a plateau. Some PLL came off, or was never fully adsorbed, when rinsing with water, but with the wax almost nothing was removed upon rinsing. This is promising for the laundering of the textiles. The same

adsorption behavior was observed when two bilayers were adsorbed, as shown in Figure 4.2.

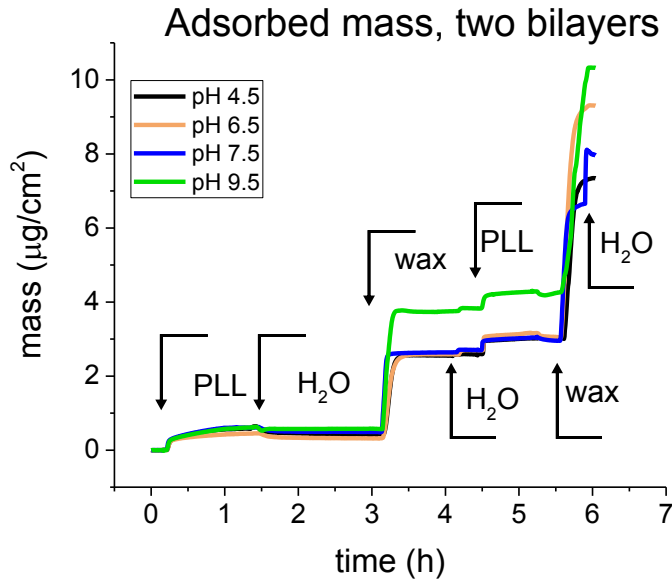


Figure 4.2. The adsorbed mass for two bilayers of PLL and wax. The pH of PLL was altered and the pH of the wax dispersion remained again unchanged.

Once again, the adsorption of PLL is higher the higher the pH is. This is most clear for the first bilayer. For the second bilayer a lot of PLL is adsorbed even at pH 6.5 and onto this layer a thick layer of wax is adsorbed. It seems that the wax adsorption increases with increasing PLL adsorption. This can explain the changes for pH 4.5-7.5, but not 9.5. A measurement of the z-potential gave a better explanation (Figure 4.3). The zeta-potential is about the same for PLL at 4.5-7.5, but notably lower for PLL at pH 9.5. This means that PLL behaves differently at different pH. When pH is 4.5-7.5 PLL adsorbs in a more flat conformation the surface, and the small variation in wax adsorption is due to the small differences in PLL adsorption, i.e. the more PLL adsorbed, the more wax is adsorbed. At high pH (9.5) the z-potential of PLL is clearly lower and it might lead to a higher adsorption of wax since the PLL molecules do not repel each other at the surface.

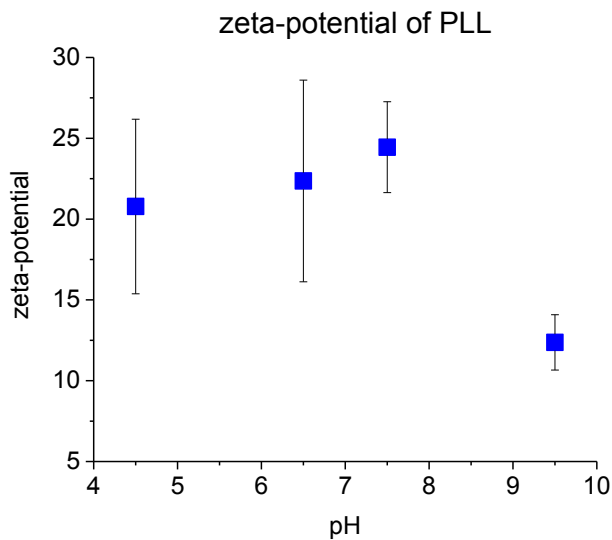


Figure 4.3. The zeta-potential of PLL at different pH.

The conformation of PLL does not change within the pH range used here. At low pH PLL exist in a coil formation, a P_{II}-helix. At pH 4 the side chains of PLL are fully ionized preventing the formation of an α -helix. At a pH above 11.6 (10°C) (Mirtic 2013) or above 10.6 (Chiou 1992) PLL turns into an α -helix, and when the α -helix is heated it turns into a β -sheet. The pH range in this work was 4.5-9.5, meaning that PLL had the same conformation the whole time.

Until the first bilayer is adsorbed the treatment for the QCM-D crystals used in the experiments with one and two bilayers (Figure 4.1 and 4.2) was the exact same, and should therefore have received similar results. Figure 4.4 shows the adsorbed mass of all PLL layers, the first ones and the third, plotted against pH. No very clear trends appear. There are variations between the first layers, and even more variations when the third layer is taken into account. Nevertheless, the adsorption of PLL is generally small, so any differences will appear more clearly. Generally, it seems that the third layer is a bit thinner than the first layer, but the differences are small and should not be over interpreted.

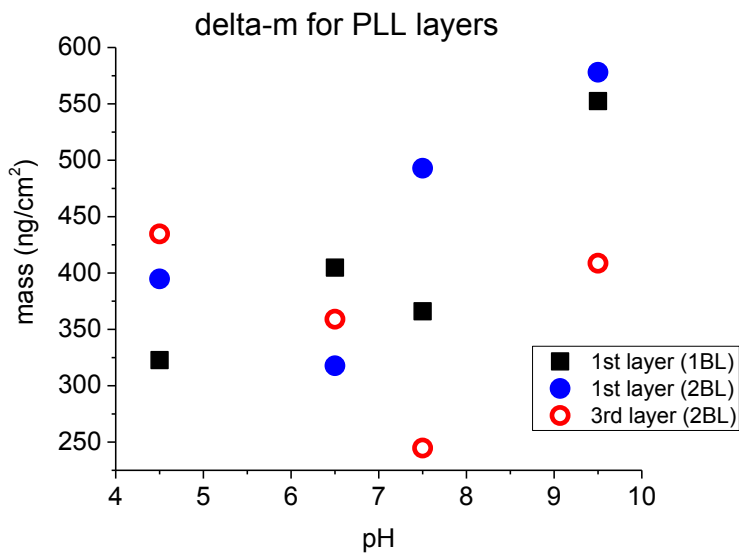


Figure 4.4. The adsorption of PLL according to pH.

When the adsorption of the wax particles is plotted against the pH of PLL trends are clearer (Figure 4.5). As established, the higher the pH the higher the wax adsorption. What is interesting is that in the fourth layer significantly more wax is adsorbed than in the second layer. This might be due to a more heterogeneous surface after the third layer (second time PLL), than after the first PLL layer. Each layer is probably not evenly spread out on the surface, thinner and thicker places are likely to appear. When the third layer (PLL) adsorbed onto the second layer (wax) it is not likely that the PLL is covering all the wax, since wax adsorption is about 10 times higher than PLL adsorption. This will create even more hills and valleys for the wax to adsorb on, which gives higher wax adsorption in the fourth layer than in the second layer. This change in thickness of the different layers might also be due to the nature of L-b-L, it has been noted that the buildup more often than not is non-linear, even exponential.

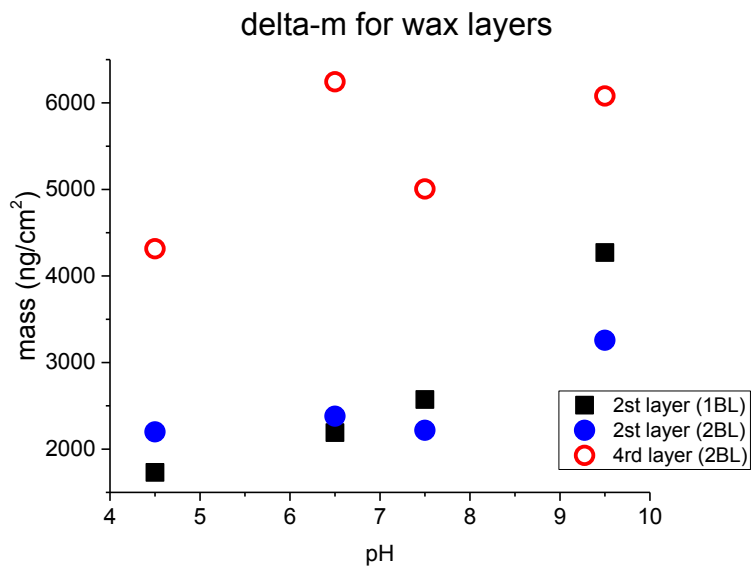


Figure 4.5. The adsorption of wax particles according to pH of PLL.

The adsorption of colloidal lignin particles was also studied with QCM-D. Figure 4.6 shows the adsorption of PLL, at pH 9.5, lignin and wax.

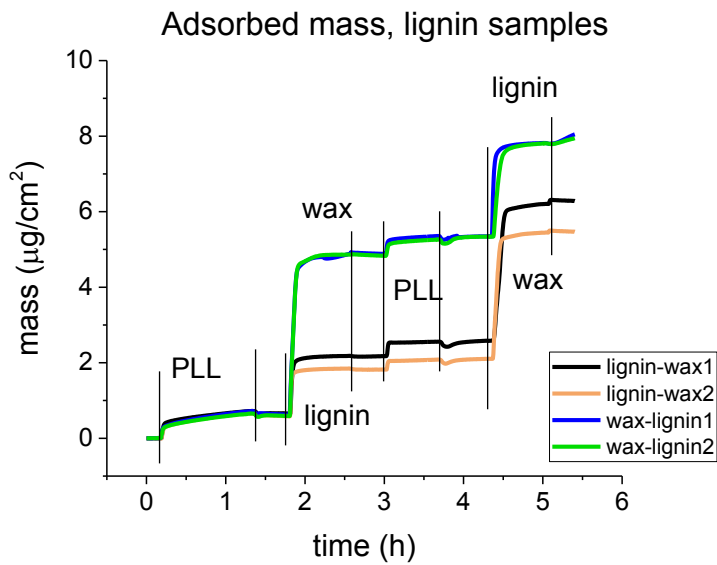


Figure 4.6. The adsorption of PLL (pH 9.5), colloidal lignin particles and wax particles. The black and orange lines show the adsorption of PLL-lignin-PLL-wax, whereas the blue and green lines show the adsorption of PLL-wax-PLL-lignin. The layers were rinsed with water before next layer was introduced.

From the graph (Figure 4.6) it is clearly seen that lignin adsorbed far less than the wax particles, even though the two solutions have the same concentration. This lower adsorption has also affected the following layers, which are thinner when lignin makes up the second layer. The amount of adsorbed lignin differs quite a bit, but since the treatment is exactly the same the only explanation for this is that lignin as a natural material is heterogeneous and does not always behave exactly the same. Nevertheless, when lignin was adsorbed as the fourth layer the adsorption pattern for the two QCM-D crystals looks more similar to each other. Another explanation for the difference in adsorbed lignin is the differences in adsorbed PLL in the first layer. The PLL adsorption for the crystal that is represented by the black line is notably higher (659 ng/cm^2) than for the crystal represented by the orange line (586 ng/cm^2), and gives more surface area for the lignin to attach to. Interesting is that in the second bilayer the lignin layer is thicker when the PLL layer is thinner. The difference in thickness in PLL in that layer is however smaller than in the first bilayer.

What also is interesting is that the fourth lignin layer is thicker than the second layer, whereas both PLL and wax are thicker in the first/second layer and thinner in the third/fourth layer. Surface roughness could perhaps explain this, e.g. more surface area for the particles to attach to, but the same should be true for PLL and wax as well.

4.1.2 Contact angle

The contact angle (CA) revealed that each of the coatings improved the hydrophobicity, compared to the very hydrophilic reference CNF (Figure 4.7). As expected, the thickness of the wax affects the CA, i.e. the more wax adsorbed, the higher the CA.

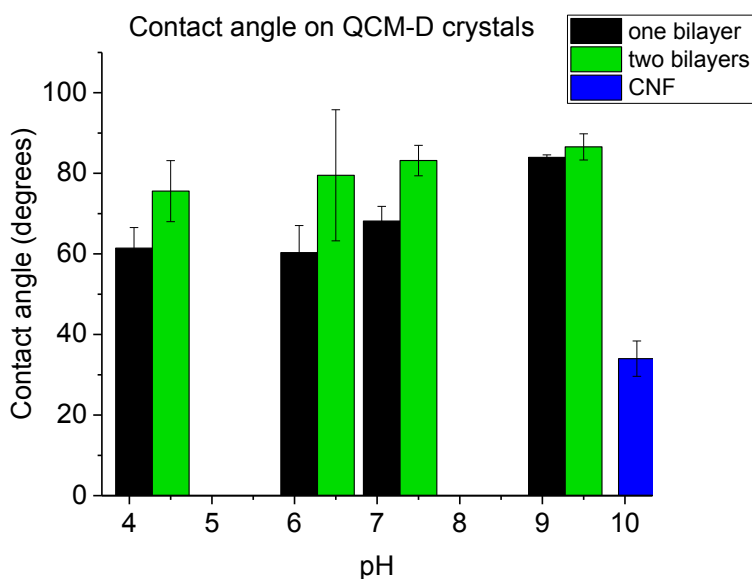


Figure 4.7 The CA of PLL-wax one bilayer and two bilayers, according to pH of PLL. CNF is an uncoated reference. Five measurements were performed on each sample.

Both for one and two bilayers the CA increased with higher pH, and more wax, and with two bilayers the CA was overall higher than for on bilayer, but the different two bilayer samples were closer in CA compared to the one bilayer samples. Interesting is that the samples with pH 9.5 had the smallest standard deviation, maybe these coatings were more uniform due to a higher wax adsorption. However, all the CAs are under 90°, and none of these samples can therefore be classified as hydrophobic, even though a notable difference in CA can be seen with bare eyes (Figure 4.8).

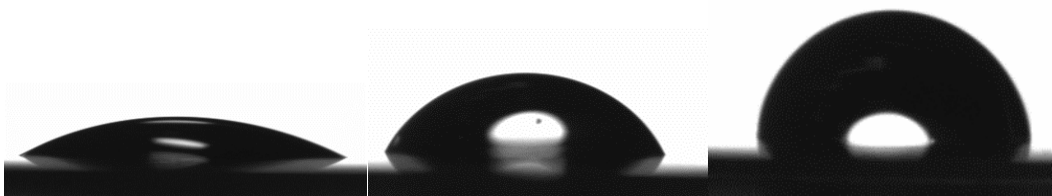


Figure 4.8. From left to right, water droplet no CNF reference, PLL-wax on bilayer at pH 4.5 and PLL-wax two bilayers at pH 9.5

For the samples with colloidal lignin particles hydrophobicity was achieved (Figure 4.9). The CA reached to around 95° when lignin made up the second layer and wax the fourth and outermost layer. When the lignin was in the outermost layer, the CA was remarkably poorer, only around 70°-50°. This big difference, and the huge standard deviation for the

first lignin-wax sample, is curious, maybe the lignin coating is uneven and therefore result in these huge CA differences.

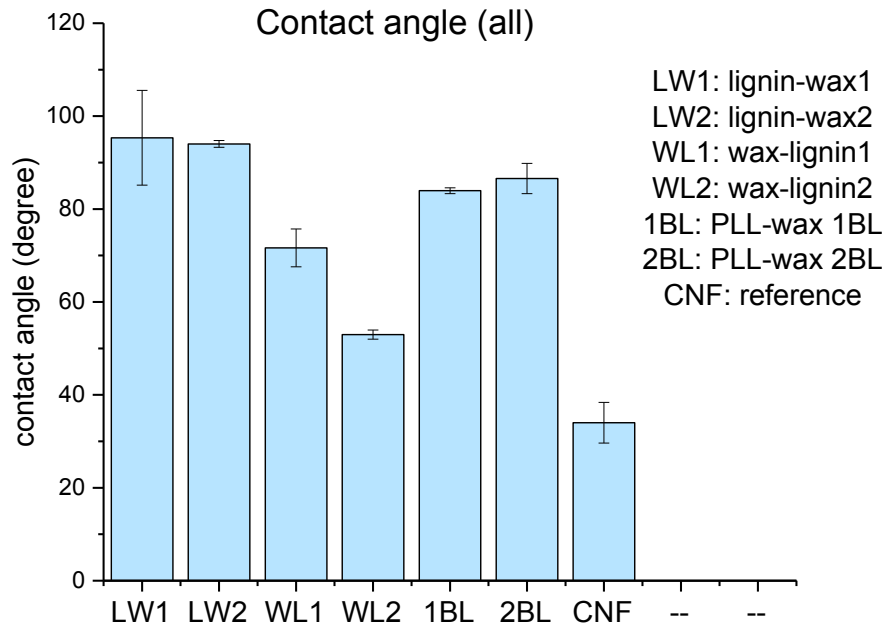


Figure 4.9. The CA, at 5 seconds, of the lignin samples compared to the PLL-wax samples at pH 9.5. 5 measurements of each sample.

Overall, the CA results show that PLL needs to be at a high pH (9.5), two bilayers are better than one and that lignin should not be in the outermost layer for achieving a high CA.

4.1.3 AFM

The morphology of the coated surfaces was investigated using AFM. On the surface of one bilayer, pH 4.5, wax particles are visible, but also cellulose fibrils (Figure 4.10). The size of the particles differs, but there are no huge particles. Theoretically the max size is $1\mu\text{m}$ (the dispersion was filtered for QCM), and the biggest particles are about half that size. But the surface is not totally covered in wax particles, cellulose fibrils are also clearly visible.

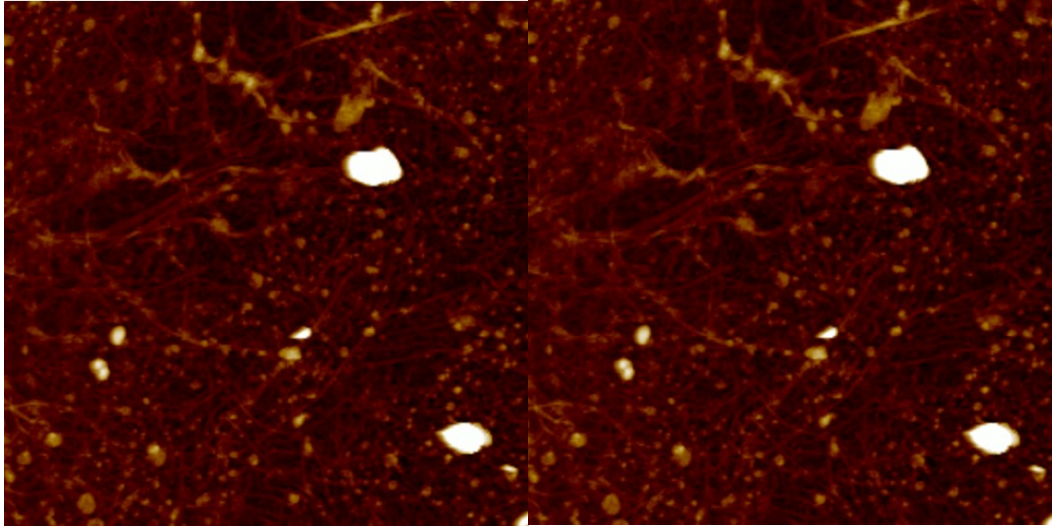


Figure 4.10. AFM height images of PLL-wax one bilayer at pH 4.5 5µm.

The surfaces of one bilayer PLL-wax at pH 6.5 and 7.5 looks very similar to the same coating but at pH 4.5 (Figure 4.11). There are both wax particles and cellulose fibrils visible. On the sample at pH 7.5 there appears to be some dirt, or particles that have clogged together. The theoretical max size for the wax particles is 1 µm, since the dispersion was filtered prior to QCM-D.

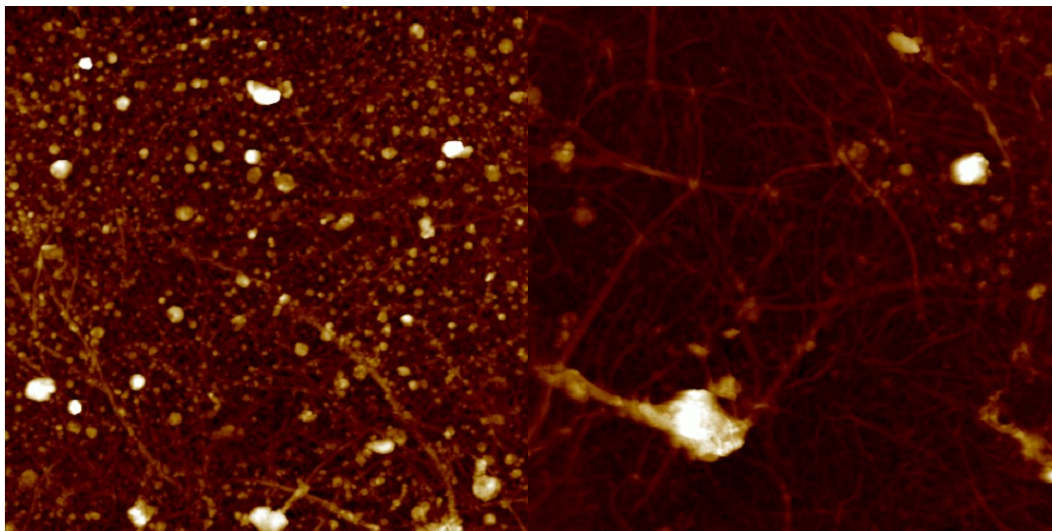


Figure 4.11. AFM height images of PLL-wax one bilayer at pH 6.5 (left) and pH 7.5 (right). 5µm.

With one bilayer and PLL at pH 9.5 there are not that many cellulose fibrils visible, but instead more wax particles (Figure 4.12). This is consistent with the other results, more wax with higher pH.

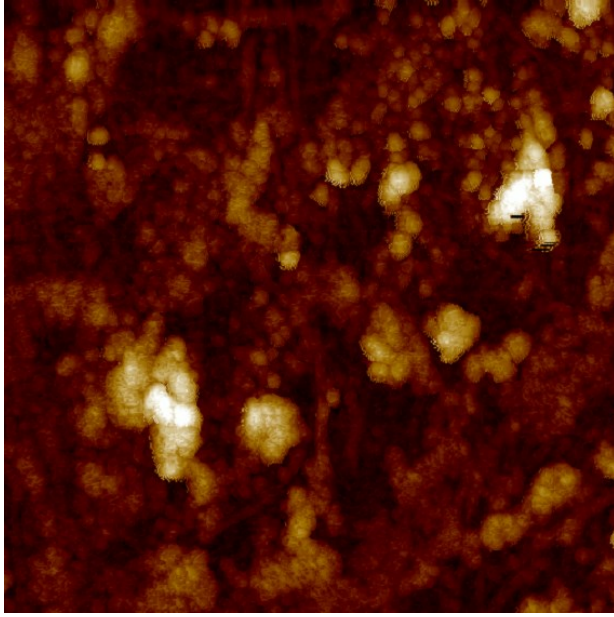


Figure 4.12. AFM height image of PLL-wax one bilayer at pH 9.5 5 μ m.

With two bilayers, even more of the cellulose fibers are covered with wax. At pH 4.5, the wax particles form a layer that covers almost all underlying cellulose (Figure 4.13). But the layer has cracked, revealing the cellulose fibers. This might be due to the wax layer drying, or to something else.

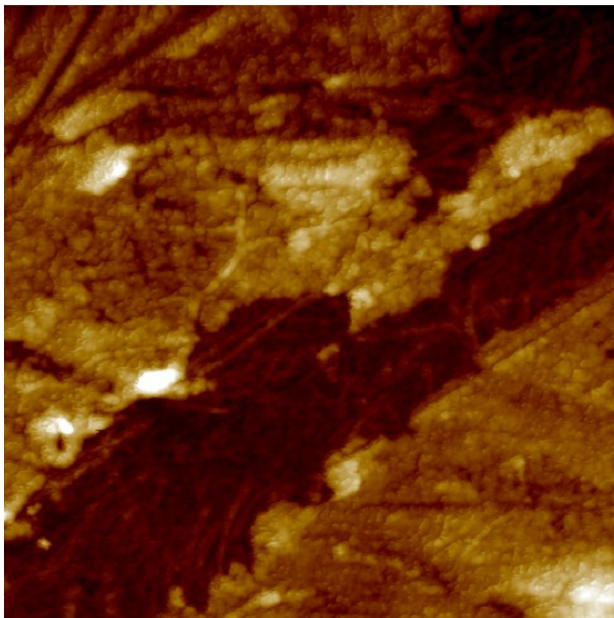


Figure 4.13. AFM height image of PLL-wax two bilayers at pH 4.5 5 μ m.

At pH 6.5 and 7.5 no cellulose is visible, but the same cracks appear on the 7.5 sample (Figure 4.14). The cracks should however not be so big that they affect the CA and hydrophobicity.

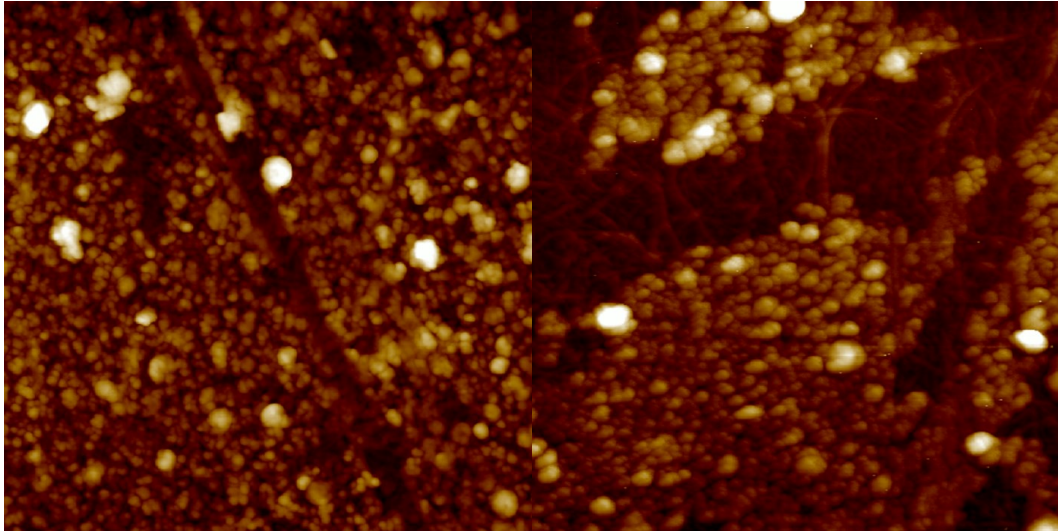


Figure 4.14. AFM height images of PLL-wax two bilayers at pH 6.5 (left) and pH 7.5 (right). 5 μ m.

With two bilayers and PLL pH at 9.5 a fully covering wax particle layer appear (Figure 4.15). There are also some bigger particles, but no cracks are visible.

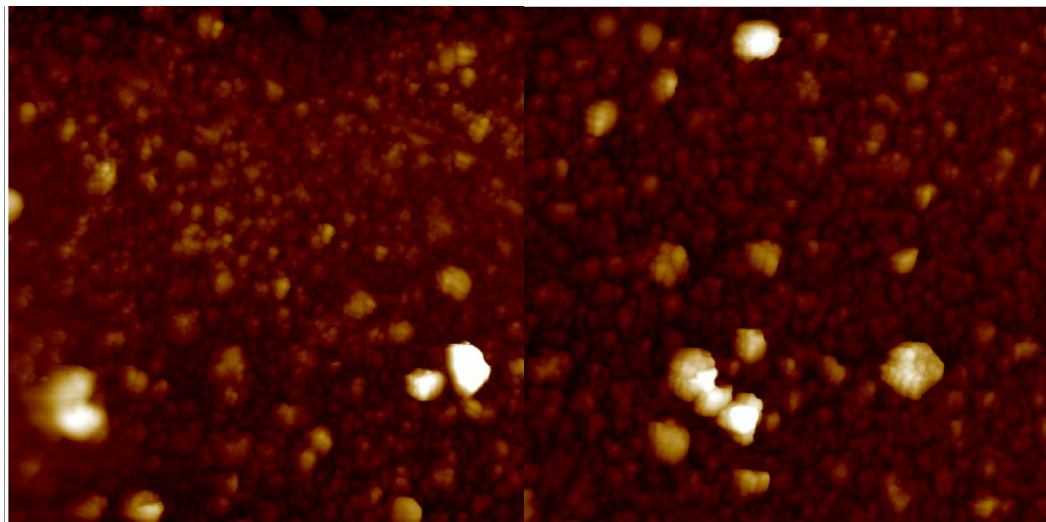


Figure 4.15. AFM height images of PLL-wax two bilayers at pH 9.5 5 μ m.

With colloidal lignin particles on top the AFM images look completely different, as they should (Figure 4.16). Besides lignin there are also chunks that look very similar to wax

particles. Perhaps the entire wax layer was not covered with lignin and is also observed. Whatever those particles are, they are not fully covering the surface, lignin is dominating.

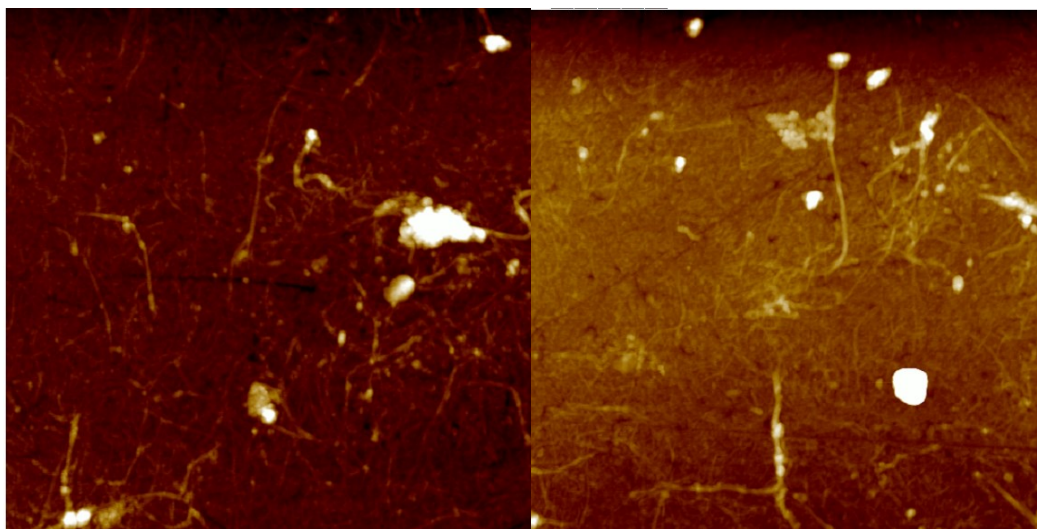


Figure 4.16. AFM height images of PLL-lignin-PLL-wax. 5 μ m.

The experiments on freestanding CNF films and fabrics were based on the data obtained from these experiments on QCM-D crystals. With the films and fabrics, the pH of PLL was always 9.5 and lignin was never in the outermost layer.

4.2 Surface modification of macroscopic samples

4.2.1 The samples

L-b-L deposition was furthermore performed on freestanding CNF films and textiles. Although the optimum pH was already found in the model experiments, the effect of wax and lignin concentration, number of bilayers and drying conditions was explored. The CA results showed that the higher the concentration the higher the CA. This difference was clearer for wax than for lignin, but that might be due to that the difference in lignin concentration was not too big (100 mg/l compared to 300 mg/l). More than two bilayers did not improve the CA, and were additionally more difficult to produce due to the more dipping needed. Two bilayers gave the best results. Overnight drying in a 50 °C oven did not improve the CA, compared to normal drying at standard conditions, but drying at 103 °C for one hour improved in some cases the CA. The samples that were tested for other

properties besides CA are presented in Table 4.1. The tests were done to learn more about the properties of the coatings, and in which applications they could be used.

Table 4.1. The freestanding CNF film and textile samples that were used for testing. The wax concentration is 1 g/l, if not else said.

Treatment	drying temperature
CNF ref (no treatment)	standard
PLL	standard
PLL-wax	standard
PLL-wax-PLL-wax	standard
PLL-wax-PLL-wax, 10 g/l	standard
PLL-lignin-PLL-wax	standard
PLL-wax-PLL-wax, 10 g/l	103 °C
Textiles	
Reference	standard
PLL-wax-PLL-wax, 10 g/l	standard
PLL-wax-PLL-wax, 10 g/l	103 °C

4.2.2 Wetting and Roughness

The CA results of the freestanding CNF films are shown in Table 4.2. Two different sets of results are shown, one set from when L-b-L was done with good solutions, and one set from when L-b-L had been done with diluted/dirty solutions that had been used for L-b-L on textiles. It was only after the experiments were done and the results analyzed that it was discovered that solutions used to coat textiles weren't suitable to coat CNF films anymore.

Table 4.2. CA of coated CNF films, one set made with good solutions, that had dried in standard condition for two days, and three measurements were done on each sample. The other set were made with diluted/dirty solutions (not PLL, it was replaced), and were dried in standard conditions for five days, and five measurements were done on each sample. CA presented at five seconds.

Treatment	drying temp.	CA (3 meas. 2 d. drying)	CA st.dev. (3)	CA (5 meas. 5 d. drying)	CA st.dev. (5)
CNF ref	standard	< 15		< 15	
PLL	standard	94.7	0.91	89.9	3.73
PLL-wax	standard	85.6	3.56	79.2	1.52
PLL-wax-PLL-wax	standard	120.5	7.55	79.7	6.63
PLL-wax-PLL-wax, 10 g/l	standard	131.5	0.42	104.4	5.02
PLL-wax-PLL-wax, 10 g/l	103°C 1h	127.6	13.96	112.9	4.30
PLL-lignin-PLL-wax	standard	104.5	3.35	76.0	3.07

The first set, made with good solutions, are considered here to be more reliable, even though they were not in the standard condition room as long and only three measurements were performed. Because of this, the set made with good solutions will be analyzed, and not the other set.

Surprisingly, PLL has a higher CA than PLL-wax. However, the difference was small and the reproducibility of CA measurements was rather poor, so not too much emphasis should be put on this difference. Both PLL-wax one bilayer and two bilayer show a higher CA on CNF films than on QCM-D crystal, but this most likely is due to the ten times higher wax concentration. In addition, when the wax concentrations get even higher, 10 g/l, the CA increases. Thermal annealing does not seem to benefit the hydrophobicity, it even lowers the CA a bit, even though the standard deviation for the sample is extremely high (13.96), and the difference between the annealed sample and the sample with the same coating but not annealed is not significantly big, so this should not be taken too much into account. For the set made with poor solutions the annealed sample clearly shows the highest CA. The lignin sample has about the same CA as for the QCM-D crystal, which is curious, since the wax concentration has increased and the CA theoretically should be

higher. However, all the samples, except PLL-wax, has a CA higher than 90 °, and can be classified as hydrophobic.

The roughness measurements were performed on the samples made with diluted/dirty solutions, but since these samples show a difference in CA, there should also be some kind of difference in roughness. Roughness and corresponding CA are shown in Table 4.3.

Table 4.3 The roughness and CA of the coated CNF samples.

Treatment	Sa (nm), avg.	St.dev. (3 meas.)	CA	CA st.dev. (5 meas.)
ref	971	247	< 15	
PLL	2322	136	89.9	3.73
PLL-wax	973	207	79.2	1.52
PLL-wax-PLL-wax	1223	441	79.7	6.63
PLL-wax-PLL-wax 10 g/l	1008	159	104.4	5.02
PLL-wax-PLL-wax 10 g/l 103C 1h	1786	113	112.9	4.30
PLL-lignin-PLL-wax	1017	105	76.0	3.07

The reference sample has the lowest roughness, so all treatments have increased the roughness of the surface, except for PLL-wax where the roughness is the same. This shows the importance of surface energy regarding wettability, since the two samples have a major difference in CA. The difference between the 10 g/l wax sample and the reference is not significantly large either, and the same goes for the lignin sample. Again, the samples were made with poor solutions and not too much emphasis should be put on these results, especially when the standard deviations are high.

Some differences are still showing, and some restrained conclusions can be drawn. The roughness of the PLL-wax-PLL-wax sample is higher than both PLL-wax and the reference, but does not have a higher CA than the PLL-wax sample. This again shows the importance of surface energy in wettability. However, the annealed sample has the highest roughness of all sample as well as the highest CA. In terms of surface energy, the annealed sample and the 10 g/l sample are the same, so surface roughness might explain their small difference in CA.

The PLL sample has the highest roughness of all samples, and this might explain the good CA of water-soluble PLL, the surface is uneven. This is also in line with previous z-potential and QCM results, PLL with pH 9.5 have plenty of loops and tails so that a lot of wax can attach to it.

The dependence of the surface roughness for the CA of the wax samples is presented in Figure 4.17. There seems to be a correlation, but CA is not the most exact measurement and between most of the samples, there is no real difference in roughness, so no far-reaching conclusions should be drawn from this.

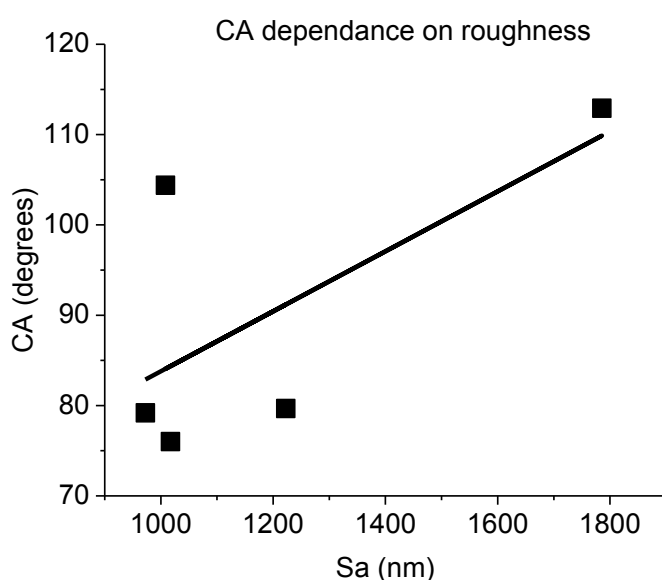


Figure 4.17. CA dependence on surface roughness of the wax samples. $R = 0.45$.

The CA of the textiles was higher than for the same coating on CNF (Table 4.4). This might be due to the material itself, a textile is more uneven than a CNF film, and therefore the roughness is higher.

Table 4.4. CA of textile samples, two bilayer PLL-wax, 10 g/l wax, 103 °C 1 h annealing.

Textile samples	CA	St.dev. (5 meas.)	Reference, CA
lightweight cotton	156.3	6.81	< 10
heavy cotton	149.2	5.83	< 10
linen	139.3	3.28	< 10

All the samples have truly good hydrophobicity, and the lightweight cotton sample can even be classified as superhydrophobic ($CA > 150^\circ$). From both the cotton samples, the water droplet rolled off, and it almost rolled off from the linen sample as well, but it is a coarser weave so it might be due to that that the droplet did not roll off. This is a huge difference to the uncoated reference samples; for all of them the water droplet was completely adsorbed in less than five seconds.

4.2.3 Moisture buffering

The moisture sorption curves are presented in Figures 4.18-4.20. Two and a third cycles were tested, where one cycle is 24 h (8 h with 75% RH, and 16 h with 33% RH). The idea was to test for three whole cycles, but the tester realized too late that the third cycle also had to be finished, and thus the last measurement was accidentally left out. The sample size was 5cm*5cm, and all six sides were exposed to the humidity changes. Four of the sides are very small and can be neglected, and since the samples are thin it can be expected that the water vapour could adsorb into/release from all of the sample from one side. The surface area was thus calculated as 5cm*5cm even though it is not according to the NORDTEST standard, however NORDTEST is not designed for textiles.

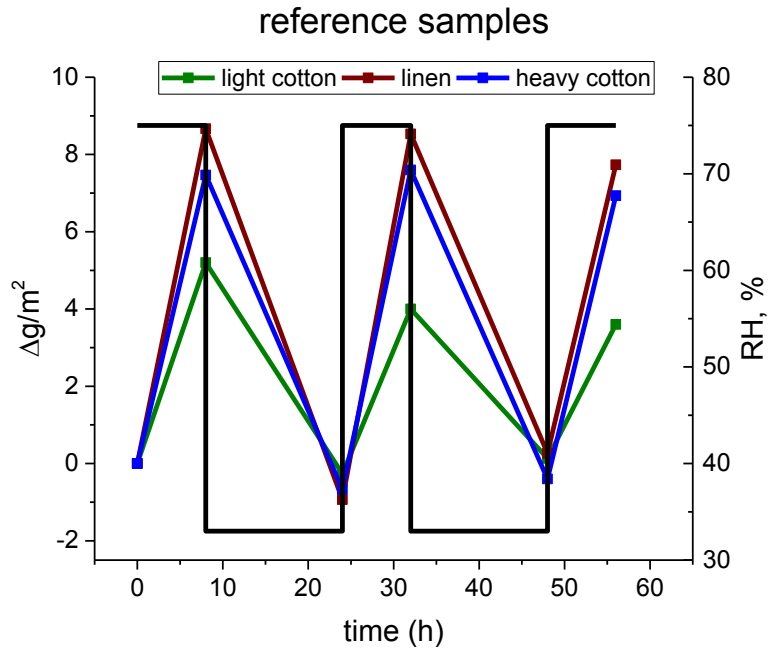


Figure 4.18. Moisture uptake and release for the reference samples. The black line represents the theoretical humidity, but in reality humidity changes are not as rapid as shown.

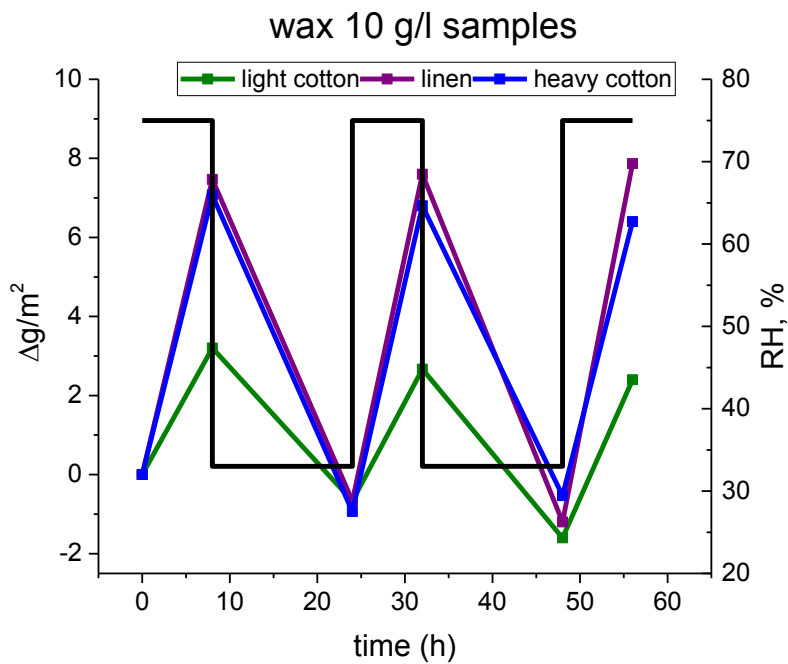


Figure 4.19. Moisture uptake and release for the samples treated with PLL-wax-PLL-wax, $c_{wax} = 10 \text{ g/l}$.

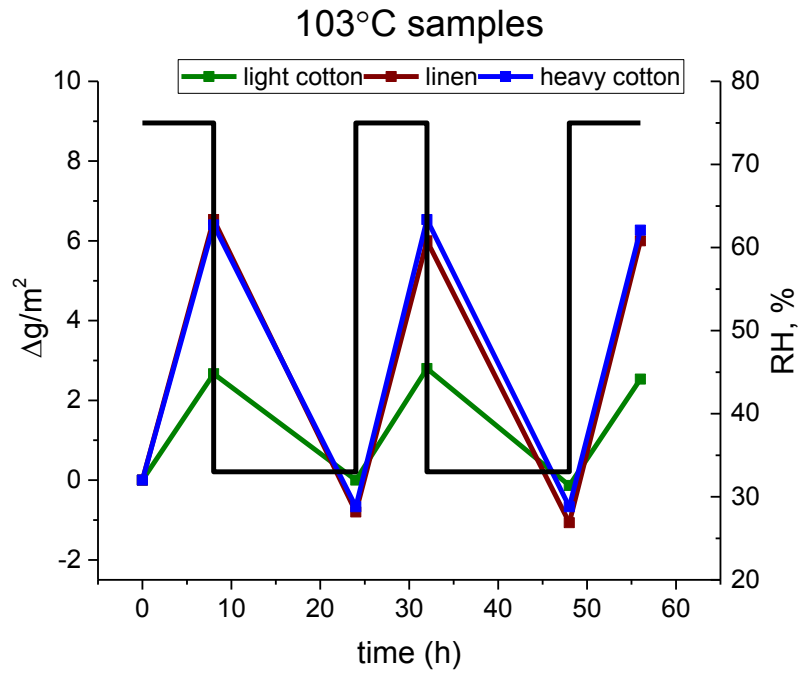


Figure 4.20. Moisture uptake and release for the thermally annealed PLL-wax-PLL-wax samples, $c_{wax} = 10 \text{ g/l}$.

The mass change per area is significantly lower for textiles than for wood (Lozhechnikova 2015), but wood is heavier than textiles and the mass of the textile sample was small, so a low mass change per unit area was expected. From these figures, it can be seen that both coatings reduce the moisture buffering of all textiles, and the annealed one reduces it slightly more. The reduction is not tremendously huge, and the coated textiles buffer moisture. In Figure 4.21 the moisture buffer values, MBV, for the textiles are presented. The reduction of MBV is presented in Table 4.5.

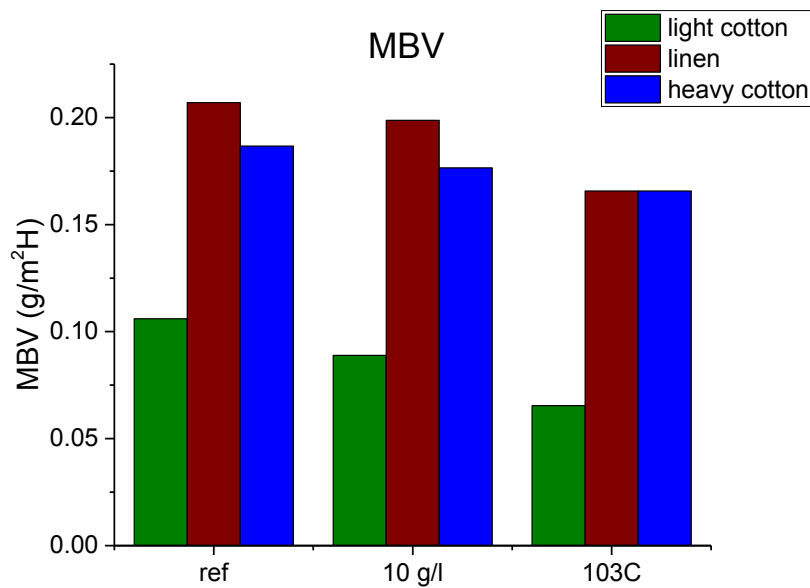


Figure 4.21. The moisture buffer values of the textiles.

Table 4.5. The MBV reduction, in percent, of the coated textile samples in relation to the references.

MBV reduction, %	10 g/l	103°C
light cotton	16	26
linen	4	17
heavy cotton	5	6

From Figure 4.21 it can be seen that the reduction of moisture buffering of the same textile with different coatings is smaller than the difference between a coated sample compared to its reference. The textile itself affects the moisture buffering more than the coating. The mass of the textile has an impact on the MBV, the lightweight cotton was the lightest sample and the heavyweight cotton was about double the mass/unit area. It makes sense that the more mass a sample has, the more water molecules can be stored in and released from the sample. Surface roughness also plays a part; the linen samples are slightly lighter than the heavy cotton sample, but coarser woven, which means more surface area for the moisture exchange to take place on. According to the NORDTEST standard, MBV levels under 0.2 (g/m² % RH) are negligible (Rode 2005), but the standard is not made for textiles so this classification should thus be taken with a pinch of salt when it comes to textiles. The percentage reduction in MBV (Table 4.5) is largest for the samples

with smallest mass, and as said, thermal annealing reduces the MBV further. This is probably due to the wax forming a more film like structure. The heaviest and most tightly woven samples were only negligible affected, even the annealed ones. However, all textiles buffer moisture, and the more cellulose mass (=pores) and surface area the better. Coatings, especially annealed coatings, slightly decrease the moisture buffering but not significantly.

4.2.4 Oxygen Transmission Rate

At 50 % relative humidity, 23 °C, all samples, except the CNF film, had an OTR value of < let almost any oxygen through. This is as expected for dense and hydrophilic CNF films (Österberg 2013). Due to the hydrophilicity unmodified CNF films usually loose their oxygen barrier ability at elevated humidity. It was expected that the hydrophobic coating could shield the CNF from humidity, thus retaining low oxygen permeability also at higher humidity levels. The results for 80 % relative humidity, 23 °C are presented in Table 4.5. Thickness of an uncoated CNF film was 70 µm (±4 µm) and 68 µm (±3 µm) for a PLL-wax-PLL-wax (10 g/l) coated film showing that the coating was very thin and within the normal variation in film thickness. Using the film thickness (70 µm for all) the oxygen permeability is calculated (Table 4.5).

Table 4.5. The OTR values (cc/m²/day) and OP values (cm³ µm m⁻² d⁻¹ kPa⁻¹) at 80 % RH.

**The sample absorbed the grease used for sealing.*

Sample	OTR	OP
Reference	12	8.4
PLL-wax-PLL-wax 10g/l, 103 °C 1h	9.47	6.63
PLL-wax-PLL-wax 10g/l	2.7 *	1.89 *
PLL-lignin-PLL-wax 1g/l	18.27	12.79
PLL-wax-PLL-wax 1g/l	17.7	12.39
PLL	17	11.9

The results show that the thickest coatings, with 10 g/l wax, had better barrier properties compared to the reference, i.e. blocked out more oxygen. It is logical that a thick coating reduces the oxygen transfer, and this is in line with the moisture buffering results. If the coating doesn't decrease ability to absorb and release humidity, it will not improve oxygen

barrier properties at elevated relative humidity either. However, since the 10 g/l sample that had not been annealed adsorbed the grease used for sealing, and thus increased its barrier properties, this particular result should not be looked at too much. It may be the grease that was enhancing the barrier properties. At least the annealed sample has better barrier properties than the reference, and even though the annealing probably increases the barrier properties due to forming of a film, the coating itself explains much of the changes in barrier properties.

The other coatings had worse barrier properties than the reference, which means they enable the oxygen transfer and are breathable. Changes between the coatings are not too big, but compared to the reference all samples coated with something other than 10 g/l wax have significantly improved oxygen transfer. Even though the annealed sample blocks more oxygen out than the reference, the change is far smaller compared to “lightly coated” samples. It would have been interesting to measure MBV for these “lightly coated” samples as well. To sum things up, all coatings are breathable in case that they transfer oxygen, and coatings with 10 g/l wax, or at least annealed coatings, slightly reduce the breathability and oxygen transfer, whereas the other coatings improve the breathability and oxygen transfer.

From a packaging application point of view, the best coatings are those with 10 g/l wax, since they inhibit oxygen flow a bit more than the reference. The other ones are not of interest when the uncoated reference had better barrier properties. The barrier properties of the 10 g/l samples (at least of the reliable annealed sample) was, however, not too great, meaning that these coatings might be less suitable for packaging applications.

5 Conclusions

Cellulosic materials, e.g. wood and natural textiles, have the ability to buffer moisture and even out extremes in relative humidity, thus providing a more convenient indoor climate. However, textiles easily get wet as well as dirty, not to mention that textiles are good breeding grounds for bacteria. Coatings that make the textiles hydrophobic and less prone to dirt and bacteria, yet preserving the breathable properties would enhance the properties of the textiles, and help to provide a more convenient indoor climate. These textiles could be used, not only in domestic applications, but also in clothes as well. Clothes that do not get sweaty but allow breathing would have a large market.

Non-renewable fabrics dominate the global textile market, even though cotton has a big market share. From an environmental point of view, this is very unfortunate. Non-renewable materials are not sustainable, and there need to be a transition from non-renewable fabrics to renewable and biodegradable fabrics, e.g. natural textiles. A coating that enhances the properties of natural textiles would give them a huge advantage, and thus help move towards a more sustainable, eco-friendly society.

In this work, cellulosic fabrics and thin freestanding CNF films were coated with poly-L-lysine, wax particles and colloidal lignin particles. The idea was to use wax particles to create a rough surface that would increase the hydrophobicity of wax by adding surface roughness. Wax particles, instead of a continuous film, would also allow air and water vapour to flow through the surface. This surface structure would also be expected to protect against dirt. Colloidal lignin particles were added to introduce antibacterial properties. The role of PLL was to attach wax and lignin particles to cellulose, as PLL is cationic and the other materials are anionic. PLL would also contribute to the antibacterial properties.

The adsorption behaviour was studied with QCM-D and the adsorption of PLL was higher with higher pH. The pH of PLL also affected the adsorption of wax particles; the higher the pH the more wax was adsorbed. More wax adsorption led to a higher CA, which is logical given the surface energy of wax. Two bilayers of PLL and wax led also to a higher CA, and since the second layer of wax was thicker than the previous this was to be expected. AFM

imaging showed a discontinuous film of wax. The higher the pH of PLL, or with two bilayers, no cellulose fibrils, only wax particles were observed in the AFM images. With lignin in the outermost layer, the CA was poor, and in AFM images lignin were observed.

The coatings were deposited onto the CNF films and fabrics using the L-b-L method, and only PLL with the pH 9.5 was used and lignin was never in the outermost layer. Different concentrations of wax were used, and the more wax the better the CA. More bilayers than two did not improve the CA. On textiles higher CA, and even superhydrophobicity, were obtained with the same coatings as on CNF films, probably due to the higher roughness of textiles. On CNF films, all coatings improved the surface roughness or kept it the same.

The moisture buffering experiments showed that all the tested fabrics buffered moisture. Both coatings that were tested decreased the MBV, but to different extents on different textiles. The lightweight cotton sample showed a reduction in MBV of 16-26%, whereas for the heavy cotton the reduction was only 5-6%. The MBV was far lower than for wood, but the moisture buffering in indoor environments also depends on the mass of the hygroscopic materials. Even though the moisture buffering of textiles is small, plenty of textiles are used in many indoor environments and thus the textiles contribute to even out the changes in relative humidity.

All coatings on CNF films were breathable and allowed oxygen to pass through at high humidity. The coatings with 10 g/l wax have a slightly worse permeability than the reference, and the other coatings have better permeability than the reference. This is a good property for textiles used as clothing, since breathable textiles enhance the comfort.

Antibacterial properties were not tested due to time issues, but there is reason to expect that the coatings provide antibacterial properties. The surface is hydrophobic which is not convenient for bacteria, and PLL and lignin have both antibacterial properties.

These coatings have shown great promises in that they, as expected, provide hydrophobic yet breathable properties for the cellulosic substrates. They can be used in many applications, e.g. packaging, and textiles is a large field of application. There is a use for hydrophobic, breathable textiles in the global textile market, both as wearable and

domestic textiles, as they would benefit the indoor climate and not get sweaty but let moisture pass through. Of course, more research needs to be done before this can be said for sure, but the coatings are at least hydrophobic and breathable. Another topic for further research would be how to coat large sheets of textiles, since dipping is not too practical. To coat the fibres before they are woven could be one way to do it. The laundering of the textiles is also a question that needs research; detergents might interact with the charged particles/polymers and cause the coating to dissolve. The antibacterial properties also need to be tested.

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