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PII: S0144-8617(19)31030-6  
DOI: <https://doi.org/10.1016/j.carbpol.2019.115363>  
Reference: CARP 115363  
To appear in: *Carbohydrate Polymers*  
Received Date: 6 June 2019  
Revised Date: 17 September 2019  
Accepted Date: 20 September 2019

Please cite this article as: Forsman N, Johansson L-Sisko, Koivula H, Tuure M, Kääriäinen P, Österberg M, Open coating with natural wax particles enables scalable, non-toxic hydrophobation of cellulose-based textiles, *Carbohydrate Polymers* (2019), doi: <https://doi.org/10.1016/j.carbpol.2019.115363>

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## Open coating with natural wax particles enables scalable, non-toxic hydrophobation of cellulose-based textiles

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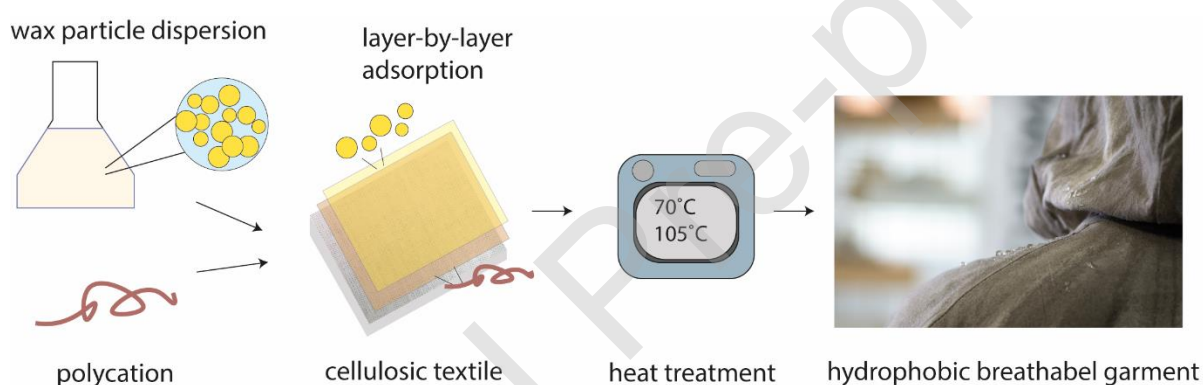
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### Graphical abstract



### Highlights

- A hydrophobic coating for textiles fully made out of natural and non-toxic materials
- Wax particles provide both low surface energy and high surface roughness, and allow gasses to pass through
- Heat treatment already below the melting point of wax increases the hydrophobicity
- The method is suitable for different cellulosic textiles and scalable for large garments

### Abstract

Environmental benign cellulosic textiles are hampered by their tendency to absorb water, which restricts their use in functional clothing. Herein we describe a method to functionalize textile surfaces

using thin, open coatings based on natural wax particles and natural polymers rendering cellulosic fabrics water-repellent while retaining their feel and breathability. The impact of curing temperature, cationic polymer and fabric properties on wetting and long-term water-repellency were studied using contact angle measurements and scanning electron microscopy. The wetting properties were correlated to roughness of the textiles using white light interferometer. X-ray photoelectron spectroscopy revealed the surface chemical composition, leading to fundamental understanding of the effect of annealing on the wax layer. Breathability was evaluated by water vapor permeability. The optimal curing temperature was 70 °C. The developed coating performed well on different natural textiles, and better than commercial alternatives. A set of garment prototypes were produced using the coating.

**Keywords:** wax particles, hydrophobic textile, surface roughness, layer-by-layer, breathability, non-toxic

## 1. Introduction

Two thirds of the textiles produced globally today are made out of synthetic materials (Lenzing Group, 2017). However, recent environmental concerns, like the accumulation of microplastics in water systems and oceans (Browne et al., 2011) urges the need to increase the use of non-harmful materials like natural or man-made cellulosic fibers. Cotton is the most widely used of the natural fibers, but despite its many benefits, cotton production requires plenty of water and pesticides.

Viscose is a versatile man-made cellulosic fiber, however the viscose process produces toxic waste, decreasing its environmental friendliness (Sayyed, Deshmukh, & Pinjari, 2019). Man-made fibers utilizing the Lyocell process, such as NMMO and Ioncell, show great promise to be used as environmentally benign textiles (Asaadi et al., 2018; Sayyed, Mohite, Deshmukh, & Pinjari, 2019).

Natural materials like cotton, linen or viscose are hydrophilic and tend to adsorb moisture, which makes them comfortable to wear but not in wet conditions, whereas synthetic textiles do not exhibit similar behavior; they are usually hydrophobic but the feel on the user's skin is not very comfortable. This promotes the use of synthetic fibers in functional clothing. Several different techniques are used to render cellulose-based textiles hydrophobic and widen their use, mainly based on the covalent bonding of fluorinated (Wu et al., 2014) or silicon compounds (Zhu, Gao, Guo, Yang, & Shen, 2011) or both (Owen, 2017; Przybylak, Maciejewski, Dutkiewicz, Dąbek, & Nowicki, 2016; Yu, Gu, Meng, & Qing, 2007). Fluorocarbons repel water excellently but are problematic from an environmental point of view, as they are very persistent and bioaccumulative, and there is an increasing concern about their environmental effects (Ahrens, 2011). Fluorocarbons with shorter chains have been proposed as an alternative, as they are not considered bioaccumulative. However, they are equally persistent as fluorocarbons consisting of longer chains (Krafft & Riess, 2015). In addition, there is not

enough data available on the long-term effect of fluorocarbons on the environment and human health (Ahrens, 2011; Krafft & Riess, 2015). The use of silicon compounds (such as silanes and siloxanes) is often suggested as a more environmentally friendly option, even though some of them might be toxic and harmful for the environment (Hogue, 2018; Hong et al., 2014). There are various silicon compounds and application methods reported (Chen, Chen, Zhang, Yin, & Zhou, 2016; Cheng, Zhao, Weng, Li, & Zeng, 2019; Hou et al., 2018; Lahiri, Zhang, Zhang, & Liu, 2019), all with their own advantages and disadvantages. Covalent binding or adsorption of inorganic materials furthermore affect the biodegradability of cellulose, contributing to textile waste. Silicon-based coatings have likewise suffered from poor durability. Harsh and toxic solvents are also frequently used during the treatments.

Since the highest hydrophobicity is reached by a combination of high surface roughness and low surface energy, there have been multiple studies on increasing the surface roughness by adding various kinds of nanoparticles onto textile surfaces. Although many methods show promising results, there are safety concerns regarding nanoparticles that cannot be neglected. Som et al. showed in a review study on the environmental and human toxicity of commonly used nanoparticles, that there are risks of varying degree associated with all investigated nanoparticles (Som, Wick, Krug, & Nowack, 2011), and that we currently lack complete knowledge of their environmental impact. Additionally, mechanical wear may damage and/or contaminate the surface, reducing the hydrophobicity (Verho et al., 2011).

More environmentally friendly options to make cloths water-resistant exist. One method is tightly woven (cotton) fabrics that keep water out, *e.g.* Ventile (Holmes, 2000; Hunter & Fan, 2009; Mukhopadhyay & Vinay Kumar, 2008). The production of Ventile requires extra long staple yarns, which are only available from 2% of the world's entire cotton crop (Ebbelsen Ltd, 2019). This limits the global use of Ventile and similar fabrics. Another method is to directly deposit a layer of wax onto clothes. For example the outdoor clothing company Fjällräven sells a wax bar intended for the user to stroke onto their garments and melt the wax by ironing, thus hydrophobizing them. The problem with this approach is that the breathability of the material suffers, and breathability is important for user comfort and crucial for performance of functional sports clothing. Breathability studies are often excluded from scientific papers on functional textiles. Hydrophobization by wax coatings has gained scientific interest, and to overcome the lack of breathability of solid wax films, different ways of producing colloidal wax particles have been recently reported (Lozhechnikova, Bellanger, Michen, Burgert, & Österberg, 2017; Morrissette et al., 2018; Wang, Qian, & Shen, 2018). However, so far very few of the methods utilize solely wax and water without any surfactants and other solvents and the scalability of the methods have not been thoroughly assessed (Forsman et al., 2017; Lozhechnikova et al., 2017).

In a previous study, we demonstrated that cellulosic fabrics can be rendered hydrophobic by layer-by-layer coating of alternating poly-L-lysine (PLL) and wax-particle dispersion (Forsman et al., 2017). However, the method was only demonstrated in small scale and not optimized for large-scale use. The high price of PLL (Sigma-Aldrich, 2019) makes it unsuitable for industrial applications. Hence, herein we investigate if PLL can be replaced by cheaper natural polycations and systematically explore the optimum curing temperature, and the effect of the fabric used applying standard textile testing methods. Furthermore, the developed wax-particle-based open coating was compared to commercially available surface hydrophobation methods and the durability of the coating during washing was tested. Combining water contact angle measurements (WCA), scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS), allows us to explain the effect of curing temperature on wetting properties by partial melting and rearrangement of molecules within the wax layer. To conclude the series of lab-scale tests, a small collection of garment prototypes was designed and produced. The aim was two-folded: to explore and test how the coating process could be up-scaled for industrial use and to obtain real garments so that the potential of this new technology could be presented for multiple audiences.

## **2. Materials and methods**

### *2.1 Anchoring agents*

#### *2.1.1 Poly-L-lysine (PLL)*

Poly-L-Lysine (PLL) 0.1 % (w/v) with a molecular weight of 150,000-300,000 was purchased from Sigma-Aldrich. The pH of the PLL was altered to 9.5 using buffer solutions, 0.1 M NaOH and 0.1 M HCl.

#### *2.1.2 Cationic starch (CS)*

Classic 145, a potato based cationized wet end starch was obtained from Chemigate Oy, Lapua, Finland. The molecular weight (Mw) of CS was not altered in any way, and the natural Mw of potato starches are over 100 000 000 (Tomasik, 2009). The degree of substitution value was 0.042. The starch was added to boiling water and boiled under stirring for ca 15 min, and then cooled down. A 5 g/l stock solution was prepared.

### *2.2 Wax dispersion*

In order to prepare the wax dispersion 1 g of solid refined carnauba wax (Sigma-Aldrich) was added to 100 ml MilliQ water at 100 °C. The mixture was sonicated for 5 min using an Ultrasonic Probe Sonifier S-450 with a 1/2" extension (Branson Ultrasonics). Immediately after sonication, the carnauba dispersion was cooled down in an ice bath, and filtered through a filter funnel with 100-160

$\mu\text{m}$  nominal maximal pore size. A detailed description of the preparation and characterization of the wax dispersion can be found elsewhere (Lozhechnikova et al., 2017). For simplicity, the carnauba wax will be further referred to as wax.

### 2.3 Textile samples

A 100% cotton fabric (here called cotton) with plain weave was purchased from Eurokangas, Espoo. A 100% tencel fabric (tencel) was obtained from Lenzing, (Lenzing, Austria). A microviscose fabric (microviscose) with satin weave, and a cellulosic blend fabric (hemp, 55% hemp 45% cotton) were obtained from the storage of textile printing and dyeing workshop of Aalto University (Espoo), and a knitted cotton material (knitted cotton) was made of raw untreated and uncolored cotton yarn from Huaifu cotton yarn supplier. The grammages, measured of textiles conditioned at 23 °C and 50 %RH for over a month, were as follows: cotton 156 g/m<sup>2</sup>, tencel 118 g/m<sup>2</sup>, microviscose 122 g/m<sup>2</sup>, hemp 283 g/m<sup>2</sup> and knitted cotton 629 g/m<sup>2</sup>. All fabrics (Figure 1) were white and were washed with ethanol and MilliQ water and dried prior to use.

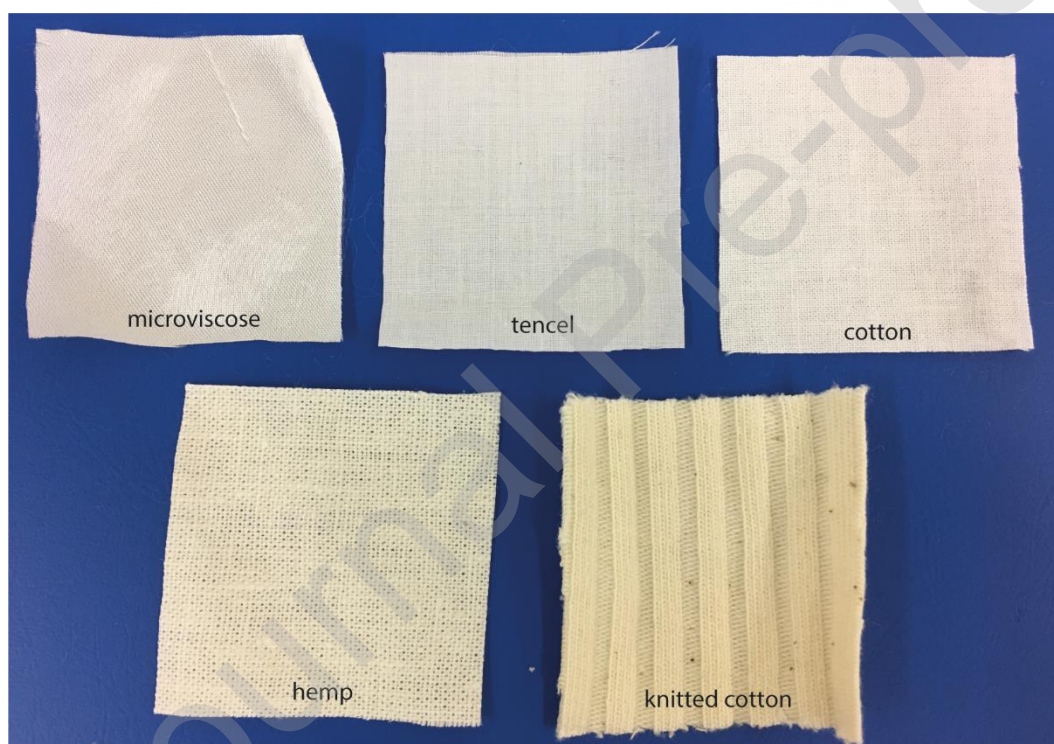


Figure 1. Photograph of the different textiles studied.

### 2.4. Layer-by-layer coating of the fabrics with the wax dispersion

The textiles were hydrophobized using the layer-by-layer method. Prior to the LbL coating, the substrates were soaked in water for a few minutes. Concentrations of the solutions were 1 g/l for PLL, 5 g/l for cationic starch and 10 g/l for wax. The substrates were thoroughly rinsed with water three



times in different beakers, to remove non-adsorbed material after adsorption of each layer and only then, the next layer was adsorbed. The immersion time was always five minutes. The samples were dried in room temperature (RT) and cured in an oven (except for one sample that was not cured at all, only dried in RT), either immediately when still wet or after they had dried. Curing time was at least 15 min.

*Table 1. Overview of the samples prepared by the LbL method with wax particles.*

<b>Fabric</b>	<b>Cation</b>	<b>Nr. of bilayers</b>	<b>Curing temperature, °C</b>	<b>In Figure</b>
cotton	PLL	2	RT, 30, 40, 50, 60, 70, 80, 90, 100, 105	2, 3
cotton	PLL	1	70	4
cotton	CS	1, 2	70	4
cotton	PLL	2	70, 105	5
cotton, microviscose, tencel, hemp, knitted cotton	PLL	2	70	6

### 2.5 Commercially available coatings

A bar of Fjällräven's Greenland wax was purchased from an outdoor supply store. The bar consists of paraffin and beeswax (Fjällräven, 2019). The bar was stroked on to the textile, and then cured at 70 °C, according to instructions. Two different samples were prepared, one with a lighter stroke of wax and one with a generous layer of wax deposited onto the textile. A Woly wet blocker spray (Melvo GmbH, Ludwigsburg, Germany), claiming to utilize nanotechnology to repel water, oil and dirt without compromising breathability, was purchased from a shoe store, and applied according to instructions.

### 2.6 Textile printing pigments

Pure textile printing pigments were obtained from Emo-tuotanto Oy, Kuopio, Finland. Two or three drops of pure pigment were added to one liter of wax dispersion.

### 2.7 Water contact angle (WCA)

The water contact angle (WCA) was measured with a CAM 2000 (KSV Instruments Ltd, Finland), and the size of the MilliQ water droplet was 6.5 µl. The static contact angle was measured for 60 seconds, with one frame taken every second, and the contact angle at 5 seconds was used for comparison. At least three parallel samples were tested for each coating.

### 2.8 Scanning Electron Microscopy (SEM)

Samples were imaged with a Zeiss Sigma VP (Carl Zeiss NTS Ltd, Germany) field emission scanning electron microscope using an acceleration voltage of 1.5 kV. Prior to imaging, the samples were attached to an aluminum SEM stubs with carbon tape followed by sputter-coating (Emitech K100X) with Pt/Pd forming a thin layer of ~10-15 nm to avoid charging and to enhance the signal from the sample.

### 2.9 Surface roughness

The roughness of coated and uncoated textiles was determined using scanning white light interference microscope (ContourGT-K, Bruker Corporation, USA). The arithmetical mean height  $S_a$  was calculated using the on-board software of the interference microscope. The area scanned was 423  $\mu\text{m}$  x 564  $\mu\text{m}$ , the focus was 20x0.55x and 640 x 480 pixels were measured. Three replicates of each sample were analyzed.

### 2.10 Fourier transform infrared spectroscopy (FTIR)

To characterize the chemical composition of the textile samples, their FTIR spectra were measured using a Nicolet Magna IR750 Fourier transform infrared with an attenuated total reflection (ATR) accessory. Each spectrum is an average of 64 measurements.

### 2.11 X-ray photoelectron spectroscopy (XPS)

Kratos Analytical AXIS Ultra electron spectrometer with monochromatic Al K $\alpha$  irradiation at 100 W was used for chemical surface analysis of the fabrics. Low resolution scans were used to determine elemental surface composition while high resolution measurements of carbon C 1s and oxygen O 1s regions were applied for a more detailed chemical evaluation. Furthermore, nitrogen contents were evaluated using long regional N 1s scans recorded with survey resolution so that they could be incorporated into survey quantifications. Pure cellulose filter paper (Whatman) was used as in-situ reference with each measurement batch and 2-3 locations were measured for each sample, with a nominal analysis area of 300 x 700  $\mu\text{m}$ . CasaXPS software was utilized for data analysis. For the carbon regions, a tailored four component fitting routine for cellulosic specimens was used (Johansson & Campbell, 2004).

### 2.12 Water vapor transmission rate (WVTR)

The water vapor transmission test was performed according to ASTM standard E 96/E 96M – 05 desiccant method in custom build chambers that comply with the standard requirements. The relative humidity in the chamber was 71 % and temperature 23 °C. The experiment was performed using two parallel samples. The treated side of the sample was placed toward the higher vapor pressure.



Thickness of the samples for calculations was determined using a Schraeder micrometer (Lorenzen & Wettre, Sweden) having 1  $\mu\text{m}$  accuracy.

### 2.13 Hydrostatic pressure

The hydrostatic pressure was measured according to standard SFS-EN 20811:1993, using 20 °C water and with a water level increase rate of 10 cm H<sub>2</sub>O/min. Five parallel samples were tested.

### 2.14 Spray test

The water-repellency was tested using the spray test, according to standard SFS-EN ISO 4920:2013. The temperature of the water was 20 °C and three samples were tested.

## 3. Results and Discussion

The scalability of the layer-by-layer method for hydrophobation of natural textiles by alternating a layer of a polycation and a layer of anionic wax-particle dispersion was evaluated. Various alternatives to replace the previously used PLL as polycation were assessed. The optimum curing temperature, the effect of the fabric properties on the performance, breathability of the treated fabrics as well as resistance to washing were systematically explored. Lastly, the coating method was combined with garment design to demonstrate the scalability of the method.

### 3.1 The effect of curing temperature on hydrophobicity of coated samples

The effect of curing temperature on water contact angle (WCA), fiber surface morphology and chemistry is shown in Fig. 2. There was no statistically significant change in WCA between curing temperatures from RT to 40 °C. However, between 40 °C and 70 °C the WCA increased systematically with increasing curing temperature. Curing at 70 °C yielded the highest WCA (Fig. 2A). At this temperature there are still individual, only partially melted, particles clearly visible on the surface (Fig 2C). There are two possible reasons for this phenomenon. Carnauba wax is a natural material and consists of different molecules, mostly wax esters, some free fatty alcohols and free fatty acids (Basson & Reynhardt, 1988; Doan et al., 2017; Zhang et al., 2016). Some of these have lower melting temperature than others. The overall melting temperature for carnauba wax in literature ranges around 84 °C, with values reported between 82 °C and 86 °C (Bayer et al., 2011; Shellhammer, Rumsey, & Krochta, 1997; Zhang et al., 2016). Despite this, some components start melting already at lower temperatures, indicated by reported melting ranges as broad as 65-90 °C (Basson & Reynhardt, 1988). This could lead to better coverage.

Another possible reason for the increase in WCA with temperature could be the rearrangement of the molecules in the outermost wax layer, with the accumulation of the more hydrophobic molecules or

parts of molecules at the wax/air interface in order to decrease the surface energy (Basson & Reynhardt, 1988; Kameda & Tamada, 2009). Carnauba wax undergoes a solid-solid transition at 62 °C, and some reorientation of methyl groups also occur (Basson & Reynhardt, 1988). XPS measurements (Fig. 2B/S1) confirm that the chemical composition of the surface changed during the curing. Samples treated at 70 °C had a higher amount of non-polar C-C bonds and lower amount of polar C-O bonds than samples treated at 40 °C or lower, explaining the observed increase in hydrophobicity. At the air-wax interface, hydrophobic alkyl chains move towards the hydrophobic air and hydrophilic groups containing C-O move away from the air. The movements are aided by the increase in kinetic energy that the increase in temperature provide. In addition, the nitrogen signal originating from the PLL beneath the wax decreased between 40 °C and 70 °C curing. Thorough inspection of the wide spectra in S1 shows a clear increase in the oxygen 1s background signal, indicating that some compounds of the wax are melting and covering the cellulosic textile substrate already at 70 °C curing (Buchert, Koljonen, Campbell, Johansson, & Kleen, 2004; Tougaard, 2002) supporting better surface coverage. No chemical reactions are likely to happen, only partial melting of the wax and rearranging of the wax molecules at the solid-air interface. It must be stressed, that wetting is affected by changes in the outermost surface layer and hence even minor changes have significant effect on the hydrophobicity of the material.

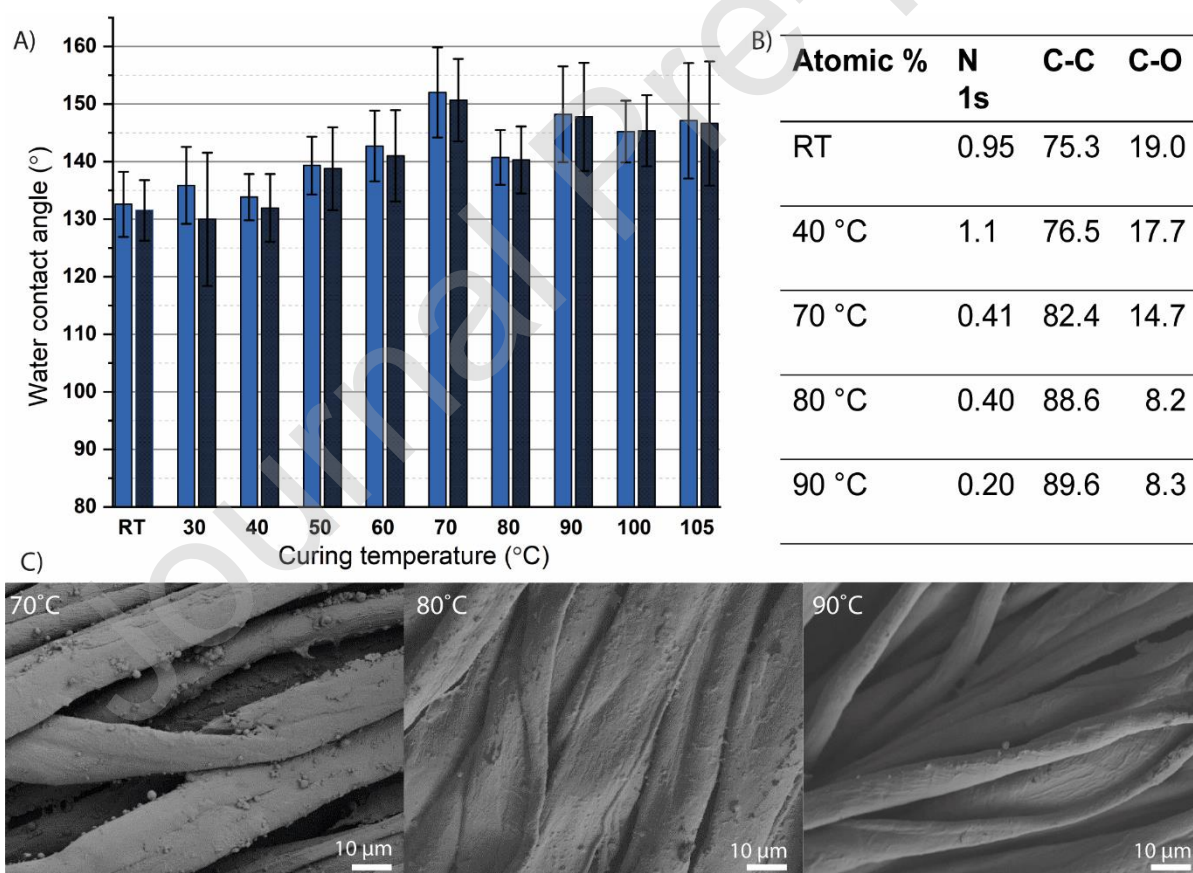


Figure 2. Cotton fabrics coated with 2BL PLL/wax cured at different temperatures. A) WCA at 5 s and 60 s (light and dark blue respectively) B) Relative atomic surface concentration of N, and relative amount of C-C and C-O of the total C content at the surface analyzed using XPS C) SEM images with 1000 X magnification.

At 80 °C the wax particles have partially melted (more than at 70 °C) as seen in the SEM images (Fig. 2C). The small decrease in the observed WCA when curing temperature is increased to 80 °C could be due to decrease in roughness of the sample. Higher temperatures than 80 °C did not significantly change the hydrophobic behavior; coatings with partially or fully melted wax behaved similarly. Melted particles means lower surface roughness and better coverage of the cellulose fibers, and this explains the slightly lower WCA compared to 70 °C. After melting, WCA stays quite similar, a bit over 140°, indicating that the surface coverage cannot be increased further.

While the initial WCA is the best measure of hydrophobicity of the coated fabrics, the water-resistance during longer exposure is of high practical relevance. The very small droplet that is used in contact angle measurements evaporates in a few minutes. Hence, we qualitatively evaluated the water-resistance of samples by following the spreading or absorption of a colored water droplet as a function of time (Fig 3A). The sample cured at room temperature absorbed the water in less than 30 min, meaning that some kind of thermal curing is necessary. The samples cured at 30 °C, 40 °C and 50 °C failed in respective order, whereas samples cured at 60 °C could withstand the water for over 2 h 30 min. At this temperature, only part of the wax could be melted so we suggest that rearranging of the molecules at the outermost surface also plays a role. The heating is furthermore likely to improve the adhesion between the wax and the underlying surface (Bayer et al., 2011). For textiles cured at 90 °C or higher, the wax has fully melted, and a more covering wax film with better long-term water-repellency, was formed.

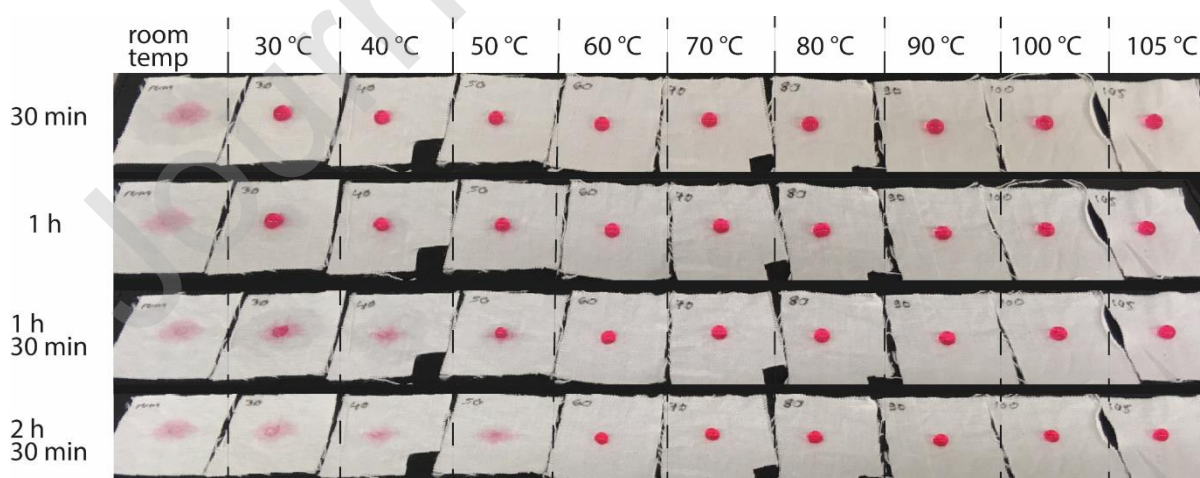


Figure 3. 2BL Photographs of PLL/wax coated cotton fabrics cured at different temperatures showing how long the coated fabric can hold a water droplet before it is absorbed.

To further evaluate the wetting properties of the coated fabrics advancing and receding WCA were measured on samples with two different curing temperatures, both showing high WCA and long-lasting water-repellence, but with clearly different surface morphology. The wax particles were fully melted at 105 °C and only partially melted at 70 °C. A surface where water easily rolls has a low WCA hysteresis (difference between advancing and receding WCA), contrary to a “sticky” surface where the water moves poorly (Balu, Breedveld, & Hess, 2008). The hysteresis was low for both curing temperatures studied, and lower for 105 °C than for 70 °C (Table 2). Water moved freely on both surfaces, and better when the wax was melted. On a structurally rough surface there is a transition from the Cassie-Baxter state to the Wenzel state over time introducing adhesion between water and the substrate (Schlaich, Wei, & Haag, 2017). With the melted wax there is no air pockets between the wax particles, meaning that the transition to the Wenzel state cannot happen and the water moves more freely. The better coverage may also decrease the hysteresis. Overall, water rolled easily of coated textiles and hence long-term wettability might not even be needed, further adding to the advantageous properties of the coating method.

*Table 2. Advancing and receding WCA, and WCA hysteresis measured on a plane with 5° slope. N = 5, except for 105°C sample, for which one drop rolled off before it could be measured.*

	<b>advancing CA</b>	<b>receding CA</b>	<b>hysteresis</b>
<b>70°C</b>	148.5 (8.3)	139.7 (5.8)	8.8
<b>105°C</b>	> 141.1 (7.6)	> 137.0 (6.6)	< 4.1

### *3.2 Effect of cation on hydrophobicity*

PLL is a rather expensive polycation, and in larger scale applications, a cheaper cation would thus be favorable. Initial tests with natural cations soy protein, wheat gluten and casein showed poor hydrophobicity, and these materials were thus abandoned from further studies. Starch is a cheap natural substance that for long has been used in the paper and textile industries (Chiu & Solarek, 2009; Ellis et al., 1998), and although starch is anionic in its natural state it can easily be cationized (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008; Vasanthan, Bhatta, Tyler, & Chang, 1997). A bilayer of cationic starch (CS) and wax had a slightly lower WCA than one bilayer PLL/wax (Fig. 4), and the WCA was not stable over time.

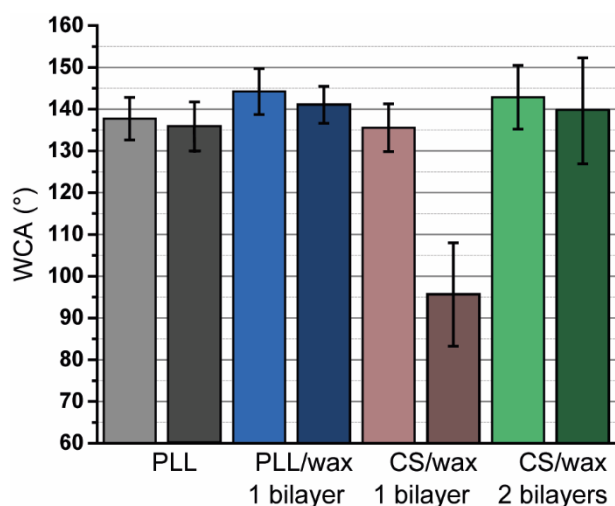


Figure 4. WCA at 5s and 60s (light and darker color shades respectively) of a single layer of PLL (grey shades), 1BL of PLL/wax (blue shades), 1BL of CS/wax (brown shades) and 2BL of CS/wax (green shades), all samples cured at 70 °C. WCA of unmodified cotton and a single layer of CS < 10° at 5s and hence no results are shown.

There are two possible reasons for this phenomenon. One reason may be the hydrophobic/hydrophilic properties of the cations themselves, PLL is hydrophobic whereas CS is very hydrophilic, and PLL thus contributes to the hydrophobicity of the PLL/wax bilayer, as opposed to CS. Secondly, the hydrophobicity of PLL may increase the affinity of wax to the cationic layer, thereby increasing the adsorption. The number of bilayers also affect the properties of an LbL-coated surface, and a greater number of bilayers has been shown to increase the WCA (Forsman et al., 2017; Lozhechnikova et al., 2017). Two bilayers of CS/wax had similar WCA compared to one bilayer of PLL/wax, indicating that PLL could be substituted with CS, but more bilayers are needed to get sufficiently high coverage of wax particles on the surface. A coating process with several layers is more time-consuming and complicated than a process with fewer layers. Coating four to six layers would still be manageable, and would allow manufacturing in a larger scale. In research papers wax particle LbL coatings with 16 layers (Lozhechnikova et al., 2017) and for LbL in general over 100 layers have been reported. However, in commercial applications the layers should be minimized. PLL is many times more expensive than both CS and wax, and in large-scale applications CS might still be a better option, even if more bilayers are needed.

### 3.3 Performance of the wax particle coating in comparison to commercial coatings

A combination of breathability and water-repellence is crucial for comfort and performance for outdoor clothing. Breathability refers to water vapor and gasses passing passively through, with no active mechanisms involved. Currently the most common approach is to combine very tightly woven synthetic fabrics (Goretex) with a spray coating reapplied when needed, but in practice, very tightly woven fabrics have limited breathability. Coating of mixed natural and synthetic fabrics with



Greenland wax is marketed as a more sustainable approach, although the Greenland wax mostly contains petroleum-based paraffin (Fjällräven, 2019). The wax bar is nevertheless popular as an easy way to hydrophobize clothes. Hence, the breathability and WCA for our open coating was compared to the performance of these two coating approaches. Although the structure of the textile affects both the hydrophobicity and the breathability, these coatings were compared on just one fabric to clearly evaluate the effect of the coating in itself. Since the amount of the anchoring polycation is small in comparison to the wax particles, only one polycation is studied.

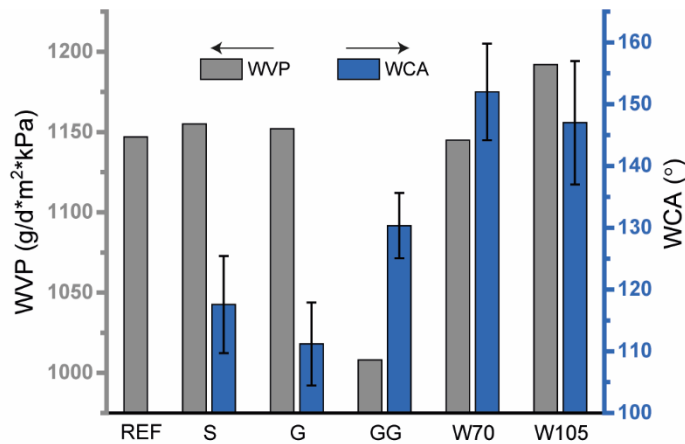


Figure 5. Water vapor permeability (WVP, gray bars, left-hand axis) and water contact angle (WCA, blue bars, right-hand axis) for uncoated cotton reference (REF), shoe spray (S), thin (G) and thick (GG) layer of Greenland wax, and 2BL PLL/wax cured at 70 °C (W70) and 105 °C (W105).

The breathability of the different coatings was evaluated by WVP. A thin layer of the commercial shoe spray (S) did not alter the breathability of the fabric, the WVP remained on the same level. However, the WCA was below 120°. Nevertheless, one has to remember that the shoe spray is intended for thicker and denser materials that are used in shoes, such as leather or suede, and not the thin breathable cotton fabric used in this study. For the Greenland wax coating the WVP and WCA were both strongly dependent on the layer thickness. For a thin layer the breathability remained good but the WCA was the lowest out of the compared samples. A thick layer resulted in WCA of 130° but deteriorated the breathability considerably. This was expected as the continuous wax layer seals the surface of the fabric. A thicker wax layer also contributed to a smoother surface, when wax filled the cavities between the textile fibers. Smooth surfaces exhibit WCAs of 120° at the highest, since the surface roughness of the surface is lost (Liu et al., 2007). Neither of the Greenland-wax coatings had outstanding WCAs, and with the Greenland wax there was a compromise between water-repellence and breathability. Both cannot be obtained simultaneously. The same phenomena has been demonstrated for coating of wood with wax (Lozhechnikova, Vahtikari, Hughes, & Österberg, 2015).

The wax-particle coating, regardless if composed of melted (W105) or only partially melted wax particles (W70), did not affect the breathability of the fabric. The coating is very thin, and space



between the particles allow for the gas flow. Additionally, the coating is deposited only on the fibers, which means that holes in the textile weave are not covered and gasses can still pass through. The open coating also adds to the surface roughness, a contributing factor to hydrophobicity and this also explains the higher WCA for the wax particle coatings compared to the Greenland wax coatings. The wax particle coating, performed better than both the continuous Greenland wax coating and the shoe spray, at the two tested curing temperatures and both in terms of breathability and hydrophobicity. Interestingly, water rolls off much easier from the LbL wax particle coated fabrics as compared to the commercial solutions, further enhancing long-term water-repellence, as seen in the video available in the online version of the article (Video 1).



Video 1.mp4

### *3.4 Evaluating the coating on different textiles*

In order for the coating to be of use in larger scale, it has to perform well on different (natural) textiles. Since the coating did not affect the breathability of the tested cotton fabric, it is expected that it will not affect the breathability of any other fabric. The coating method relies on adsorption to the cellulose fibers, hence pores available in the fabric will not be sealed and overall breathability will be purely dependent on the porosity of the fabric. In contrast, different fabrics can have very different surface roughness, a contributing factor to hydrophobicity, and therefore the hydrophobicity will be affected by the fabric texture. The fiber dimensions, yarn and fabric structure also alter, at least to some extent, the surface properties of the fabric. Additionally, the chemical composition of fabrics made from different plants or man-made cellulosic fibers produced with different technologies, might slightly vary. Due to these reasons, the hydrophobicity of different fabrics coated with two bilayers of cation and wax particles was evaluated.

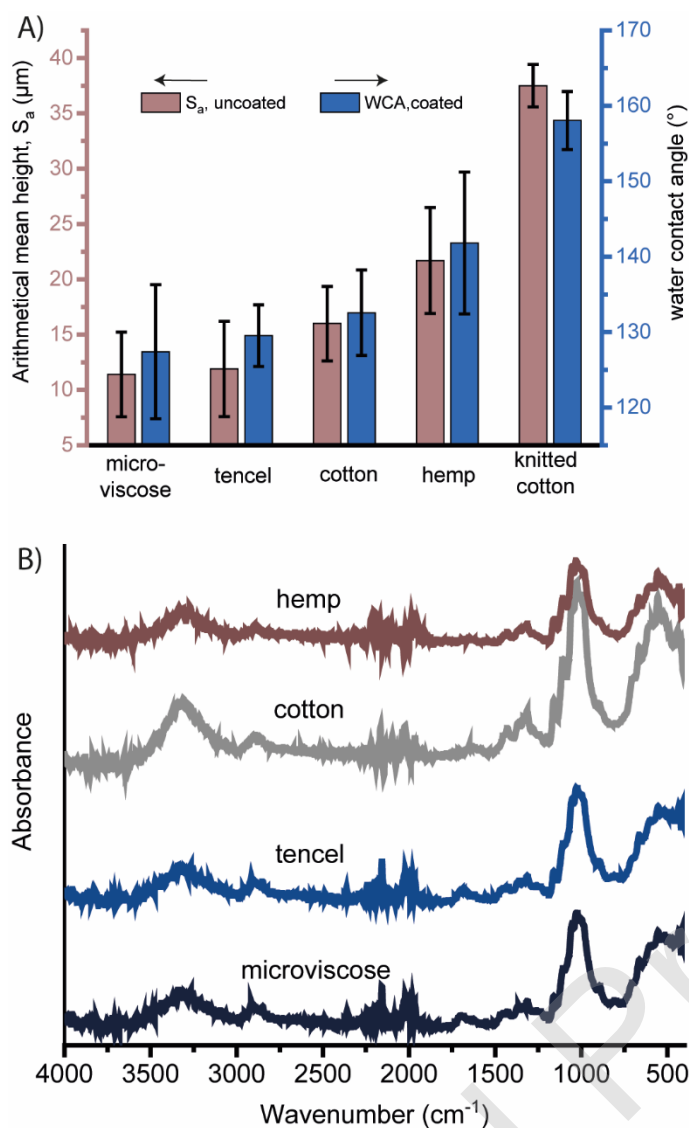


Figure 6. A) Arithmetical mean height ( $S_a$ , brown, left-hand axis) of uncoated microviscose, tencel, cotton, hemp and knitted cotton and water contact angle (WCA, blue, right-hand axis) of the same fabrics coated with 2BL PLL/wax. B) FTIR spectra of microviscose, tencel, cotton and hemp.

There is a clear correlation between surface roughness of the uncoated fabrics and the achieved hydrophobicity after coating. The WCA increased with increasing surface roughness of the fabrics (Fig. 6A), which is in agreement with the theory about hydrophobic surfaces. This indicates that the main roughness contribution comes from the textile itself and the wax-particle coating only modestly increases the roughness. Coated fabrics were measured, however no wax particles can be seen in the images. Moreover, due to the limitations of the instrument, and hairy surface of some of the samples the  $S_a$  values should be treated with some caution, and due to the geometry of the sample it was impossible to receive data from the whole area of the sample. However, the general trend is qualitatively reasonable and correlates with what is observed by naked eye.

It is also questionable how much change in surface roughness could be seen using this method, as the smoothest fabric (uncoated microviscose) had a roughness value around 10  $\mu\text{m}$  and the wax particles, as stated, are below 1  $\mu\text{m}$ . This method measures the microlevel roughness, whereas the wax particles affected the sub-microlevel roughness, however, both are needed to produce a hydrophobic surface. To fully understand the change in roughness and the effect on the hydrophobicity either dimensionless parameters of the fabric and coatings (Kleingartner et al., 2015) or model films can be used. Results from the latter have already been published elsewhere and they support our conclusion that the roughness of the fabric is the most important roughness contribution to the wetting properties but the submicron roughness added by the wax particles further enhance hydrophobicity of the material (Forsman et al., 2017). In extension, by tuning the roughness of the fabrics during manufacturing the hydrophobicity (after coating) can be increased. This is something that could be easily utilized in the textile industry.

FTIR spectra of the textiles (Fig. 6B) revealed that there are no observable differences in the chemical composition of the textiles. The spectra for all textiles resembles that of pure cellulose, as is expected of plant-based textile fibers, suggesting that chemical differences cannot explain the observed differences in WCA. The WCA is more likely related to the differences in the structure of the textiles.

### *3.5 Scalability of the coating method*

The coating can be applied by dipping, spraying or brushing, and all these approaches were tested in practice on the prototype garments. Dipping is suitable for small-scale coating, and spraying and brushing for garments, e.g. jackets and other clothes. For industrial scale, the coating process could be developed to be part of the fabric finishing process, especially if the wax and dye would be combined. Other studies on upscaling of LbL show that spraying could be an option (Krogman, Cohen, Hammond, Rubner, & Wang, 2013). The coating did not withstand standard washing using detergents. Hence, the coating is more suitable for outdoor clothing and similar garments that are not very often washed. Due to the simplicity of the process, the coating can be reapplied after washing. However, this will require further research and development.

For clothes, hydrophobicity is usually not reported as WCA, but hydrostatic pressure or a value according to the spray test (Table 3). The coating with CS as anchoring agent performed as well as the commercial shoe spray, and the coating with PLL performed even better. Different temperature of the heat treatment did not affect the performance indicating that WCA is a more sensitive method to show small changes. A coating is not independent of the underlying substrate, and the cotton textiles used for this experiment was thin and quite porous. With a thicker and denser fabric, the results might have been different, but then again the breathability might not have been as good.

*Table 3. Spray test of LbL textiles with different cations and curing temperature, compared to a commercial shoe spray. Hydrostatic pressure of 2BL PLL/wax, 105 °C: 17 mbar = 17 cm H<sub>2</sub>O.*

<b>sample</b>	<b>result (scale 0-5)</b>
<b>2BL PLL/wax, 105 °C</b>	2-3
<b>2BL PLL/wax, 70 °C</b>	2-3
<b>2BL CS/wax, 105 °C</b>	1-2
<b>commercial shoe spray</b>	1-2

The scalability was tested in practice by coating a small collection of prototype garments (Fig. 7) by spraying. The garments were designed and produced as a part of a Master's thesis collection by a fashion and textile design student, who was part of the multidisciplinary research team throughout the project. Two different textile materials were selected for the final prototypes: knitted cotton knitted with raw untreated and uncolored cotton yarn from Huafu cotton yarn supplier, and uncolored and unbleached plain weave cotton fabric purchased from a local fabric store Eurokangas. An interesting finding regarding the design process was that colors can be incorporated by adding pigments to the wax dispersion. It also helps to observe which parts of the textiles are already treated. This approach would enable the designers and even users to customize their products with specific colors and patterns. The spraying method functioned well in this prototype scale. In prototyping pure textile printing pigments were used together with wax dispersion to help the spraying process. Pure textile pigments are strong enough to give a vivid shade of colors only with two to three drops of pigment added in one liter of wax dispersion. By using the layer by layer spraying method and several shades of color it is possible to achieve lively color gradients and surfaces on garments.



*Figure 7. Jackets spray-coated with the wax dispersion and cured at 70 °C. The colors used were textiles printing pigments added to the wax dispersion.*

#### **4. Conclusions**

In this work the effect of cationic binder, curing temperature of wax coating and fabric roughness on water-resistance and breathability of wax dispersion coated cellulosic textiles was evaluated. It was found that a curing temperature of 70 °C gave the highest WCA, and a curing temperature of 60 °C or higher gave good long-term water-repellency. The explanation for this behavior lies in the changes in carnauba wax below its melting temperature. Some of the molecules in the wax melted at lower temperatures than others, increasing the surface coverage, while molecular rearrangement within the wax coating moreover enhanced the hydrophobicity. CS was not as efficient as PLL as an anchoring agent, but good water-repellency was still obtained with two bilayers. The price of CS is considerably lower than the price of PLL, and CS is already commercially used, which motivates its use for large-scale application. The roughness of the fabric affected the hydrophobicity on the coated material, with

the highest WCA observed for the fabric with higher roughness. The developed coating performed better than two commercially available hydrophobization methods, both in terms of WCA and breathability. Application via spray-coating and brushing was also possible, the wax could be mixed with color and textiles or even ready-made garments could be treated during the production process and again after the washing cycle. This method can become an option as a non-toxic and degradable finishing to achieve water-repellency of natural or man-made cellulosic materials. The spraying of wax-color mix could enable visually customized products, either by producers or by users.

### **Acknowledgements**

The authors wish to thank Aalto University, for funding of this project via the Greenex project. This work made use of Aalto Bioeconomy facilities and the textile workshops at the School of Arts, Design and Architecture. The authors acknowledge the provision of facilities and technical support by Aalto University at OtaNano - Nanomicroscopy Center (Aalto-NMC) and Chemigate for providing the cationic starch used in this work.

Design Matilda Tuure, photographs Valeriya Azovskaya.

**Declarations of interest:** none.

**Funding:** Aalto University. The funding source did not have any influence on study design; in the collection, analysis and interpretation of data; in the writing of the report; and in the decision to submit the article for publication

### **Data availability**

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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