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Abstract. All-cellulose composites were prepared by dispersing kraft fibers in a matrix made from pulp dissolved in NaOH-water. To hydrophobize the composite surface while maintaining the material fully bio-based and biodegradable, layer-by-layer deposition of cationic starch and carnauba wax was performed. Various options of surface coating, drying, and curing were tested, including partial and complete melting of the wax. The composite surface was characterized by water contact angle, roughness and scanning electron microscopy, and material properties by adsorption and absorption of water (in vapor and liquid form) and tensile testing. The highest water contact angle was obtained when the layer-by-layer deposition was performed by dipping the dry composite into cationic starch solution, then in wax dispersion, and partially melting the wax after coating. However, it was demonstrated that the dipping approach was detrimental to material tensile properties, due to heterogeneous swelling of cellulose during the treatment and multiple drying sequences. Process optimization via spraying resulted in composites with Young's modulus of 6 GPa and hydrophobic surface with water contact angle 122 °C.

Keywords: biopolymers, biocomposites, cellulose, carnauba wax, hydrophobization, tensile properties

1. Introduction

The demand for sustainable materials has shown to increase due to the globally growing environmental awareness. One of the main goals in creating 'green' alternatives for conventional and novel applications is to replace petroleum-based raw materials with renewable ones. Cellulose is one of the most attractive options as it is an abundantly available, renewable, and biodegradable natural polymer. Cellulose fibers have been used for centuries for different applications such as paper and board, but due to its inability to melt, dissolution is often required to produce films and textile fibers. Additionally, cellulose fibers can be used as reinforcement in polymer composites due to their low density and good mechanical performance [1]. The main challenge in conventional polymer composites reinforced with natural fibers is the lack of adhesion between the hydrophilic cellulose and hydrophobic polymer matrix. This leads to problems in stress transfer, which results in poor composite mechanical properties and requires the use of compatibilizers. One of the solutions is the single-polymer composite approach, where both the reinforcement and the matrix are made from the same material, and thus no chemical incompatibility is observed [2, 3].

All-cellulose composites are single polymer biocomposites based on cellulose, where dissolved and coagulated cellulose forms a matrix reinforced by non-dissolved fibers [4, 5]. They can be produced via i) partial dissolution of fiber surfaces [6–11] or by ii) dispersing short fibers in cellulose solution

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[12–16], with the first approach studied more extensively. The benefit of the second approach is that it mimics the processing of conventional short fiber composites and could thus have the potential for upscaling. These materials provide a wide range of properties depending on the processing parameters and raw materials [5].

The hydrophilicity of cellulose is seen as one of the main challenges when using cellulose-based materials as sustainable alternatives for petroleum-based products [17]. Hydrophobization of cellulose can be achieved with several approaches, which are reviewed in detail elsewhere [18, 19]. Generally, hydrophobization methods can be divided into chemical and physical treatments depending on the interactions between cellulose and the hydrophobizing component. In chemical treatments, covalent bonds are formed, whereas physical treatments rely on adsorption, the attraction between charges, or other kinds of physical interactions [18].

A physical method for surface hydrophobization of cellulose is layer-by-layer (LbL) deposition of oppositely charged polyelectrolytes onto the surface of the material [20]. This method can also be extended to charged particles or other polyelectrolyte systems [21]. Recently, Forsman *et al.* [22] proposed an environmentally friendly LbL method using cationic poly-L-lysine and anionic carnauba wax particles as a coating of nanocellulose films and textile fabrics; it leads to a hydrophobic surface but maintains the moisture buffering properties of cellulose. However, polylysine is expensive, which limits the possibility of industrial applications, and thus other cations are preferred. Lozhechnikova *et al.* [23] used ZnO as a cation for carnauba wax LbL hydrophobization of wood, but ZnO is not environmentally benign. Additionally, cationic starch has been shown to work as a cationic layer between cellulose and carnauba wax for textiles [24] and pulp sheets [25]. In most cases, the coating is introduced by dipping the cellulose material first into the cationic system, followed by dipping into the carnauba wax dispersion.

Hydrophobization of all-cellulose composites has gained little attention so far even though they are clearly hydrophilic materials with the highest water contact angle reaching 55° [26, 27]. Adak and Mukhopadhyay [28] altered the hydrophilicity by increasing the density of the all-cellulose composites reporting a maximum 76° water contact angle, which is not achieving the commonly accepted limit of contact angle 90° for hydrophobic surfaces. To the best of our knowledge, only Yousefi *et al.* [29] reported the hydrophobization of all-cellulose nanocomposites by silane treatment achieving a water contact angle of 93°.

The goal of this work was to perform surface hydrophobization of all-cellulose composites keeping their fully biobased nature and not altering their initial mechanical properties. To do this, we used carnauba wax particles as hydrophobic coating and cationic starch as an anchoring layer between cellulose and wax. In order to select the highest hydrophobization effect, various approaches were used for surface coating, drying, and curing, including partial and complete melting of the wax. The samples were characterized by their surface properties (water contact angle, roughness), moisture sensitivity, and mechanical properties. The latter were correlated with surface treatment, and optimization was performed to achieve a high contact angle with water without compromising the mechanical properties of the composites.

2. Experimental section
2.1. Materials
Birch dissolving pulp (degree of polymerization (DP) 1100, composition: 92% cellulose, 7% hemicellulose, <1% lignin) and softwood kraft pulp (DP 2550, composition: 80% cellulose, 19% hemicellulose, <1% lignin) used in composite preparation were provided by Stora Enso Oyj. Pulp composition and DP were determined as described in the next section. Sulphuric acid (product number 1.00731.2511) was purchased from Merck (Merck, Darmstadt, Germany) and diluted with water. Analytical grade NaOH pellets (product number 28244.295) were purchased from VWR International (Czech Republic) and dissolved in water to prepare 8 wt% solutions used as cellulose solvent. In all preparations, deionized water was used unless otherwise mentioned.

Hydrophobization was performed using layer-by-layer deposition of cationic starch and carnauba wax. A potato-based cationized starch (Classic 145) was kindly donated by Chemigate Oy, Lapua, Finland. According to the producer, the degree of substitution of quarternary ammonium groups was 0.042. The starch was added to boiling water and left boiling under stirring for *ca* 15 min, and then cooled down. A 5 g/l stock solution was prepared.

Refined carnauba wax (100952382) was purchased from Sigma-Aldrich (Sigma-Aldrich Chemie, Steinheim, Germany). The wax dispersion was prepared by adding solid wax to hot water at 100 °C and sonicating the mixture for 5 min using Ultrasonic Probe Sonifier S-450 with 1/2" extension (Branson Ultrasonics, Lawrenceville, GA, USA). Wax particles in water were thus formed. After sonication, the dispersion was immediately cooled down in an ice bath, ensuring that the wax particles remained stable in the water. To remove large particles and undispersed material, the dispersion was filtered through a filter funnel with 100–160 µm nominal maximal pore size and measurements with a Zetasizer Nano ZS90 (Malvern Instruments, Worcestershire, UK) confirmed that the average particle size was 0.5 µm. A detailed description of the preparation and characterization of the wax dispersion can be found elsewhere [23]. For simplicity, the carnauba wax will be further referred to as wax.

A never-dried bleached birch kraft pulp was used to prepare cellulose nanofibrils (CNF) to be used for AFM experiments. The pulp was washed with 0.01 M HCl to remove residual metals and treated with 0.005 M $NaHCO_3$ to facilitate disintegration by changing carboxyl groups to sodium form. CNF was obtained using 6 passes in a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int. Co., Newton, MA). To prepare ultrathin CNF films for AFM, the CNF dispersion was diluted to 1.67 g/l and mixed for homogenization, and then centrifuged for 45 min at 10 400 rpm. The upper phase containing the thinnest fibrils was collected for spin-coating.

30% aqueous polyehtlyeneimine (PEI) solution with a molecular weight of 50 000–100 000 (06090) was purchased from Polysciences (Warrington, PA, USA). For AFM sample preparation, 0.34 g of 30% PEI solution was diluted with 100 ml MilliQ water, and used as an anchoring agent for CNF.

2.2. Methods

2.2.1. Characterization of the pulps

The initial dissolving pulp was acid hydrolyzed (3% consistency, 60 min, 0.1 M H_2SO_4, 300 rpm mixing) to decrease the DP to 650; see Korhonen *et al*. [12] for more details. This DP was selected because of the best mechanical properties of all-cellulose composites prepared via the dispersion of kraft fibers in dissolving pulp-8% NaOH-water [12]. The DP of the pulps was determined according to the standard SCAN-CM 15:88 via intrinsic viscosity measurement based on cellulose dissolution in cupriethylenediamine.

The composition of the pulps was determined according to the NREL/TP-510-42618 method. Monosaccharides were detected via high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD, Thermo Scientific, Sunnyvale, CA, USA) in a Dionex ICS-3000 column and they were recalculated to carbohydrates' content according to Janson [30].

2.2.2. Preparation of all-cellulose composites

All-cellulose composites were prepared via a short-fiber dispersion approach using a method previously reported by Korhonen *et al*. [12]. Briefly, 5 wt% of cellulose (DP 650) was dissolved into 8 wt% NaOH (aq) at –7 °C for 2 h using an overhead mixer at 300 rpm. After dissolution, 2.4 wt% of softwood kraft fibers were added into the solution at 125 rpm. This concentration was selected as it resulted in the best tensile properties of all-cellulose composites made with this procedure [12]. The suspension was placed into 50 °C oven for 1 h to gel the sample prior to coagulating and washing in water for 2 days (water changed twice per day). Drying was performed in two steps. First, the sample was pressed at room temperature for 2 min at 0.37 MPa, in a pneumatic sheet press (L&W SE 040, Ab Lorentzen &Wettre, Sweden) to remove most of the water. Then the rest of the water was evaporated in hot press at 100 °C for 2 h (Carver Laboratory Press, Fred S. Carver Inc., Wabash, IN, USA). The concentration of kraft fibers in dry composite was 60 wt%.

2.2.3. Surface hydrophobization using the layer-by-layer method

The composites were hydrophobized using the layer-by-layer method by dipping the samples first into aqueous cationic starch solution (5 g/l) and then into aqueous wax dispersion (10 g/l). Two bilayers were shown to be sufficient for the hydrophobization of cellulose nanofibril films and textiles using a similar approach with poly-L-lysine [22].

Two options were tested for hydrophobization. In the first one, a never-dried (or wet) sample was treated with the LbL dipping method before drying. This approach will be called a 'single drying method (1-dry)'. In the second approach, the coagulated composite was first dried in a hot press, and then the composite
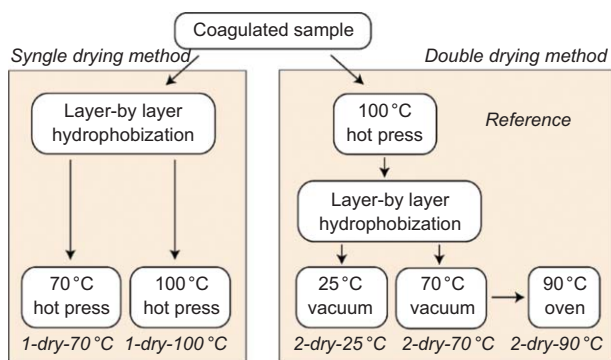
Figure 1. Summary of the two hydrophobization approaches of all-cellulose composites together with samples' codes.

was hydrophobized by dipping. Since the dipping rewetted the samples, they were dried again, and this approach is called the 'double drying method (2-dry)'. Figure 1 shows the different hydrophobization approaches and lists the prepared samples. The impregnation time of each dipping was either 5 minutes or 22 hours per layer. After each dipping, samples were rinsed with water to remove non-adsorbed matter before the next layer was adsorbed onto the surface.

In both cases, after the deposition of two bilayers, the samples were dried to remove the absorbed water. Samples from the single drying method were dried first at room temperature with 0.37 MPa and then at 70 or 100 °C in a hot press. Samples from the double drying method were dried in a vacuum under a 3 kg weight (corresponding to about 1.5 kPa pressure) either at 25 or at 70 °C. In order to study if the morphology of the wax influenced the surface properties of the treated sample, after drying at 70 °C vacuum, the samples were placed in a 90 °C oven for 10 minutes to melt the wax particles. All treated samples were stored in plastic bags for further analysis. All-cellulose composites were prepared as disks of about 16 cm in diameter and 0.2–0.3 mm thickness from which samples were cut for characterization.

In addition to hydrophobization by dipping, layer-by-layer spraying was used to compare the effect of the treatment method on the properties of the hydrophobized composites using the double drying method. One bilayer of 7.5 g/l cationic starch solution/12.6 g/l wax dispersion or two bilayers of 3.3 g/l cationic starch solution/5.6 g/l wax dispersion were sprayed using 3 ml of each compound onto the surface of the dry composite using air-pressurized painting spray. As opposed to the dipping deposition, the samples were not rinsed in between the deposition of the layers. Subsequently, the samples

were dried at 70 °C vacuum to remove the absorbed water.

2.2.4. Differential scanning calorimetry

The melting behavior of the carnauba wax was monitored using differential scanning calorimetry (DSC) (Mettler Toledo, DSC 3$^+$, Columbus, Ohio, USA). Wax was placed in hermetically sealed aluminum pans, and the thermal behavior was measured from 23 to 120 °C at a rate of 5 °C/min using 100 ml/min nitrogen flow. An empty pan was used as a reference.

2.2.5. Characterization of composites

Water contact angle
The water contact angle (WCA) of composite surfaces was measured with a CAM 2000 (KSV Instruments Ltd, Finland). The volume 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. At least 5 measurements were performed for each sample.

Scanning electron microscopy (SEM)
Samples' morphology was investigated with a Zeiss Supra 40 SEM FEG (Field Emission Gun) (Jena, Germany) scanning electron microscope using an acceleration voltage of 3 kV. Prior to imaging, the samples were attached to aluminum SEM stubs with carbon tape followed by sputter-coating Q150T Modular Coating System (Quorum Technologies, Ashford Kent, UK) with platinum forming a thin layer of 7 nm.

Atomic force microscopy (AFM)
Ultrathin model CNF films were used to study the influence of curing temperature on surface roughness. Silicon wafers were immersed in 0.102 mg/l polyethyleneimine solution for 15 min, rinsed with MilliQ water, dried with N$_2$ gas and spin-coated at 3000 rpm with ultrathin CNF dispersed in water. The films were then immediately coated with 2 bilayers of cationic starch and wax as described for the composites. The films were left to dry at room temperature and cured at 70 and 100 °C. The films were imaged in air using a Nanoscope V MultiMode scanning probe microscope (Bruker Corporation, Billerica, Massachusetts, USA). Images were recorded in tapping mode. Silicon cantilevers (NSC15/AIBS, MicroMasch, Tallinn, Estonia) with driving frequencies

around 270–340 kHz were used. According to the manufacturer, the radius of the tip was less than 10 nm. At least 3 different areas of the sample were imaged. For the calculation of roughness, the size of the images was 10 μm×10 μm, and at least two to three images per formulation were analysed.

Tensile properties and density

Tensile properties of the composites were tested using a universal tensile testing device (Instron model 4204, Massachusetts, USA) equipped with a 1 kN load cell (0.5 mm/min). Dog-bone shaped specimens (EN ISO 527: 1996; specimen 5A) were conditioned for at least 24 h (25 °C and 50% relative humidity) prior to analysis and measured in the same conditions. Minimum 5 specimens per formulation were tested.

The density of the composites was determined by simply measuring the mass of the sample and its volume; two specimens from each sample were analyzed.

Water uptake and sorption isotherms

The influence of hydrophobization and the wax layer morphology on water uptake and water vapor sorption was tested for samples that were hydrophobized with the double drying method. Water uptake [wt/wt%] was studied by placing a sample in water at room temperature and measuring the weight increase over time; water uptake was calculated as $100\% \cdot \Delta W / W_0$ where ΔW is the difference between sample weight at a certain time and weight of dry sample W_0. Sorption isotherms were measured using a dynamic vapor sorption device (DVS Intrinsic, Surface Measurement Systems Ltd., Wembley, UK). The measurements were performed at 25 °C. The relative humidity (*RH*) was decreased to 0% to determine the dry weight of the specimen and then increased to 95% by the first step of 5% followed by 10% steps. Desorption was measured by a decrease from 95 to 0% in the reverse order. Vapor sorption or desorption [wt/wt%] was calculated using the same approach as for water uptake. Each relative humidity step was maintained until the weight change was less than 0.002%/min for 10 minutes.

3. Results and discussion
3.1. Phase transitions in carnauba wax

Before presenting the results on surface hydrophobization of all-cellulose composites, the properties of the hydrophobizing component, carnauba wax,
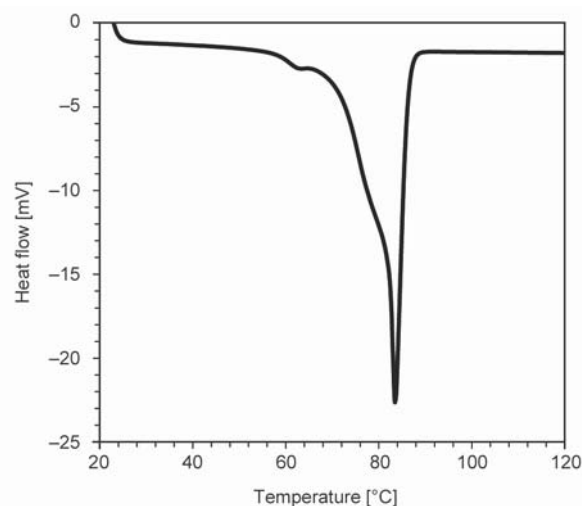
Figure 2. DSC traces of carnauba wax.

must be understood. While a hydrophobic surface can be achieved by decreasing the surface energy, the highest hydrophobicity is achieved by a combination of high surface roughness and low surface energy. Carnauba wax particles can provide both. As it will be demonstrated later, micron-size wax particles naturally contribute to surface roughness.

As a natural material, carnauba wax consists of several different molecules, mostly esters (84–85%), but also fatty acids (3%) and fatty alcohols (3%) [31, 32]. It is also known that carnauba wax is melting in the interval of 65–90 °C and at 62 °C, it undergoes solid-solid transition with the reorientation of methyl groups [31]. Thus, the melting behavior of the chemically heterogeneous carnauba wax was studied using DSC (Figure 2). Three main peaks were found: the onset temperature of the first peak was at 59.4±0.2 °C, the second at 69.8±0.5 °C and the third at 78.9±1.3 °C. Based on these results, we chose three curing temperatures: no melting (*RT*), partial melting (70 °C), and full melting (90 °C). Using X-ray photoelectron spectroscopy, it has previously been demonstrated that at 70 °C there is a higher amount of non-polar C–C bonds and a lower amount of polar C–O bonds at the outermost surface of the wax than at room temperature, further suggesting both partial melting and rearrangement of the molecules at the surface [24].

3.2. Hydrophilic/hydrophobic properties of surface-hydrophobized all-cellulose composites

The water contact angles of the treated all-cellulose composites are presented in Figure 3. For the non-treated reference composite, it is around 43°, and it
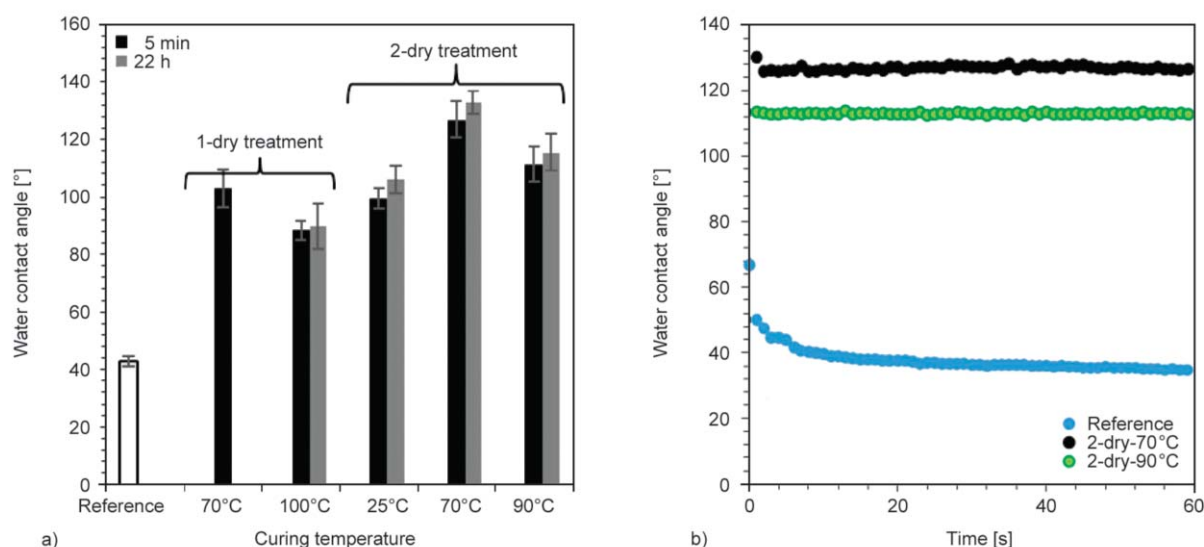
Figure 3. Water contact angle of the composites made with different LbL treatments and curing temperatures: (a) at 5 s and (b) evolution as a function of time during the first minute for the reference (non-hydrophobized) and two hydrophobized samples with partially melted (2-dry-70 °C) and completely melted coating (2-dry-90 °C).

decreased by about 20% during the first minute (Figure 3b) until the water was completely absorbed. Layer-by-layer hydrophobization (recall Figure 1) increased the WCA for all studied samples, as shown in Figure 3a. The duration of dipping, 5 min, or 22 h per layer, did not influence the WCA within the experimental errors. The absorption of water droplets during the first minute was negligible for the treated samples as droplet volume decrease was in the range of 2–3%. The untreated reference exhibited 11% decrease in the water droplet volume.

A surface can be classified as hydrophobic if the water contact angle is above 90° [33]. The lowest WCA, 88–90°, was obtained for the case of 1-dry-100 °C, all other treated samples are more hydrophobic with WCAs from 100 to 133°. The single drying method resulted in an overall lower WCA than the double drying method, while the main effect within each drying type was caused by the curing temperature. In both drying approaches, curing at 70 °C resulted in the highest WCA, with a value of 133° obtained for the 2-dry treatment.

The reason for different water contact angles is not only the low surface energy and thus intrinsic hydrophobicity of the wax but also the different surface morphology of the composites. The latter, in turn, depends on the wax response to the curing temperature, see DSC results in Figure 2. The wax starts to melt at 60 °C, while all wax particles are expected to have melted at 90 °C. The SEM images of the reference (non-treated) and double dried samples are presented

in Figure 4. The reference sample had a relatively smooth surface; the adhesion between the reinforcing kraft fibers and the cellulose matrix was very good (Figure 4a). After hydrophobization and curing at 25 or 70 °C the composite surface was well covered with wax particles (Figure 4b and 4c, respectively).

The DSC results (Figure 2) show that the wax is partly melted at 70 °C. However, from Figure 4c it is evident that there are still a lot of particles left on the surface. This situation is optimal for good surface water-resistance because of the combined roughness and low surface energy. The partial melting ensures better wax coverage over the sample surface, while the non-melted wax particles give additional surface roughness. The cracks observed after drying at 25 °C are not visible after drying at 70 °C. At 90 °C all wax had melted (Figures 2 and 4d), leading to a rather smooth surface of the composite with no visible particles; some of their traces, resembling craters, can be detected. This leads to a smoother surface and slight decrease in WCA.

To provide more details on the influence of curing temperature on surface roughness, AFM experiments were performed. In order to separate the roughness due to wax from that due to reinforcing fibers (see Figure 4a), model ultrathin CNF films were used. The results are presented in Figure 5 and Table 1 with R_a being the arithmetic average height (Equation (1)) and R_q the root mean square height representing the standard deviation of the distribution of surface heights (Equation (2)) [34]:
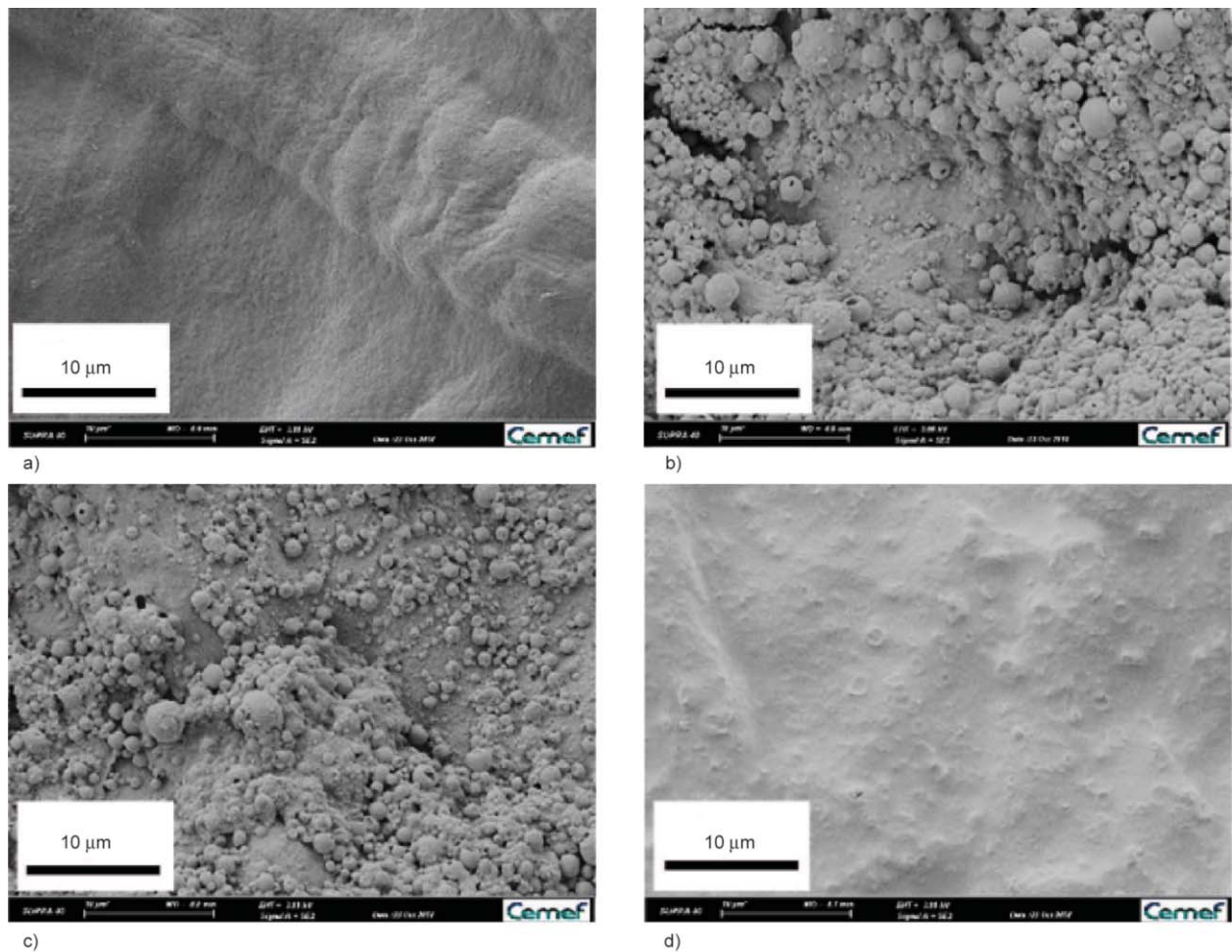
Figure 4. Morphology of the (a) reference sample, (b) 2-dry-25 °C, (c) 2-dry-70 °C and (d) 2-dry-90 °C. All hydrophobization treatments correspond to double drying method with 5 min dipping time per layer.

$$R_a = \frac{1}{l} \int_0^1 |y(x)| \, dx \qquad (1)$$

$$R_q = \sqrt{\frac{1}{l} \int_0^1 \{y(x)\}^2 \, dx} \qquad (2)$$

The surface roughness of neat CNF is very low, as expected (Table 1). The values for the samples cured at 25 and 70 °C (Figure 5a and 5b, respectively, and Table 1) are very similar and much higher than that of reference sample due to the presence of wax particles. The difference in WCA of the samples cured at 25 and 70 °C cannot be explained by surface

Table 1. The values of R_q and R_a with the standard deviation in parenthesis

Sample	R_q [nm]	R_a [nm]
CNF	5.0 (0.0)	4.0 (0.0)
CNF + wax at *RT*	251 (133)	167 (109)
CNF + wax at 70 °C	268 (121)	207 (107)
CNF + wax at 100 °C	45 (14)	35 (12)

roughness only. Instead, differences in surface energy must be the reason, as when cured at 70 °C, wax has a higher amount of hydrophobic C–C and a lower amount of hydrophilic C–O on the surface [24]. The partial melting of the wax particles increases the wax coverage of the surface, while still providing necessary surface roughness. After curing at 100 °C the wax particles are completely molten based on both DSC (Figure 2) and SEM (Figure 4), and the surface roughness has decreased in one fifth as compared to 25 and 70 °C (Table 1). Overall, an increasing amount of C–C bonds due to heat-induced reorientation of the wax molecules [24] coupled with surface roughness and better coverage of partially molten particles provide the optimal conditions for having the highest surface hydrophobization effect.

While the as-prepared all-cellulose composites show enhanced surface hydrophobicity, it was of interest to test their bulk properties in terms of water vapor adsorption/desorption and water uptake. Water vapor sorption isotherms (Figure 6) show that the surface
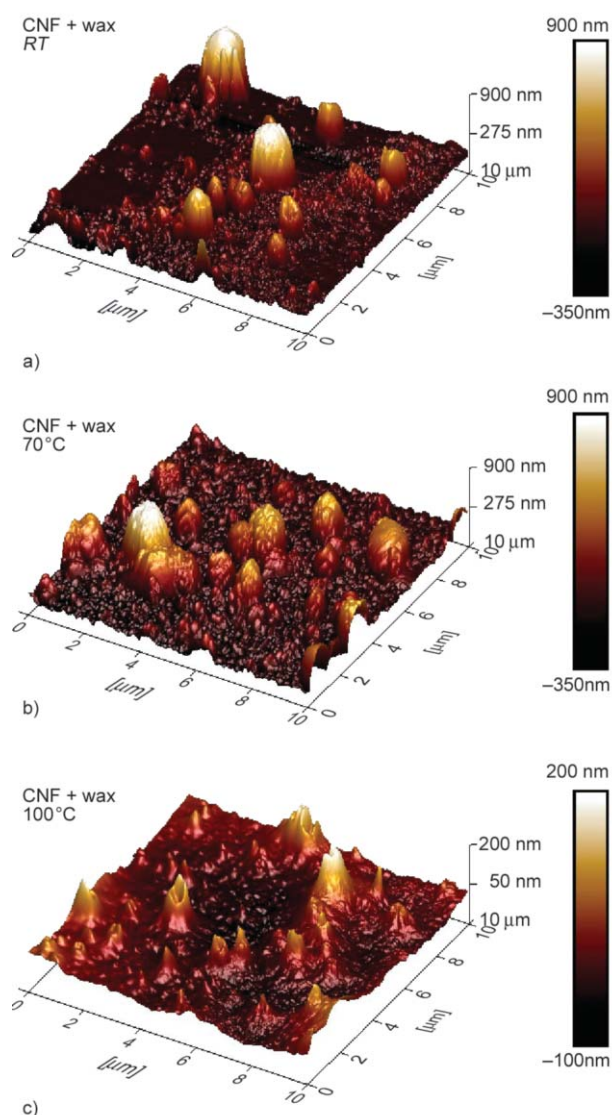
a)

b)

c)

Figure 5. AFM images model CNF film coated with wax and cured at (a) *RT*, (b) 70 °C and (c) 100 °C.

Figure 6. Water vapor isotherms [wt/wt%] of the reference and double dried hydrophobized all-cellulose composites. Closed markers are for sorption and open markers are desorption. Lines are given to guide the eye.

Figure 7. Liquid water uptake [wt/wt%] of the reference and two surface hydrophobized all-cellulose composites with particle-like (2-dry-70 °C) and completely melted coating (2-dry-90 °C).

treatment has minimal effect on the adsorption behavior as compared to the non-treated sample and no effect at all for the desorption behavior. Sorption was slightly higher for the treated samples, and there was no difference between the partially molten and non-molten surfaces (70 and 90 °C). At the same relative humidity treated composites adsorb 1–1.5% more water vapor than its non-treated counterpart, and no influence of curing temperature on vapor sorption and desorption can be noticed. Desorption occurs with a slight hysteresis as it is usually observed for cellulose-based materials [35, 36]. Maximum adsorption at 95% *RH* is very similar, around 19% for the reference composite and 21% for the treated ones. Even though the surface was shown to be hydrophobic by WCA, the treated composites react to the humidity changes in the same way. The reason for the
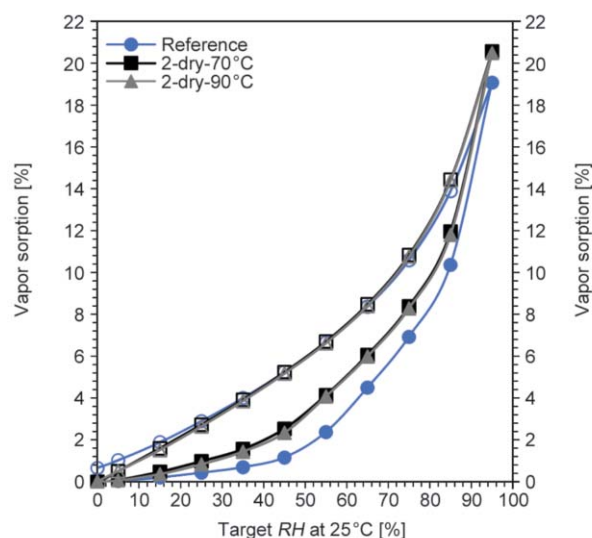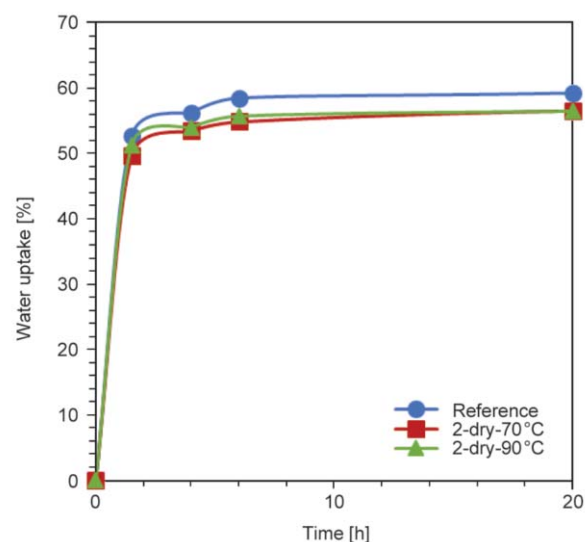
slightly increased vapor adsorption by the treated samples is most likely due to the presence of the cationic starch used for LbL deposition of wax, as hypothesized by Lozhechnikova *et al*. [23] for the case of ZnO.

Water uptake by the reference and surface-treated composites is also very similar (Figure 7). Non-treated composite absorbed 61% of water during 48 h exposure time, whereas samples 2-dry-70 °C and 2-dry-90 °C absorbed 58 and 57% during the same exposure time, respectively. About 90% of the total

absorption occurred during the first two hours of exposure; there was no significant difference between the absorption rate of the reference and the treated samples (Figure 7). Overall, all-cellulose composites with a hydrophobic surface were obtained without changing their sorption behavior. This treatment is suitable for applications where a non-toxic, breathable, water-repellent coating is desired.

3.3. Mechanical properties of surface hydrophobized all-cellulose composites

Mechanical properties are key characteristics of any composite material, and thus the influence of the treatments used for surface hydrophobization on the material's tensile properties was studied. Young's modulus and tensile strength for single and double drying methods are shown in Figure 8. It was found that the double drying method, *i.e.* drying/rewetting(dipping)/drying is detrimental for the mechanical properties of all-cellulose composites. Tensile strength and Young's modulus of the reference sample were around 48 MPa and 6.4 GPa, respectively, which were maintained for the samples hydrophobized by the single drying method. However, the tensile strength and Young's modulus of the composites with the highest water contact angle made with the double drying method were around 37 MPa and 4.5 GPa (Figure 8), respectively, which corresponds to a roughly 30% decrease in the mechanical performance as compared to the reference sample.

In order to understand the obtained results and to further improve the mechanical properties of composites with the highest water contact angle, the following experiment was performed. Four non-hydrophobized samples were prepared and the double drying method was imitated but without the addition of the cationic starch and wax. Two samples were simply dried (without dipping) under a hot press and in a vacuum, and two were dried under a hot press, dipped in water according to the '5 min' dipping protocol and dried again with final drying performed also under a hot press and in a vacuum. Figure 9 shows that both Young's modulus and tensile strength are decreased if the sample is dried, dipped and dried again. We hypothesize that when wetting a dry composite followed by drying, the composite is swelling and contracting
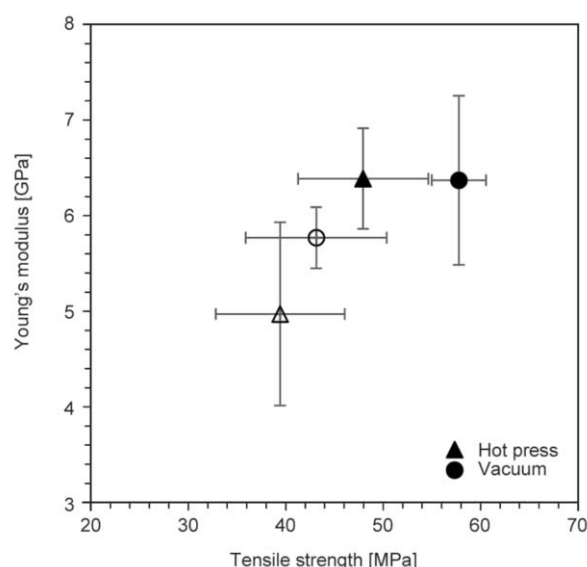

Figure 9. Comparison of the mechanical properties between non-hydrophobized samples made in different ways: open points correspond to 2-dried samples and filled point to 1-dried samples.
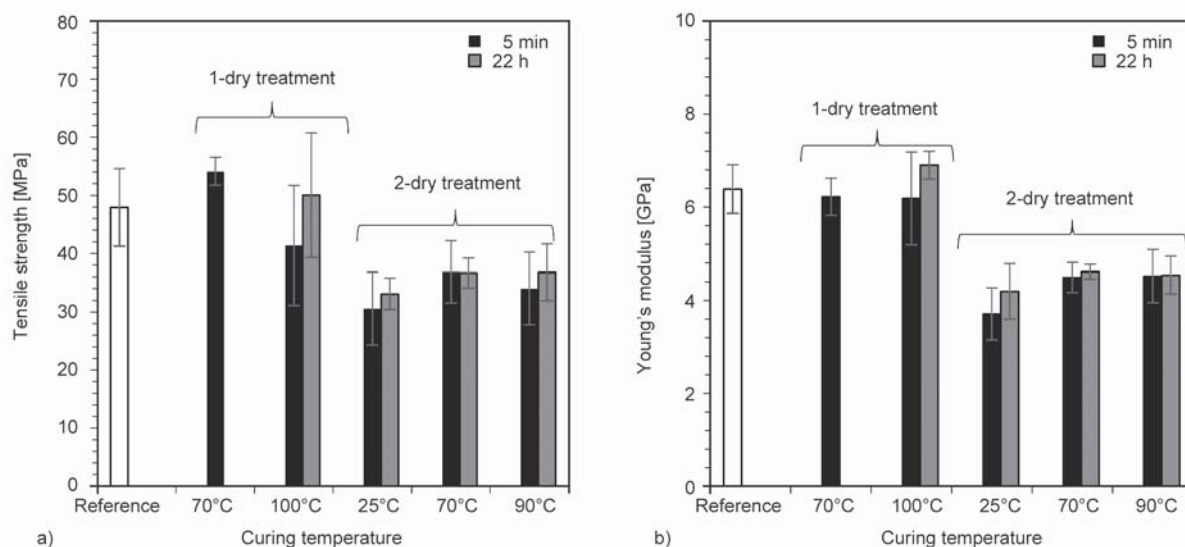

Figure 8. Tensile strength (a) and Young's modulus (b) of the composites.

in a heterogeneous way due to the presence of different celluloses: cellulose II in the matrix and native cellulose in the kraft fibers. Indeed, the sample significantly swells during '5 min' dipping protocol (20 minutes of total exposure to water) as its' thickness increased by 1.8 times compared to that before dipping. The residual stresses caused by the drying of the swollen composite may induce material distortions and, potentially, the appearance of microcracks, accentuated by drying in a hot press. Hence, extensive wetting of the dry composite should be avoided.

3.4. Optimization of the process

Since it was found that dipping (sample swelling) followed by a second drying is decreasing the mechanical properties of the composite, but the highest WCA was achieved using this approach, optimization of the process was performed. The goal was to reduce the contact of the composite with water to minimize swelling, but still having a high WCA. Spraying was chosen for this purpose. One bilayer and two bilayers of aqueous cationic starch and wax dispersion were sprayed on top of the composites. One bilayer was used to test if it is still sufficient to obtain a hydrophobic surface. The sprayed samples were dried in a vacuum at 70 °C.

Figure 10 summarizes all the studied samples by comparing their water contact angle and Young's modulus. As shown above, the highest contact angles were obtained when the samples were treated with the double drying method and cured at 70 °C, but this approach sacrificed the tensile properties. The single drying method maintained the mechanical performance of the composites, but the increase in the water contact angle was modest. When using the spraying method, a water contact angle of 120° was achieved for a sample with two bilayers while almost maintaining the mechanical performance of the reference composite. The spraying of two bilayers induced slight swelling of the composite: sample thickness increased by 20% compared to the initial dry sample. This is considerably less than swelling occurring during dipping. This confirms that by controlling composite swelling, high water contact angle can be achieved without the reduction in tensile properties. When comparing the spraying method with one or two bilayers, one bilayer resulted in similar tensile properties as the reference composite, however, WCA was lower, 110°, than with two bilayers.
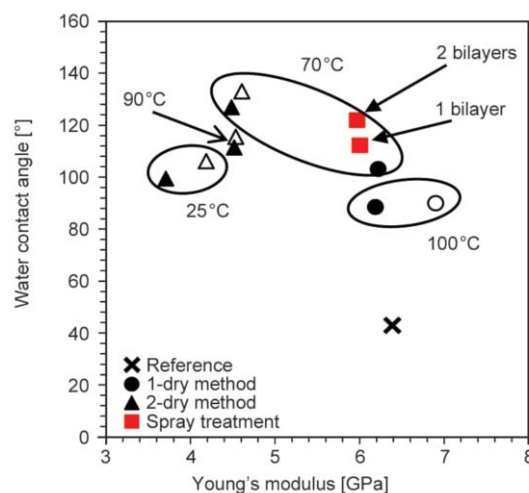

Figure 10. Water contact angle and Young's modulus for all samples studied. Closed markers are for the samples with impregnation time of 5 min and open markers of 22 h.

All-cellulose composites with good tensile properties have the potential to be used in a range of applications as a 'greener' alternative of plastics that are widely used today. However, the use of cellulosic materials has been hampered by poor performance when interacting with water. The hydrophobized composites overcome this issue, and the hydrophobization process used does not compromise the eco-friendliness of the material.

4. Conclusions

The surface of all-cellulose composites made by dispersion of short kraft fibers in cellulose-NaOH-water solutions was hydrophobized via the layer-by-layer method. Natural materials, cationized starch, and carnauba wax were used for this purpose. It was demonstrated that the phase behavior of wax is important for controlling hydrophobization. Optimal conditions, combining highest surface coverage, lowest surface energy and highest surface roughness was achieved with curing at 70 °C.

While two bilayers applied by dipping of a dried composite resulted in the highest hydrophobicity, uncontrolled swelling and a second drying process decreased the mechanical performance of the material. As the extensive swelling negatively affected the mechanical properties, optimization of the layer-by-layer method was performed. Spraying was used as a way to maintain both high contact angle and good tensile properties, the latter being similar to the reference non-hydrophobized material. Easy processing and widely available components make all-cellulose

composites surface-hydrophobized by spraying very attractive as fully bio-based materials, for example, for food packaging, furniture and covers for electronic units.

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