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A fast method to produce strong NFC films as platform for barrier and functional materials

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Abstract

In this study we present a rapid method to prepare robust, solvent resistant nanofibrillated (NFC) cellulose films that can be further surface modified for functionality. The oxygen, water vapor and grease barrier properties of the films were measured and in addition mechanical properties in dry and wet state, and solvent resistance were evaluated. The pure unmodified NFC films were good barriers for oxygen gas and grease. At relative humidity below 65%, oxygen permeability of the pure and

unmodified NFC film was below $0.6 \text{ cm}^3\mu\text{mm}^{-2}\text{d}^{-1}\text{kPa}^{-1}$, and no grease penetrated the film. However, the largest advantage of these films was their resistance to various solvents, like water, methanol, toluene and dimethylacetamide. Although they absorbed a substantial amount of solvent, the films could still be handled after 24h of solvent soaking. Hot-pressing was introduced as a convenient method to increase not only the drying speed of the films but also enhance the robustness of the films. The wet strength of films increased due to the pressing. Thus they can be chemically or physically modified through adsorption or direct chemical reaction in both aqueous and organic solvents. Through these modifications the properties of the film can be enhanced introducing e.g. functionality, hydrophobicity or bioactivity. Herein a simple method using surface coating with wax to improve hydrophobicity and oxygen barrier properties at very high humidity is described. Through this modification the oxygen permeability decreased further and was below $17 \text{ cm}^3\mu\text{mm}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ even at 97.4 % RH and the water vapor transmission rate decreased from 600 to 40 $\text{g}/\text{m}^2\text{day}$. The wax treatment did not deteriorate the dry strength of the film. Possible reasons for the unique properties are discussed. The developed robust NFC films can be used as a generic, environmentally sustainable platform for functional materials.

Keywords: Nanofibrillated cellulose, barrier, film, oxygen permeability, solvent resistance, wet strength

Introduction

Nanofibrillated cellulose (NFC) is one of the most interesting renewable nanomaterial obtainable in nature. In addition to the obvious environmental reasons; the renewability, non-toxicity and availability of cellulose, the growing interest for this material is due to its extraordinary high specific strength, thermal stability, hydrophilicity and broad capacity for chemical modification. Recently the development in cellulosic fibrillation methods has facilitated the production of nano-scaled NFC from cellulosic sources like wood and crops with reasonable low energy consumption.¹⁻³ The width of the nanofibrils depends on the production method but is typically around 5-20 nm. The length of the fibrils

is more challenging to determine but may exceed 5 μm and thus the aspect ratio of NFC is more than 250. The high aspect ratio is advantageous and contributes to the high strength of network structures and composite materials prepared from NFC.

There is a great demand for flexible, strong, transparent, thermally stable films with excellent barrier properties for various packaging applications, like food, medicine and electronics. Especially the gas barrier properties are important since even a very small amount causes most products to deteriorate. Petroleum-derived polymers have been extensively used due to their simple processing, low manufacturing costs and excellent barrier properties. However, the increased environmental consciousness has promoted the utilization of biopolymers. Starch and regenerated cellulose films like cellophane have been explored but their strength properties are not always sufficient and thus they are traditionally mixed with synthetic ones or chemically modified⁴ to improve their properties. The strong interaction between nanofibrils during drying can be utilized to prepare NFC-films.⁵ The inherent strength of the cellulose crystals combined with the strength of interactions between the fibrils leads to the formation of very strong films based on NFC. NFC films also show excellent oxygen barrier properties in dry conditions. For a comprehensive review on the potential of NFC as a barrier material the reader is referred to the recent review by Lavoine et al.⁶ However, most practical applications demand that the film can stand at least 50% relative humidity. Only a few attempts have been made to enhance the barrier properties of NFC at elevated humidity. Spence et al⁷ found that lignin present in the NFC actually increased the water vapor transmission through the film although the opposite was expected. This was concluded to be due to the increased porosity of the film. Similarly acetylation of cellulose nanofibrils prior to film formation enhanced the barrier properties only at very low degree of substitution and had a deteriorating effect at higher levels of substitution.⁸ Nanocomposite films containing nanoclay and NFC were found to retain good oxygen barrier properties even at high humidity.^{9, 10} Although the barrier properties of NFC films have gained much attention lately the films resistance to solvent has not been explored earlier.

Another disadvantage of most approaches reported in the literature is the extremely slow dewatering of NFC. NFC-films are typically prepared from water suspensions by film casting and water evaporation.^{9, 11} Alternatively, the suspension can be gradually pressed in a mould with porous plates, where the water can pass through.¹² Afterwards, the moulded compound is freeze-dried to a moisture content of 2 %, followed by hot-pressing. Filtration on a Büchner funnel followed by drying can also be used.¹³ With these approaches the film preparation takes from several hours to a few days, which is not practically feasible.

We introduce a method based on over-pressure filtration and hot pressing for fast preparation of NFC films. The formed film is surprisingly robust and resistant to many solvents, which opens up numerous application and functionalization possibilities. For example, through simple surface modification the film could be a platform for diagnostic assays. The effect of hot pressing on both dry and wet strength, water absorption, and barrier properties is discussed and finally an example of a simple, cheap and environmentally friendly method to further increase the water resistance is shown.

Experimental section

Materials

The cellulose nanofibrils (NFC) were prepared in the Finnish Centre for Nanocellulosic Technologies. Never-dried industrial bleached hard wood kraft pulp was washed into sodium form following a procedure introduced by Swerin et al¹⁴ to control both the counter-ion type and ionic strength. The washed pulp was disintegrated through a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int. Co., Newton MA) 6 or 20 passes. No chemical or enzymatic pretreatment was used prior to disintegration. If not otherwise specified the six-pass sample was used. The charge density of the pulp used was 0.065 meq/g and the zeta-potential of the corresponding NFC gel was -3 mV¹⁵ Paraffin wax (Sigma-Aldrich, m.p. 54-56 °C, CAS: 8002-74-2) was used for surface modification of films.

Film preparation

The films were prepared by pressurized filtration. 150 ml of 0.84 % NFC suspension was filtrated through a Sefar Nitex polyamine monofilament open mesh fabric with 10 μm pore size at 2.5 bar pressure. Using this technique 120 μm thick (dry thickness) and 137 cm^2 large films (corresponding to a diameter of 13.2 cm), that were dry enough to handle, were prepared in less than one hour. The films were wet pressed for 4 minutes whereupon they were further pressed in a Carver Laboratory press (Fred S. Carver Inc., New Jersey, USA) at about 100 °C and 1800 Pa varying the pressing time between 0.5-2 h. The basis weight of the films was about 55 g/m^2 . There was always about 40 % loss of material during the filtration. The dry films were stored for at least 48 h at 23 °C and 50 % relative humidity until further measurements. For comparison some of the dry film was treated with paraffin wax by melting the wax and dipping the film into the melted wax, removing excess wax from the surface and allowing the films to dry in 23 °C and 50 % relative humidity without any further treatments.

Apparent film density

The apparent film density was calculated from the 2×4 cm strips of about 70 μm thickness used for solvent absorption measurements by dividing the mass with the sample dimensions. The thickness was measured tree times/per sample with a Lorenz Wetter paper thickness meter.

Oxygen transmission rate

The oxygen transmission rate (OTR) through the films was determined according to the standard ASTM F1927 using Ox-Tran 2/20 Oxygen transmission rate tester (Mocon, Modern Controls Inc., USA). The test area of the sample was 50 cm^2 . The tests were carried out at 23 °C and different relative humidity using 100 % oxygen as a test gas. The OTR was multiplied with the thickness of the film and the corresponding oxygen permeability (OP) was reported.

Water vapor transmission rate

Water vapor transmission rates of the films were determined gravimetrically using a modified ASTM E-96 procedure. Samples with a test area of 25 cm² were mounted on a circular aluminum dish (H.A. Buchel V/H, A.v.d. Korput, Baarn-Holland 45 M-141), which contained water. Dishes were stored in test conditions of 23 °C and 50 % relative humidity and weighed periodically until a constant rate of weight reduction was attained.

Grease resistance

Grease resistance was determined according to modified Tappi T 507 method. First, standard olive oil was colored with Sudan II dye and applied onto 5 cm×5 cm sized blotting paper. Stain saturated piece of blotting paper was placed against the films and a piece of blank blotting paper (stain absorber) was placed against the other side. The whole stack was pressed between two plates and kept in oven at 60 °C for 4 h. At the end of the test period, the assembly was removed and the stain absorbers were examined. For each absorber the area and the number of stained spots, if any, were determined.

Solvent resistance and solvent absorption

Pieces of the films were immersed in solvent for at least 18 hours whereupon they were photographed and removed from the solvent and photographed again after a few minutes of drying. The absorption of solvent was determined by immersing 2×4 cm strips in solvent removing them periodically and weighting them. The samples were equilibrated in 50% RH and 23 °C for at least 72 h before measurements and the measurements were performed in the same conditioned room. The thickness of the dry films was around 70 μm, but thickness and weight was measured for each sample strip before solvent immersion. Average values from four measurements are shown. The solvent uptake (%) was calculated from Equation 1:

$$\text{Solvent uptake (\%)} = (m_t - m_0) \times 100/m_0.$$

Equation 1

Mechanical properties in dry and wet state

The mechanical properties of the dry films were determined with a tensile test using Instron 4204 testing machine. Strips with dimensions of $5.3 \times 30 \text{ mm}^2$ were cut from the uniform film, and the thickness was separately measured for each sample before measurements. To avoid slippage at the sample holders, small pieces of paper was glued to the edges of the samples. The grip distance was 20 mm, maximum cell load 1 kN and testing speed 1 mm/min. Wet films were measured using a MTS 400/M vertical tester. Strips with dimensions of $50 \times 15 \text{ mm}^2$ were cut from the uniform film, and the thickness was separately measured for each sample before measurements. The samples were immersed in water for 1h and measured immediately after removal. The grip distance was 40 mm, maximum cell load 200 N and testing speed 0.5 mm/min. For both dry and wet strength at least 7 parallel samples were tested, and the samples were conditioned for at least 3 days at 23 °C and 50 % before testing or alternatively soaking in water and testing under wet conditions. Average results are shown.

Contact angle measurements

The contact angle of water on the films was determined using the sessile drop method employing a CAM 200 (KSV Instruments Ltd, Finland) video camera based fully computer controlled contact angle meter. The determination of contact angles is based on the analysis of drop shape using the full Young-Laplace equation. The measurements were performed at room temperature using pure water and at least three areas were measured on each sample. The drop volume was $\sim 6 \mu\text{l}$.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM), employing a LEO 1450 SEM equipped with a W-cathode (Carl Zeiss Inc.) was used to characterize the cross sections of the films. Slices of the film were dried in liquid nitrogen and quickly cleaved to obtain a clean cut. A thin layer of gold/palladium was sputtered on the specimen before imaging.

Atomic force microscopy

For the characterization of NFC fibril dimensions and film surface morphology, atomic force microscopy (AFM) imaging in air was applied. The Nanoscope IIIa multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA) operating in tapping mode was used. Silicon cantilevers (NSC15/AIBS, MicroMasch, Tallinn Estonia) with a driving frequency around 300-360 kHz were used. The radius of the tip according to the manufacturer was less than 10 nm. At least three different areas on the sample were scanned.

Wide angle X-ray scattering

Wide angle x-ray scattering measurements (WAXS) were made for determining the crystallinity and the width of cellulose crystallites. The measurements were made using the perpendicular transmission geometry with the equipment and methods described by Svedström et al.¹⁶ The average width of cellulose crystallites was determined from the measured diffraction patterns from the cellulose I β 200 reflection using Scherrer's equation.¹⁷ The relative crystallinity was determined by fitting the amorphous background and the theoretical intensity of crystalline cellulose to the experimental diffraction pattern.¹⁷ The accuracy was ± 5 %.

Results and Discussion

Film formation

Nanofibrillated cellulose forms dense films with good barrier properties.^{18, 19} Still, the slow dewatering is one main challenge limiting industrial use of these films. Solvent casting and evaporation^{7, 19} or filtration^{18, 20} have been used to produce NFC films. However, the film formation using these approaches may take from several hours to days depending on technique and NFC used. Hence possibilities to speed up the dewatering were evaluated. A technique based on over-pressure was employed to filtrate the gel. Surprisingly the dewatering was rather rapid and 130 mm diameter films, having a dry thickness of 120 μm , were formed in less than 30 min for the six times fluidized NFC

sample. After 0.5-2 h hot pressing the film was ready for use. The most time consuming step in this approach is not the dewatering, as is the case in most other preparation methods, but rather the hot pressing. The total film preparation time was 1–2.5 h depending on time in hot press. This is comparable with the fastest preparation method reported for NFC films using a Rapid Köthen equipment.²¹ They reported a total film preparation time of 1-2 h for 200 mm diameter and 45 μm thick films.

Effect of applied load on the mechanical properties of pure and dry NFC films

The drying at elevated temperature and under high load was initially employed in order to avoid wrinkling of the NFC films. However, in addition to leading to smooth, rather transparent films (Figure 1), this treatment also increased the strength and barrier properties of the film as demonstrated below. The structure of the fabric used in filtration and pressing gives some nanometer scale roughness to the film surface (Figure 1b).

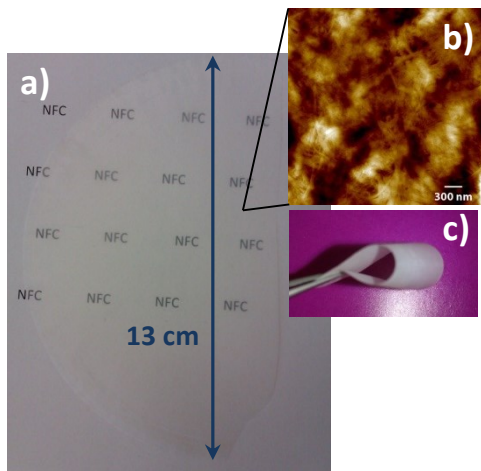


Figure 1. a) Photograph of the translucent free –standing film on top of a conventional copy paper. b) $25 \mu\text{m}^2$ AFM height image showing the surface topography of the film and c) photograph illustrating the flexibility of the sample. The film was prepared from NFC passed 6 times through the fluidizer (F6).

In Figure 2 the tensile stress-strain curves of pure NFC films as a function of time in the hot press is shown. If the film was dried without the hot pressing step it was too wrinkly to measure, thus the first measured point is after 0.5h hot pressing. In general the films were strong and comparable to previously reported values.^{18, 19, 21-23} However, here we note that measurements procedures, relative humidity and sample dimensions strongly influence the results and thus mechanical properties obtained in different studies should be compared with some caution. The 0.5 h pressed film has lower Young's modulus and tensile strength suggesting that indeed the pressing increases the strength of the film. However, no remarkable change was observed between the one and two hours pressed films. The corresponding modulus, tensile strength and elongation are shown in Table 1. The modulus and strength increases upon hot pressing. We speculate that a denser film with higher amount of bonds and less voids is formed when the film is dried at high applied load and elevated temperature. A slight decrease in film thickness from 74 ± 3 μm for non-pressed to 65 ± 4 μm for 2 h pressed sample indicates densification during pressing. The thickness of the 0.5 and 1 h pressed samples was in between these two extremes ($67-68\pm 3$ μm). Nevertheless the changes in density were within the error limits and clear correlation between hot pressing and density was consequently not found.

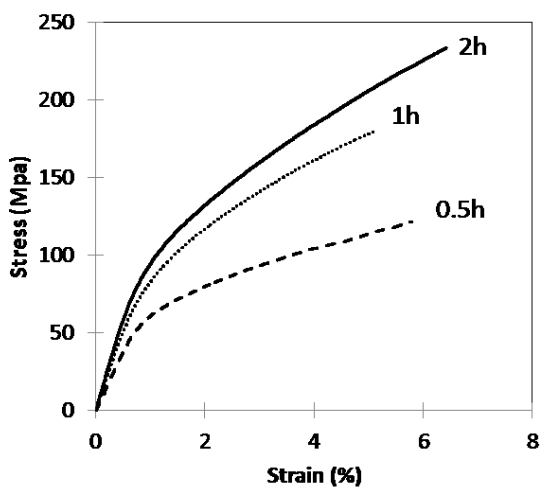


Figure 2. Effect of the time in hot press on the tensile stress – strain curves for the free-standing NFC films prepared from F6 NFC.

Table 1 Mechanical properties of NFC (F6) films

Sample	Young's modulus (GPa)*	Tensile strength (MPa)*	Elongation (%)*
NFC (0.5 h pressed)	8.1±0.7	121±16	7.9±0.8
NFC (1 h pressed)	11±1.0	180±19	5.1±0.4
NFC (2 h pressed)	11.2±2.3	230±23	7.2±2.1
NFC (2 h pressed)+wax	11±0.8	180±19	5.1±1.0

* The standard deviation from 7-11 parallel measurements is indicated.

Oxygen barrier properties of pure NFC films

In Figure 3 the effect of fibril size on the oxygen transmission rate through the film is shown. Films were made from NFC dispersion after six (F6) and 20 passes (F20) through the Fluidizer. The increased fibrillation led to more homogeneous samples, with smaller amount of thick fibrils in the size range 50-100 nm, but the major part of the fibrils were already in the width range of 5-20 nm in both samples (Figure 3 b and d). The fibrils are many micrometers long and it is difficult to evaluate the length of the fibrils, thus the width of fibrils and fibril aggregates are compared. The size of the fibrils affected the dewatering time, which was clearly slower for the F20 sample, further supporting that indeed there is a difference in fibril size range between the two samples. However, no significant difference in the barrier properties between the samples could be observed (Figure 3e). The scarce thicker fibrils do not deteriorate the very dense network that is formed during drying and pressing. Consequently the rest of the experiments were conducted with the F6 sample, due to the clear advantage of quicker dewatering.

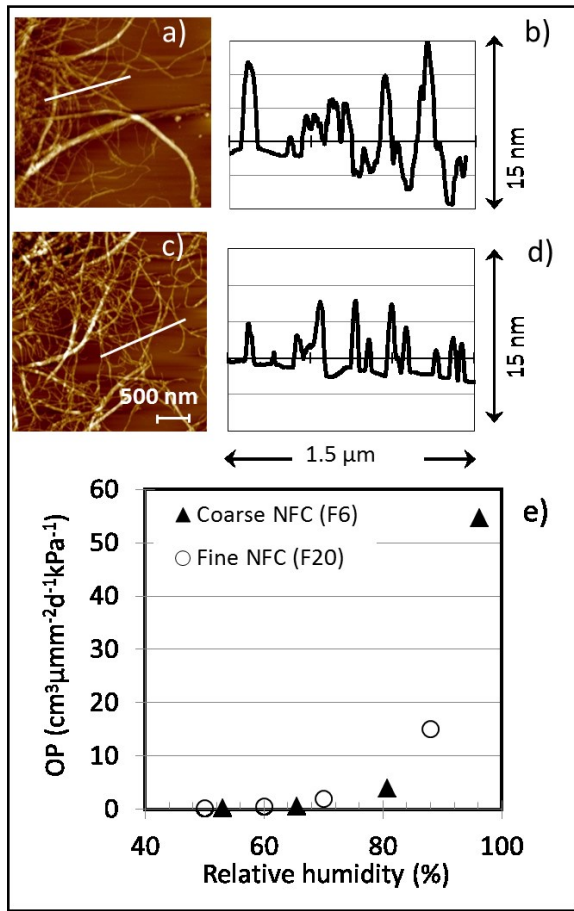


Figure 3. Comparison between coarse NFC and fine NFC. The coarse NFC corresponds to 6 passes and fine NFC to 20 passes through the Fluidizer. In a) and c) $9 \mu\text{m}^2$ AFM height images of diluted fibril dispersions dried on clean mica sheets are shown for F6 and F20 NFC samples. The corresponding $1.5 \mu\text{m}$ line scans are shown in b) and d). The oxygen permeation (OP) as a function of relative humidity for the two different NFC grades is shown in e). Both films were hot pressed 2 h.

The effect of hot pressing time on barrier properties was evaluated for the F6 sample (Figure 4). The measurements shown in the figures are representative values and some variation in parallel measurements was observed. Thus the difference between 0.5 h and 1 h samples are within the error range. However, the 2 h pressed sample clearly differs from these, having a lower oxygen transmission rate at elevated humidity than the samples pressed for shorter times. The OP for 2 h hot pressed NFC film is below $0.2 \text{ cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$ at 53 % RH and even at 96 % RH the OP is $55 \text{ cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$. From these results we can conclude that all the films prepared had very good oxygen barrier properties

at humidity below 70 % as compared to previously published results for NFC films and other biopolymer or polymer films.⁶ The high degree of crystallinity of the fibrils (60 %, see Supplementary Information) prevents oxygen transmission through a fibril and close packing of the fibrils during film formation reduces the free volume and thus prevents the transmission of oxygen through the film. The high surface polarity of nanosized fibrils results in enhanced fibril-to-fibril attraction at low humidity. The fibrils are strongly bound to each other by hydrogen bonds and van der Waals attraction and the movement of fibrils is efficiently restricted, thus preventing the oxygen permeation. Typically the barrier properties of biopolymers are very sensitive to moisture variations. Water enters the polymer and breaks the hydrogen bonds that hold the chains together. At high humidity conditions, the nanocellulose film swells, thus allowing permeation to increase.

Our results have significant practical relevance since most applications require the material to retain its barrier properties in a large humidity range. Nevertheless, most OP values reported in literature are for 0% RH and are thus difficult to compare to the results presented here. As comparison we note that oxygen permeability of $3.5\text{-}5^{18}$ and $0.85\text{ cm}^3\mu\text{m m}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ ¹⁹ have been reported at 50 % RH for unmodified NFC and carboxymethylated NFC (MFC) respectively. Using a film formation approach that, similar to the method presented here, involved elevated heat and pressure Liu et al¹⁰ reported OP as low as $0.47\text{ cm}^3\mu\text{m m}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ at 50 % for unmodified NFC but the value increased to $175\text{ cm}^3\mu\text{m m}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ at 95 % relative humidity showing the sensitivity of the film for increase in humidity. In a recent study, a OP value of $45\text{ cm}^3\mu\text{m m}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ was reported for NFC film at 82 % RH.²⁴ NFC films are in most cases superior in respect to strength and oxygen barrier properties compared to other biodegradable or synthetic films.¹⁹ Only the flexibility is slightly low. For example the OP of the often used barrier plastic ethylene vinyl alcohol is $0.01\text{-}0.1\text{ cm}^3\mu\text{m m}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ at dry conditions¹ and for poly(lactic acid) around 200.²⁵ It has been argued that carboxymethylation prior to fibrillation gives improved oxygen barrier properties because thin, well dispersed fibrils are easier to obtain and thus the film is denser.¹⁹ While excess of carboxylic groups indeed facilitates fibrillation, and thin fibrils are

obtained both by carboxymethylation³ or TEMPO mediated oxidation², these films are more sensitive to water and increased humidity. Fukuzumi et al reported that OP increases exponentially with humidity for films made from TEMPO oxidized nanofibrils.²⁶ We did not find clear effect of the fibril size on the barrier properties of the films (Figure 3), provided most of the fibrils are nanosized. On the contrary, the properties of unmodified native NFC films are sufficient for many applications and modification of the NFC prior to film formation may not only increase the cost of the NFC but also deteriorate the properties of the film. The reason for this being that the modifications may hinder the hydrogen bonding ability of the fibrils, thus introducing pores, and leading to decreased barrier properties, as was seen for highly acetylated⁸ and lignin containing⁷ NFC.

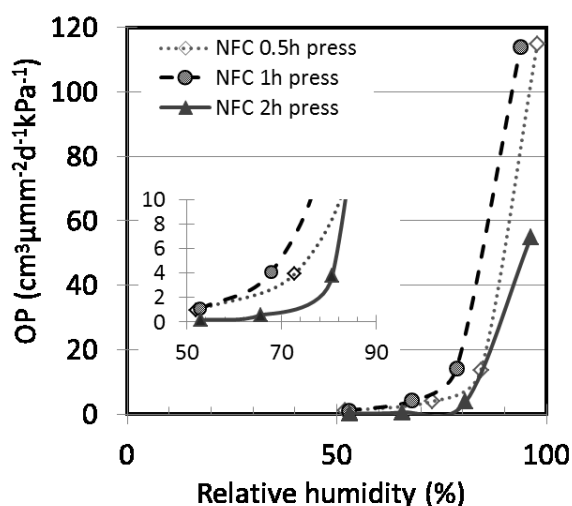


Figure 4. OP as a function of relative humidity for NFC films after varying pressing time. To emphasize the differences between the samples a close-up of OP below $10 \text{ cm}^3\mu\text{mm}^{-2}\text{d}^{-1}\text{kPa}^{-1}$ is shown in the inset. The lines are only guides for the eye.

Robustness of the NFC film

The strength and oxygen barrier properties reported above already indicate that the films are strong and dense. The density of the films was estimated from mass/volume from the samples used for water absorption testing and it was about 1250 kg/m^3 , but the standard deviation (100 kg/m^3) between samples pressed the same time was higher than the difference between samples. Nevertheless, the values are in

accordance with literature values.⁵ The robustness and resistance to solvents was further tested by soaking the film in various solvents. Chemical modification of NFC prior to film formation is often used to increase the compatibility to organic matrix,²⁷ however, these modifications interfere with the strong self-association tendency of NFC and may lead to a weaker and more porous film. Henriksson et al have shown that nanopaper made from less polar solvent is more porous and consequently weaker.⁵ To retain the advantageous properties of the NFC film it would be beneficial to conduct chemical modification on the film surface and in this manner improve barrier properties or induce reactivity. Water, methanol, and acetone were chosen as cellulose compatible solvents and toluene as a common nonpolar solvent. Surprisingly enough, no visible change in the films was detected after 18 h in solvent. The 0.5, 1 h and 2 h hot pressed films were all tested but in this time period they could all withstand the solvents and thus only the 2 h samples are shown in Figure 5. Attempts to systematically determine how long the films could withstand the solvents were not made, since most treatments of interest can be done in a few hours. However, samples have been stored for weeks without visible changes. The films were less transparent after re-drying (Figure 5b) indicating some swelling in the solvent as will be discussed later. Nevertheless, the surface topography was similar as prior to solvent treatment (Figure 5c). The strength of 2 h pressed wet films was measured to illustrate the robustness of the film. (Figure 5d) Only water was tested as solvent, since from an environmental point of view that is the most desired solvent to use in further applications. For comparison the wet strength of standard copy paper is also shown. Without the use of wet strength additives the strength in wet state is about 3-10 % of the dry strength.²⁸ For the copy paper used here the wet strength (1.8 ± 0.3 MPa) was 4 % of the dry strength (50 MPa). The NFC film retained more than 10 % of its original strength.

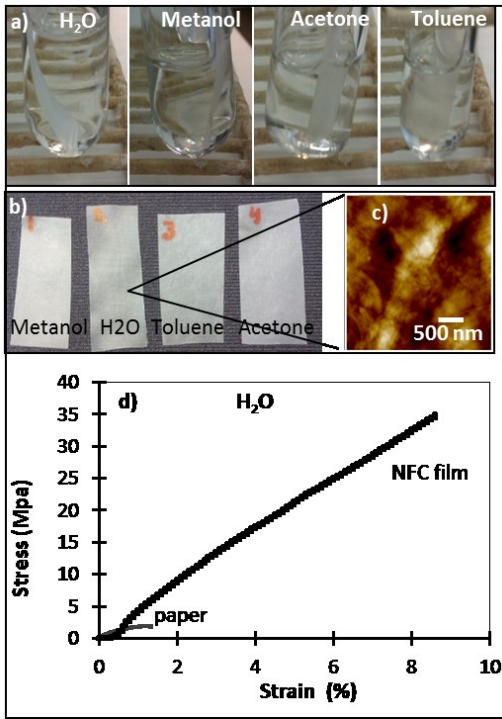


Figure 5. a) 2h pressed F6 films after 18h of soaking in various solvents, b) the corresponding re-dried films and c) a 9 μm^2 AFM height image showing that no noticeable change in the surface has occurred during solvent soaking. d) Wet strength of 2 h pressed films after 1 h soaking in water.

The extreme resistance to solvents, even to water, is a very advantageous property of the NFC films and opens up many application possibilities. For example a normal pulp sheet interacts strongly with water through hydrogen bonds and becomes very weak after soaking in water and may even decompose into individual fibers. The NFC films on the other hand remained robust. Thus efforts were made to understand the mechanism behind this property.

One possible explanation is that the combination of heat and load applied to the film induces additional bonding between fibrils, hindering solvent penetration into the film. Drying of cellulose is known to induce irreversible agglomeration decreasing the swelling ability of dried pulp as compared to never dried pulp. This phenomenon is called hornification and has been suggested to be due to formation of additional hydrogen bonds in the amorphous regions of cellulose.^{29, 30} The aspect of hornification of NFC gel upon drying has recently been discussed.³¹ The effect of elevated temperature

and pressing on the strength properties of normal pulp sheets made from macroscopic cellulose fibres has also been investigated. The most pronounced effects are found on lignin containing pulp.³¹ In contrast, no significant effect on dry sheet properties was found for pulp containing only cellulose and hemicellulose, which is most comparable to the NFC used in this study. However, interestingly enough a clear increase in wet-strength properties was found.³² The phenomenon was explained by a decrease in the moisture content of the press-dried sheets as compared to wet pressed sheets. It was speculated that this could be due to covalent cross-linkages (only applicable to pulp containing lignin) or irreversible hydrogen bonding. Due to the substantially larger specific surface area of NFC compared to the macroscopic fibers studied by Seth et al. the effect observed here is even stronger and a very strong and resistant film is formed. In Figure 6 the effect of the hot-pressing on film structure is shown. Clearly the film becomes very dense due to the pressing, supporting that indeed the enhanced properties are due to a decrease of the film porosity which restricts the solvent diffusion through the film. Nevertheless, the crystallinity does not change (Supporting Information), due to the treatment. Our previous investigations have shown that the media affects the surface chemistry of cellulose³¹ and Rodinova et al.⁸ recently also showed the effect of surface hydroxyl group passivation on water vapor transmission, thus confirming our hypothesis. Hence, we cannot rule out the possibility that in addition to the densification of the film, the hot pressing also affects the hydroxyl groups at the surface further restricting solvent penetration.

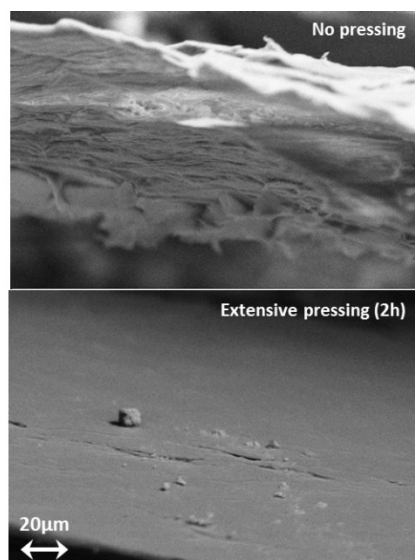


Figure 6. SEM images of the cross section of the films. The upper image shows the freely dried film and the lower image NFC film after 2h in hot press.

Systematic solvent absorption tests were conducted to quantify the interaction with solvent. In Figure 7 the water uptake is shown for films after varying pressing time. All films absorb substantial amounts of water, their weight increases by several hundred percent. Hot pressing decreases the water absorption, but the difference between samples pressed 1 h or 2 h is not significant. This correlates well with barrier and strength properties, were these two samples were comparable (Figures 2, 4 and Table 1). The thickness of the films increased correspondingly and the increase was $160\pm 5\%$ for un-pressed film, $110\pm 5\%$ for 0.5 h, $100\pm 8\%$ for 1h and $110\pm 10\%$ for 2 h pressed film. Regardless of the large scatter in results there is still a clear difference between pressed and un-pressed samples. Similar experiments were also performed for acetone and toluene (Supplementary data). The trends are similar, the 1 and 2 h pressed films absorbed less solvent than the un-pressed film. As expected the mass increase was not as high for these solvents as for water. After 18 h in toluene the increase for 2 h pressed sample was only $\sim 80\text{ wt-}\%$ as compared to $\sim 190\text{ wt-}\%$ in water (Table S1, Supporting Information).

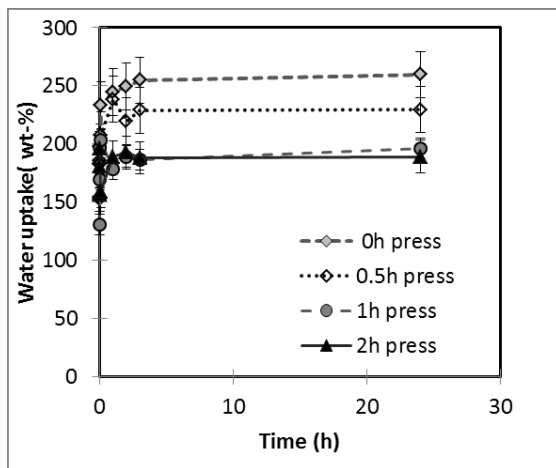


Figure 7. Effect of hot pressing on water uptake for NFC films (F6). Standard deviation for 3 measurements is indicated.

Densification and possibly partial hornification during hot pressing may explain the difference between hot pressed and un-pressed samples, but clearly most of the film still is accessible to solvent. For comparison we note that the water uptake for a standard copy paper is in the same range as the hot pressed sample (Supplementary data). We conclude that although the relatively high degree of crystallinity (60 %), and density of the film can explain the good barrier properties, the robustness in solvent must be due to the very high contact area between fibrils in the entangled network of nanoscaled fibrils.

Effect of surface treatment on film properties

Although the unmodified NFC showed good oxygen barrier properties and excellent resistance to solvents we explored the possibility to enhance the barrier properties even further, especially at high humidity. Our goal was to employ a simple method that would not deteriorate the properties of the film. Thus we surface-coated the film using a commercial Parafin wax. The strength of the film stayed unchanged after the wax treatment (Table 1), however, both oxygen transmission and water vapor transmission rate decreased considerably (Figure 8). The values are comparable and at high humidities even lower than what has been obtained for NFC nanoclay composites.^{10, 33,34} To facilitate comparison with OP values in literature the results were normalized with the film thickness as in Figure 4. However,

we recognize that this is not strictly correct. The wax treated film has a tree-layered structure where the dense NFC film is the main oxygen barrier while the role of the wax layers is to protect the NFC from the destructive effect of moisture. Thus one could argue that the oxygen transmission rate should be normalized with the pure NFC film thickness. Nevertheless, since it is experimentally challenging to distinguish between the layers and they are partly mixed the results are normalized with the whole film thickness, which leads to slightly higher OP values.

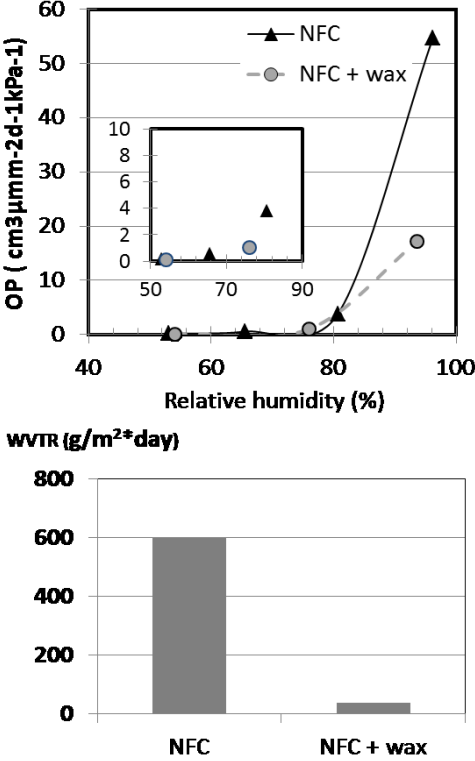


Figure 8. Upper graph: effect of wax treatment on oxygen transmission rate (OP) as a function of relative humidity for NFC film (F6). The lines are only guides for the eyes. In the insert the very low oxygen permeability region is enlarged. Lower graph: WVTR for unmodified and wax treated films.

Wax treatment decreased the OP of NFC film by 70 % at 96 % RH. The water vapor transfer ratio also decreased substantially due to the wax treatment from 600 to 40 $\text{g/m}^2 \cdot \text{day}$. Wax is highly nonpolar and thus a very good barrier to polar permeants such as water. The amount of wax was about 10 wt-% and it formed a hydrophobic surface layer hindering water vapor to penetrate through the film (Figure

9). Possibly the wax also closed some pores in the film, however due to the very dense structure of the unmodified film the closing of the surface is the main reason for the enhanced barrier properties. The water contact angle increased from 40 to 110° due to the wax surface treatment. Both untreated and wax treated films were resistant to olive oil, *i.e.* no stains were visible on the blank blotting paper after testing.

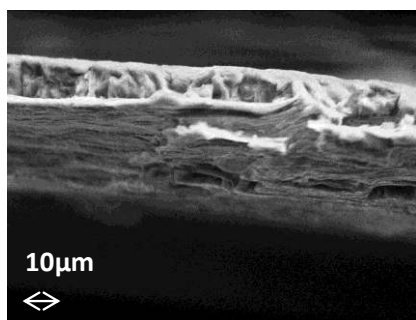


Figure 9. SEM image of cross section of NFC film coated with wax.

The simple wax coating demonstrated here was efficiently enhancing the water vapor barrier properties of the NFC films without loss in film strength. However, the resistance to solvents facilitates plenty of other possibilities for topological modifications and the possible functionalities are not restricted to hydrophobicity.

Conclusion

A method to produce strong, dense and robust biofilms from nanofibrillated cellulose was described. Drying of the films using elevated pressure in combination with heat resulted in a film with unforeseen resistance to solvents. The films could be soaked in both polar and nonpolar solvents for more than 18 h. Although the films swelled considerably in the solvents, the wet strength of the films was high and they were thus easy to handle also in wet state. The wet strength of the films allows for further topological surface functionalization which is beneficial in several applications. Due to their very dense structure, the films, in addition to the high resistance to solvents, also showed excellent barrier properties against oxygen and grease. At relative humidity below 65 % oxygen transmission rate of the pure and

unmodified NFC film was below $0.6 \text{ cm}^3\mu\text{mm}^{-2}\text{d}^{-1}\text{kPa}^{-1}$. By further surface modification, in this case a wax layer, the resistance to water vapor or oxygen at very high humidity could be increased without deteriorating the strength of the film. The film, made from fully renewable resources without chemical modification, can be used as generic platform for functional materials.

The authors declare no competing financial interest

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Supporting Information Available:

Supporting information includes fits of the theoretical intensity of crystalline cellulose to the experimental diffraction pattern from the wide angle x-ray scattering measurements (WAXS, Figure S1), a table of amount of solvent uptake for NFC films (Table S2) and comparison of water uptake for a standard copy paper and NFC film (Figure S3). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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