

Supporting Information

Direct Interfacial Modification of Nanocellulose Films for Thermoresponsive Membrane Templates

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Materials

Never dried bleached softwood pulp obtained from a pulp mill in Finland was 2,2,6,6-tetramethylpiperidine (TEMPO) oxidized according to a procedure by Saito et al.¹ The charge of the oxidized pulp, measured by a standard conductometric titration method (SCAN-CM 65:02, 2002), was found to be approximately 1.13 mmol g⁻¹. Oxidized pulp was fibrillated using a high pressure fluidizer Microfluidics M-110EH-30 (Microfluidics Int., USA) equipped with two Z-type chambers. The chambers had diameters of 400 µm and 100 µm and the pulp was passed through the fluidizer once at 1850 bar operating pressure. The final consistency of the TEMPO-CNF was approximately 2 wt.-%. Poly(vinyl alcohol) (PVA) with degree of hydrolysis of 98 % (Mowiol 56-98, M_w 195 000 g/mol, DP 4300), amine-terminated poly(NIPAM) (M_n 5500) and all other reagents were purchased from Sigma-Aldrich. Ethanol (Aa grade, 99.5 % (w/v)) was purchased from Altia Corporation (Rajamäki, Finland). Deionized water was further purified using a Milli-Q system (Millipore Corporation, Molsheim, France, resistivity 18.2 MΩ) and was used in all experiments unless otherwise stated.

Preparation of nanocellulose films

A 5 wt.-% solution of PVA in water was prepared by dissolving PVA in water at 95 °C during 4 hours under constant stirring. TEMPO- CNF suspension and PVA solution were diluted to 0.3 wt.-% and mixed together thoroughly in 9:1 weight ratio. This casting dope was degassed under vacuum and cast onto poly(styrene) petri dishes with areas of approximately 5000 mm². Petri dishes filled with casting dope were left to dry at 23 °C and 50 % relative humidity for at least 5 days to form TEMPO-CNF-PVA films.

Surface modification of nanocellulose films

Both sides of the TEMPO-CNF-PVA film were cleaned and activated using a UV/ozone cleaning procedure². The treatment was performed using a UV/ozone ProCleaner (Bioforce Nanosciences) and the treatment time for each side was 10 min. The distance between the sample and the radiation source was 2 cm.

Dry TEMPO-CNF-PVA films were subjected to esterification reaction and following poly(NIPAM) attachment. Films were submerged in ethanol with a catalytic amount of concentrated H₂SO₄ (0.145 ml 98 % H₂SO₄/100 ml ethanol) and the reaction was continued at room temperature under mild stirring for 24 hours. Films were washed in three steps with ethanol and finally they were dried in air and activated again using the UV/ozone cleaning protocol.

1 g of amine-terminated poly(NIPAM) was dissolved in 100 ml of ethanol or ethanol-water mixture with 3:1 volume ratio at room temperature. Esterified films were submerged in the solution and the reactions were continued for 24 hours in room temperature or at 50 °C. Films were washed in three steps using ethanol to remove unreacted poly(NIPAM).

Water permeance of TEMPO-CNF-PVA films

The unmodified and modified TEMPO-CNF-PVA films' permeance was determined in a Sterlitech HP4750 dead-end stirred cell (Sterlitech, Kent, USA) with deionized water. Discs of nanopapers with a diameter of 49 mm were cut, soaked in deionized water for at least three days to ensure equilibration and placed on a sintered steel plate. Water was forced through the nanopapers using nitrogen at a head pressure of 0.2 MPa. The water permeance for the active filtration area (1460 mm²) was obtained by measuring the volume permeated per unit area per unit time per unit pressure (L m⁻² h⁻¹ MPa⁻¹).

To determine the temperature dependence of the water permeance for each film type, the permeance was tested at various temperatures as shown in Figure S1. For this, the whole dead-end cell set-up was placed in a water bath. The temperature of the water bath was controlled with a magnetic stirrer connected to a temperature controller (RCT classic IKAMAG® safety control with VT-5 contact thermometer, VWR, UK). Five different temperatures were set (20, 30, 40, 50, 60 °C) and the permeance at each temperature was collected until it did not change more than one % per hour (Figure S1). The resulting permeances for the various temperatures were normalized to the permeance at 20 °C. For data points below and above 40 °C, respectively, a linear regression was performed and the slope was determined.

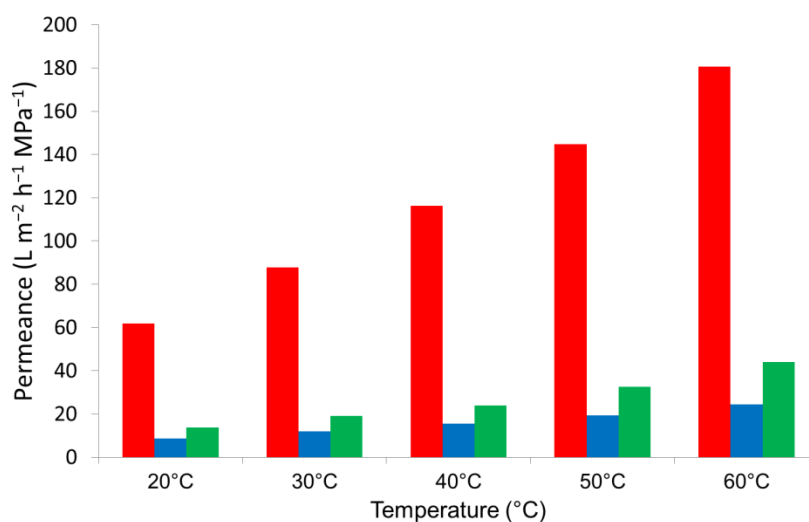


Figure S1. Permeance of water through membranes as a function of temperature for unmodified TEMPO-CNF-PVA film (red), esterified film (blue) and poly(NIPAM) modified film (green).

Fourier transform infrared spectroscopy (FT-IR)

A Nicolet iS50 FT-IR spectrometer (ThermoScientific, USA) equipped with a built-in diamond iS50 ATR was used to characterize the chemical structure of the modified films. The spectra were

scanned within the range of 350 to 4000 cm^{-1} with a total of 32 scans with resolution 4 cm^{-1} . Esterified films were subjected to counterion exchange at (pH 10) and to saponification (pH 13)³.

Solid state nuclear magnetic resonance (^{13}C NMR)

The ^{13}C cross polarization (CP) magic angle spinning (MAS) NMR measurements were performed using an Agilent 600 NMR spectrometer with magnetic flux density of 14.1 T, equipped with a 3.2 mm triple-resonance MAS NMR probe operating at double resonance mode. Dry film samples were cut into small pieces before packing them into MAS rotors. In all experiments the MAS rate was set to 10 kHz. For all samples 30,000 transients were accumulated with a 3.0 s delay between successive scans. Cross polarization contact time was 1.0 ms, and a 70 kHz proton decoupling (spinal-64) was used. The chemical shifts were externally referenced via adamantane by setting the low field signal to 38.48 ppm. Rf-field strengths for cross polarization and decoupling were calibrated using α -glycine. All spectra were recorded at ambient temperature. Processing of the spectra was carried out with Bruker TopSpin 3.5 software.

Contact angle

The sessile drop method was employed for determination of water contact angles with a video camera based fully computer-controlled contact angle meter (CAM 200 from KSV Instruments Ltd., Finland). The measurements were performed at room temperature using deionized Milli-Q water. At least five separate measurements were performed for each sample at room temperature and the measurements were performed within 15 minutes of the UV/O₃ treatment².

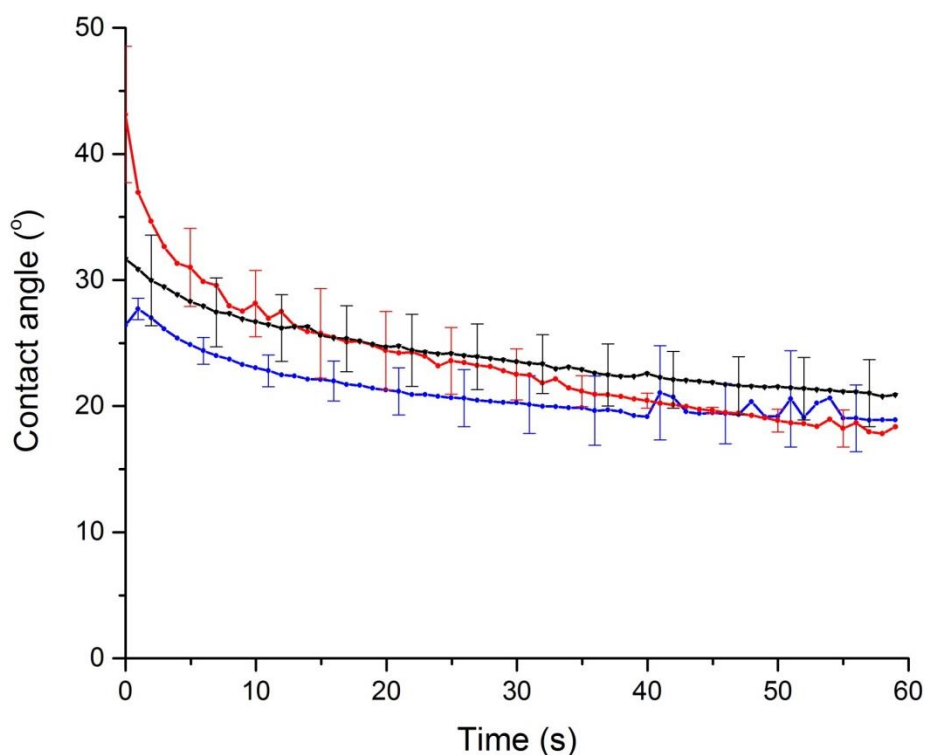


Figure S2. Water contact angle values as a function of time for the unmodified TEMPO CNF-PVA film (black curve), esterified film (blue curve) and poly(NIPAM) modified film (red curve).

Water contact angles presented in Figure S2 show that the surfaces of TEMPO CNF-PVA film, esterified film and poly(NIPAM) modified film are very similar and clearly hydrophilic at room temperature. Despite of the modification procedures, the equilibrium contact angles of the membrane templates are $\sim 30^\circ$. Fukuzumi et al.⁴ reported water contact angle values of $\sim 30^\circ$ for TEMPO oxidized CNF, which is in good accordance with the contact angle values of the TEMPO

CNF-PVA films. The addition of PVA (10 wt-%) did not appear to generate surfaces of higher hydrophobicity although contact angles as high as 79° have been reported for pure PVA.⁵ The contact angle of pristine poly(NIPAM) ranges from approximately 30° to 90° depending on the temperature⁶. Here the poly(NIPAM) modified films display high hydrophilicity at room temperature giving the static water contact angle values $<30^{\circ}$ which is a value well supported by the literature.

X-ray photoelectron spectroscopy (XPS)

Analysis of the elemental composition on the surface of the film samples was studied using X-Ray photoelectron spectroscopy (XPS). Measurements were performed with a Kratos Analytical AXIS Ultra electron spectrometer with monochromatic Al K α irradiation at 100 W and effective charge neutralization with slow thermal electrons. The experimental set-up including acquisition parameters is reported in detail by Johansson et al.⁷ Low resolution survey spectra and high resolution elemental spectra of carbon (C 1s) and oxygen (O 1s) were collected from the film samples at least from three different areas. The reported elemental concentrations are average values. The XPS analysis area was 0.2 mm \times 0.8 mm in this study and the analysis depth is less than 10 nm. Ash-free 100 % cellulose filter paper was analyzed and used as a reference with each measurement batch. The surface coverage values were calculated using nitrogen as the elemental marker for poly(NIPAM). Based on the molecular formula of the repeating unit of poly(NIPAM), the ratio of nitrogen to the total number of atoms in NIPAM visible in XPS (carbon, nitrogen, oxygen) was assumed to be 1:8.

Figure S3 shows the survey spectra of the TEMPO-CNF-PVA film in unmodified, esterified and poly(NIPAM) modified stage with high resolution spectra for nitrogen, sulfur and carbon. The low resolution wide spectrum and high resolution spectrum for carbon revealed a typical spectrum of TEMPO-CNF (black line)⁸. Wide spectrum for esterified film (blue line) does not reveal any

differences compared to the reference TEMPO-CNF-PVA film spectrum (black line). In the high-resolution carbon signal the main feature is the “cellulose signature” with peaks for C-O, C-C and O-C-O bonded carbons. Successful esterification can be seen as an increase in the carbonyl (O-C=O) component in the high resolution spectrum after esterification⁹ (blue line). As suggested by the presence of N 1s and S 2p peaks arising after poly(NIPAM) modification (red line), the attachment of poly(NIPAM) has successfully occurred on the surface of the film.

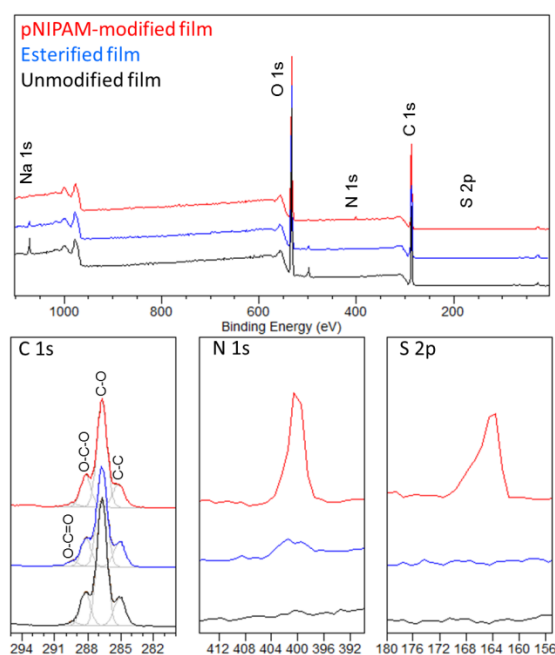


Figure S3. Low resolution XPS survey spectra (top) of unmodified film (black curve), esterified film (blue curve) and poly(NIPAM) modified film (red curve) showing peaks due to emission of Na 1s, O 1s, N 1s, C 1s and S 2p. Regional spectra (bottom) showing C 1s, N 1s and S 2p regions.

Atomic Force Microscopy (AFM)

Surface morphology and roughness of the films was studied by atomic force microscopy (AFM). Imaging was carried out using Nanoscope IIIa Multimode scanning probe (Digital Instruments Inc., Santa Barbara, CA, USA) in tapping mode. Dry films were imaged in air using aluminum coated

silicon cantilevers (Bruker Corporation, Billerica, MA, USA) with nominal resonance frequencies of 70 kHz. Image processing was performed using Nanoscope Analysis (Version 1.40, Bruker, Billerica, MA, USA). Root mean square roughness values (R_a) were extracted from topographic $1\ \mu\text{m} \times 1\ \mu\text{m}$ AFM images. No other image processing other than flattening was performed. Three areas of each sample were scanned and the average roughness values are reported in Figure 1e.

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