

SUPPORTING INFORMATION

Topochemical acetylation of cellulose nanopaper structures for biocomposites - mechanisms for reduced water vapour sorption

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S1. CHARACTERIZATION OF THE ACETYLATED NANOPAPERS

i) Solid-state CP/MAS ¹³C NMR

Bulk degree of substitution (bulk-DS) from NMR: Calculation of the DS values was made by spectral integration. The integrated methyl signal intensity (about 30 to 5 ppm) was divided by the integrated signal intensity of the entire cellulose region

(about 120 to 40 ppm). The ratio of these two intensities was taken as an estimate of the average bulk-DS. The meaning of this parameter is the degree of substitution that would result if all hydroxyl groups were initially accessible to the acetylating reagent.

SSA from NMR: Solid-state CP/MAS ^{13}C NMR can be employed in the assessment of the SSA of cellulosic samples.¹ Therefore, the SSA of control CPD-dried NFC and BC nanopapers was also estimated based on the respective NMR spectra. For this purpose, samples were wetted with deionized water to 40-60% water content and packed uniformly in a zirconium oxide rotor. Recording spectra on wet rather than dry samples gives a higher apparent resolution.² Computations of SSA are based on integrated signal intensities as obtained from the spectral fitting.³ Cellulose I SSA was calculated from the lateral fibril aggregate dimensions by assigning a density of 1500 kg/m^3 to cellulose I.¹

ii) XRD

Table S1. Crystallite dimensions, C_1 and C_2 , and crystallinity index (CrI) of the control and acetylated nanopapers, as estimated from XRD data.

Sample	C_1 (nm)	C_2 (nm)	CrI (%)
NFCcpd-Ref	2.5	3.8	64.9
NFCcpd-Ac1	2.5	4.0	63.0
NFCcpd-Ac2	2.5	3.9	57.8
NFCfd-Ref	2.8	3.2	55.4
NFCfd-Ac1	2.6	3.6	57.0

NFCfd-Ac2	2.8	3.2	53.2
NFCd-Ref	2.6	3.2	58.6
NFCd-Ac1	2.5	3.3	59.6
NFCd-Ac2	2.7	3.2	59.5
BCcpd-Ref	5.9	7.5	76.6
BCcpd-Ac1	5.9	7.3	80.2
BCfd-Ref	5.2	5.9	70.2
BCfd-Ac1	5.1	5.9	67.3

iii) Estimation of the surface-DS

First, the number of total hydroxyl groups per gram of cellulose (number of total OH/g) was calculated from equation S1:

Equation S1. Number of total OH/g = $\left(\frac{N_A}{M_{(AGU)}}\right) \times n_{OH}$

where N_A stands for the Avogadro's constant (number of constituent particles per mole of a given substance, $N_A = 6.022 \times 10^{23}$), $M_{(AGU)}$ for the molecular weight of an anhydroglucose unit (AGU, Mw=162 g/mol) and n_{OH} for the number of hydroxyl groups per AGU, which is 3.

Then, the number of surface/available hydroxyl groups per gram of cellulose (number of surface OH/g) was estimated on the basis of the BET SSA data, according to:

Equation S2. Number of surface OH/g = $\left(\frac{SSA}{A_{(AGU)}}\right) \times n_{OH}$

where SSA stands for the specific surface area of the nanopaper, $A_{(AGU)}$ for the area of an AGU (estimated to be $3.2 \times 10^{-19} \text{ m}^2$ according to cellulose I β unit cell parameters data determined by Nishiyama *et al.*⁴) and n_{OH} stands for the number of hydroxyl groups per AGU at the surface/available regions. Here, n_{OH} was assumed to be 3. This may be true for disordered cellulose regions, but is twice the number of available hydroxyls at the surface of crystalline regions.

The surface-to-bulk ratio was then calculated according to:

Equation S3.
$$\text{OH ratio} = \frac{\text{Number of surface OH/g}}{\text{Number of total OH/g}}$$

Finally, the surface-DS values can be calculated from:

Equation S4.
$$\text{Surface-DS} = \frac{\text{bulk-DS}}{\text{OH ratio}}$$

where bulk-DS stands for the bulk degree of acetylation obtained from the solid-state ¹³C-NMR data.

iv) Reduction in moisture sorption upon acetylation of the nanocelluloses

Table S2. Fraction of moisture content in the acetylated samples compared to the precursor samples.

Sorption of acetylated sample/Sorption of precursor								
RH	NFCcpd-Ac1	NFCcpd-Ac2	NFCfd-Ac1	NFCfd-Ac2	NFCd-Ac1	NFCd-Ac2	BCcpd-Ac1	BCfd-Ac1
53%	0.91	0.43	0.95	0.58	0.83	0.57	0.89	0.20
84%	0.96	0.68	0.98	0.68	0.84	0.81	0.88	0.55
100%	0.89	0.74	0.82	0.74	0.98	0.91	0.93	0.91
Liquid water	0.72	0.63	0.86	0.68	0.83	0.78	0.85	0.63

S2. DEMONSTRATION 1: POST-TREATMENT OF CONTROL AND ACETYLATED CPD-DRIED NFC NANOPAPERS

Table S3. BET SSA and porosity of the non- and post-treated NFCcpd-Ac2 samples.

Sample	Post-treatment	BET SSA (m ² /g)	Porosity (%)
NFCcpd-Ac2	—	173.29±6.30	85.8±2.4
NFCcpd-Ac2-p	Pressing in dry-state	104.21±4.20	75.3±0.3
NFCcpd-Ac2-wp	Pressing in wet-state	0.18±0.01	33.1±3.2

Table S4. Moisture sorption at different RH and water uptake of the non- and post-treated NFCcpd-Ac2 samples.

RH	Sorption (%)		
	NFCcpd-Ac2	NFCcpd-Ac2-p	NFCcpd-Ac2-wp
53%	2.06	0.81	0
84%	6.84	6.02	5.40
100%	51.85	49.06	29.81
Liquid water	444	423	244

Table S5. Fraction of moisture content in the non- and post-treated NFCcpd-Ac2 samples compared to the precursor sample.

RH	Sorption of acetylated sample/Sorption of precursor		
	NFCcpd-Ac2	NFCcpd-Ac2-p	NFCcpd-Ac2-wp
53%	0.43	0.17	0
84%	0.68	0.60	0.53
100%	0.74	0.70	0.42
Liquid water	0.64	0.60	0.35

S3. DEMONSTRATION 2: PREPARATION OF NANOCELLULOSE-BASED COMPOSITES

Control and acetylated CPD-dried NFC nanopapers (NFCcpd-Ref and NFCcpd-Ac2) were impregnated with Bisphenol A ethoxylate diacrylate, an acrylic resin monomer, previously mixed with 1 wt% of a photo-initiator (2,2-dimethoxy-2-phenylacetophenone, DMAP), under vacuum during 24 h. After impregnation, the composites were cured with a 365 nm UV-lamp.

Nanocomposites were also prepared by impregnation of both nanopapers with 2,2-Bis(4-glycidyloxyphenyl)propane, an epoxy resin monomer, previously mixed with 65 wt% of a curing agent, Jeffamine D-400, under vacuum during 24 h.

After impregnation, the nanocomposites were cured at 80 °C for 2 h, and, finally, post-cured at 105 °C for 3 h.

In all cases, the cellulose content of the nanocomposites was *ca.* 20 wt%.

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