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The structural amphiphilicity of cellulose nanocrystals characterized from their cohesion parameters

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Abstract

Cellulose nanocrystals (CNCs), usually considered as isotropically polar nanoparticles, are sheet-like crystalline assemblies of cellulose chains. Here, we link the anisotropy of the CNC structure to an amphiphilic behavior in suspension. The Hansen solubility parameters (HSP: δ ; ρ ; H) of wood-based H_2SO_4 -hydrolyzed CNCs were measured from sedimentation tests in a wide set of 59 solvents and binary mixtures. Two sets of cohesion parameters corresponding to a polar surface (18.1; 20.4; 15.3) (0.5; 0.5; 0.4) $\text{MPa}^{1/2}$ and to a mildly non-polar one (17.4; 4.8; 6.5) (0.3; 0.5; 0.6) $\text{MPa}^{1/2}$ were determined, with respective solubility radii of 7.8 and 2.1 $\text{MPa}^{1/2}$. The polar sphere is thought to correspond to the (110)&(1 $\bar{1}$ 0) surfaces of cellulose I nanocrystals, while the smaller non-polar sphere is coherent with the exposure of (200) surfaces. The HSP graph provides new insights on the amphiphilic nature of CNCs and **a mapping of their chemical affinity for solvents and polymer matrices.**

Keywords:

cellulose nanocrystals, surface properties, structure-property relationships, **chemical affinity**, amphiphilicity, Hansen solubility parameters

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1. Introduction

D-glucopyranose polymerization produces, through a dehydration, polysaccharides such as starch, glycogen, dextran, and cellulose (Dufresne, 2017; French, 2017). In (1,4)-linked macromolecules, anhydroglucose rings are locked in a chair conformation where all their hydrophilic hydroxyl groups are in equatorial position while all their more hydrophobic C-H bonds are axial. For α -(1,4)-linked polysaccharides, such as dextrans, it results in an apolar behavior in solution (Dufresne, 2017), a feature famously exploited in cyclodextrins whose structure forms a cavity rich in C-H bonds that may be used to encapsulate hydrophobic chemicals (Marques, 2010), including for delivery in living organisms (Chaturvedi et al., 2011).

Although being insoluble in water, amorphous cellulose, α -(1,4)-linked polymer of anhydroglucopyranose (Fig. 1.a&b), does not display such a marked apolarity in solution (Medronho et al., 2012; Dufresne, 2017). Its structural anisotropy, and its resulting amphiphilicity (Medronho et al., 2012), are however reflected in the crystalline networks cellulose chains form in living organisms such as plants, fungi, algae, bacteria, or tunicates (Moon et al., 2011; Hamad, 2017). From the various allomorphs (Moon et al., 2011; Dufresne, 2017), cellulose I (Nishiyama et al., 2003) and II (Nishiyama et al., 2002) are the only ones that may be found naturally in land plants (Moon et al., 2011). They both reproduce on the nanocrystal level the anisotropy of their monomeric unit. Indeed, cellulose chains assemble in sheets, parallel to the equatorial planes of the anhydroglucose rings, which then stack up to form multilayer crystalline structures, crystallites (Fig. 1.c) (Jarvis, 2003; Li & Renneckar, 2011). Intra and intersheet cohesions are respectively insured by interchain OH-O hydrogen bonds and by weaker interchain CH-O and van der Waals interactions (Jarvis, 2003; Nishiyama, 2017). The formation of these van der Waals interactions is thought to be the initial step through which cellulose chains crystallize (Cousins & Brown, 1995).

Hydrolysing cellulosic feedstocks in acidic conditions, usually with sulfuric acid, digests their amorphous and non-cellulosic contents while mostly preserving their crystalline parts (Dufresne, 2017; Moon et al., 2011; Hamad, 2017). Under harsh enough conditions, the treatment yields highly crystalline cellulose-made particles, cellulose nanocrystals (CNCs). They are hypothesized to be made of several adjacent crystallites (Uhlig et al., 2016; Ding et al., 2012, 2014) assembled with a right-handed chirality (Usov et al., 2015). Introduction of sulfate half-ester groups at CNC surface during the

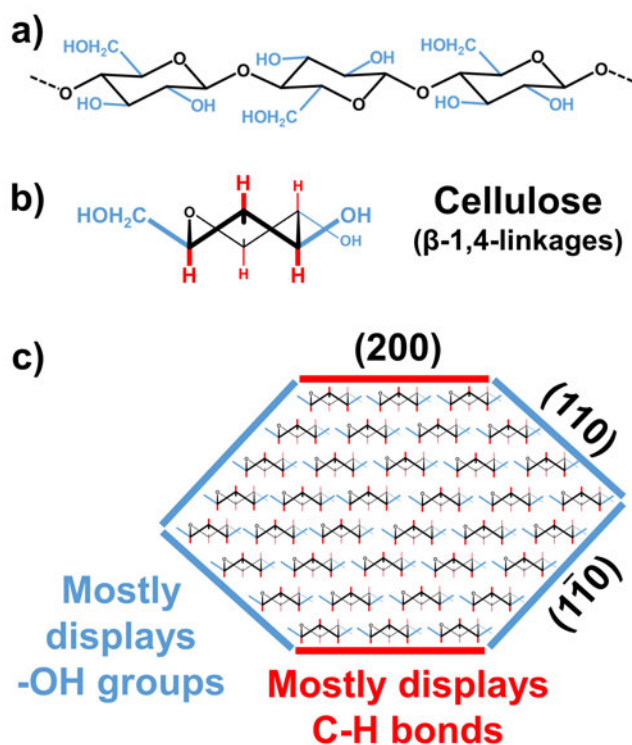


Figure 1: Anisotropy of cellulose. (a) Cellulose, a β -1,4-linked polymer of anhydroglucopyranose (French, 2017), has its monomeric units locked in a conformation where all their hydroxyl substituents (in blue) are in equatorial position while their C-H bonds (in red) are axial as exemplified in a Haworth projection (b). (c) The structure of cellulose I crystallite reflects this anisotropy as cellulose chains are arranged in sheets held together by OH-O hydrogen bonds, which then stack-up through the formation of CH-O H-bonds and van der Waals interactions (Jarvis, 2003; Li & Renneckar, 2011). Based on Ding and Himmel's model (Ding & Himmel, 2006), the resulting crystallite displays up to three kind of surfaces corresponding to the lattice planes (110), $(\bar{1}\bar{1}0)$, and (200) of its crystalline unit. The latter displays mostly C-H bonds, while the two former are rich in hydroxyl groups.

hydrolysis provides them with an electrostatic stabilization upon suspension in water and with interesting self-organization properties (Liu et al., 2011; Hamad, 2017).

CNCs, especially sulfated ones, are usually described as polar particles, which stems from the difficulty encountered to disperse them in non-polar solvents and polymer matrices (Hamad, 2017). Although arising from experimental observations, this description is at odd with the amphiphilic behavior that can be expected from CNC anisotropic structure. Analysis of wide

(WAXS) and small angle X-ray scattering (SAXS) (Elazzouzi-Hafraoui et al., 2008; Sèbe et al., 2012) as well as high resolution atomic force microscopy (AFM) (Ding et al., 2006; 2012; 2014) indeed suggests that up to three kinds of lateral surfaces are displayed by the nanocrystals extracted from cellulose I sources (Fig. 1.c), by far the most common allomorph in higher plants –wood included (Atalla & Vanderhart, 1999; Habibi et al., 2010). Within the crystalline unit, they correspond respectively to the lattice planes (110), (1 $\bar{1}$ 0), and (200) (Ding & Himmel, 2006; Brown, 1996). The latter, parallel to the sheets plane, displays mostly C-H bonds, while the two former intersect the plane of the sheets and thus display hydroxyl groups (Fig. 1.c). Molecular dynamic simulations suggests that (110) and (1 $\bar{1}$ 0) surfaces have similar hydrophilicity (Heiner et al., 1998; Matthews et al., 2006) and surface energies (Yamane et al., 2006), while (200) surfaces are expected to be more hydrophobic, with higher water contact angle (Mazeau & Rivet, 2008) and lower surface energies (Yamane et al., 2006) (Table 1).

Table 1: Cellulose nanocrystal surface properties according to the lattice plane displayed. τ is the total solubility parameter. δ , ρ , and μ are its decomposition in term of dispersive, polar, and hydrogen bonding components, respectively (Hansen, 2007). R_0 is the HSP radius.

Lattice plane		(110)	(1 $\bar{1}$ 0)	(200)
Surface energy ^a	mN m ⁻¹	155	155	92
Water contact angle ^b		43	-	95
τ	MPa ^{1/2}	31.3	1.4	19.2
δ	MPa ^{1/2}	18.1	0.5	17.4
ρ	MPa ^{1/2}	20.4	0.5	4.8
μ	MPa ^{1/2}	15.3	0.4	6.5
R_0	MPa ^{1/2}	7.8		2.1

^a Modeled values as calculated by Yamane et al. (2006).

^b Modeled values as calculated by Mazeau & Rivet (2008).

Chemically, a proof that CNCs display **hydroxyl groups rich surfaces – which would correspond to the (110) and (1 $\bar{1}$ 0) lattice planes–** may be provided easily by attempting to functionalize them (Eyley & Thielemans, 2014). (1 $\bar{1}$ 0) lattice planes have furthermore already been observed by atomic force microscopy on cellulose I samples (Kuutti et al., 1995). The detection of unreactive **C-H bonds rich surfaces –which would correspond to the (200) lattice plane–** is, however, harder to achieve. The main clue is that the display of (200) lattice planes by CNCs should result in a certain level of amphiphilic-

ity, as experimentally confirmed : stable suspensions of CNCs in chloroform have been reported (Yu & Qin, 2012; Yu et al., 2012). This mildly non-polar solvent may also form inclusions in cellulose I fibers (Wade & Creely, 1974). It is worth noting that not every work reports a good dispersion in chloroform (Yoo & Youngblood, 2016; Petersson et al., 2007) and it remains to be seen whether this divergence has to be attributed to differences in feedstock, hydrolysis conditions, or protocol of dispersion, such as the intensity of the ultrasonication for instance. Other hydrophobic interactions of cellulose include those with cellulases (Himmel et al., 2007; Mazeau & Rivet, 2008) and congo red (Mazeau & Wyszomirski, 2012; Conley et al., 2017b,a) whose aromatic parts are both thought to adsorb primarily on the (200) surfaces.

Although these preliminary results point toward a chemical influence of (200) surfaces for some CNC suspensions, thus conforming WAXS, SAXS, and AFM observations, none of them really isolate their potential contribution from the stronger influence of the (110) and (1 $\bar{1}$ 0) surfaces.

In this work, we apply a thermodynamic approach based on the Hansen solubility parameters (HSP) and on sedimentation tests using 59 solvents and binary mixtures, to isolate experimentally the influence of the hydrophobic (200) surfaces from the predominant one of the more hydrophilic (110) and (1 $\bar{1}$ 0) surfaces (as reported in Table 1). These investigations result into a mapping of CNC affinity for common solvents and polymers. The identification of an amphiphilic behavior for the nanocrystals establishes a direct link between their structure and their surface properties.

2. Materials and methods

2.1. Materials

CNCs, provided by Celluforce (Montreal, QC, Canada) as a spray-dried powder, were obtained from Kraft wood pulp by a sulfuric acid hydrolysis treatment followed by a neutralization with sodium hydroxide (NaOH). Previous work from our team on CNCs from the same batch demonstrated that these particles are in average 165 nm long and 13 nm wide with a sulfur content equivalent of 3.4 sulfate half ester (O SO₃H) per 100 anhydroglucose units (Beuguel et al., 2018b). The X-ray diffractogram is typical of I cellulose (Elazzouzi-Hafraoui et al., 2008; Sèbe et al., 2012) and the crystallinity index was found to be of 81 %.

To obtain the dimensions of the CNCs the following procedure was applied (Beuguel et al., 2018b). A drop of a sonicated water suspension of

105 CNCs, diluted at $10 \mu\text{g}_{\text{CNCs}} \text{ mL}_{\text{water}}^{-1}$, was deposited on a copper TEM grid
 106 covered by a 5 to 6 nm-thick layer of pure carbon. Average dimensions, with
 107 standard deviations in the range of 10 %, were obtained from measurements
 108 of over 100 particles performed on transmission electronic microscopy (TEM)
 109 micrographs obtained at 200 kV with a bright field imaging Jeol JEM 2100F
 110 (Beuguel et al., 2018b). The sulfur content was measured from X-Ray energy
 111 dispersive spectroscopy (EDX) analysis performed on the CNC spray-dried
 112 powder with a Tabletop Hitachi TM3030+ scanning electron microscope.
 113 Scanning of three samples on different locations, for a total of ten scans,
 114 yielded a sulfur over carbon (S/C) atomic ratio of 0.0057 with a standard
 115 deviation of 0.0005 (Beuguel et al., 2018b). The oxygen over carbon (O/C)
 116 atomic ratio was of 0.79 ± 0.02 , very close to the theoretical value of 0.83
 117 for cellulose, and is indicative of a high level of purity for the nanocrystals
 118 (Siqueira et al., 2010). The CNC crystallinity was measured through X-ray
 119 diffraction (XRD) with a X'pert instrument (Philips) operating with Cu K
 120 radiations (wavelength of 0.1542 nm generated at 50 kV with a current of
 121 40 mA. Scan type was continuous with an angle 2θ varying from 5.01 to
 122 49.99 with steps of 0.02 and a scan time of 1 s per step. The crystallinity
 123 index, IC , was measured as $IC = 1 - I_{\text{AM}} / I_{200}$, according to Segal's empirical
 124 method (Segal et al., 1959). I_{AM} and I_{200} are the intensities of the amorphous
 125 peak ($2\theta = 18.85^\circ$) and of the peak corresponding to the (200) lattice planes
 126 ($2\theta = 23.01^\circ$), respectively.

127 Organic solvents employed were purchased from commercial suppliers at
 128 high purity grade (purity >99 %, see Table A.1). The only exceptions are
 129 ethanol, used in its denatured form (purity of 95 %), and d-limonene (purity
 130 of 96 %), as higher purity grades of d-limonene are generally not available
 131 commercially. Distilled water was employed. Binary mixtures were prepared
 132 by mixing pure solvents. Densities and viscosities of solvents and mixtures
 133 at 25 °C were obtained by averaging experimental values reported in the
 134 specialized literature (Tables A.1 & A.2).

135 2.2. Sedimentation tests

136 2.2.1. Protocol

137 10 mL of the different solvents and binary mixtures were added to 0.1 g
 138 of CNCs in a glass vials of radius 2.1 cm. An ultrasonic probe (Cole-Parmer)
 139 operating at a frequency of 20 kHz with a CV334 converter and a tapered
 140 microtip was used to disperse the CNCs. The treatment had a power of
 141 25 W and was applied with a pulse cycle ON OFF of 5 s 2 s for a total

142 energy of $10,000 \text{ J g}_{\text{CNCs}}^{-1}$. Previous experimentation demonstrated that such a
 143 treatment do not result into desulfation of the CNCs (Beuguel et al., 2018b).
 144 The vials were placed in an ice bath to avoid any overheating during the
 145 ultrasonication. CNC suspensions ($10 \text{ mg}_{\text{CNCs}} \text{ mL}_{\text{solvent}}^{-1}$) were then allowed
 146 to rest at 25°C for a relative sedimentation time, $\text{RST} = 1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$.
 147 Calculated with Eq. 1 (Hansen, 2007), it corresponds for instance to an
 148 absolute sedimentation time, t_{sed} , of 12.1 h in acetone, 48.0 h in water, or
 149 1140 h in ethylene glycol (Tables A.1&A.2). Once the time of sedimentation
 150 had elapsed, three kinds of qualitative behaviors were observed for CNC
 151 sedimentation. Graded on a scale from best, 2, to worst, 0, they correspond
 152 respectively to: 2- a suspension without formation of any sediment (as shown
 153 in Fig. 2.a for DMSO), 1- a turbid suspension in which a sediment is formed
 154 (dichloromethane), and 0- all remaining cases in which a sediment is formed
 155 and the suspension is clear enough for text to be read through (toluene).
 156 The only exception to the aforementioned protocol is the sedimentation in
 157 triethanolamine, which was interrupted after a RST of $1.18 \cdot 10^{10} \text{ s}^2\text{m}^{-2}$ (10%
 158 of the standard RST). Due to the very high viscosity of triethanolamine, it
 159 corresponds to a time of sedimentation t_{sed} of 4100 h. Its behavior is clearly
 160 that of a 0-grade solvent (Fig. A.1).

$$t_{\text{sed}} = \text{RST} \frac{\text{solv}}{\text{CNCs} \cdot \text{solv}} \quad (1)$$

161 2.2.2. *RST calibration*

162 Sulfating CNCs provides them with surface charges, generating electro-
 163 static stabilization. It is a kinetic effect: the thermodynamically favored
 164 outcome of a colloidal suspension is the coagulation of the particles (Kron-
 165 berg et al., 2014). For electrostatic stabilization to manifest, there has to
 166 be dissociation between the negatively charged CNCs and their counter-ions,
 167 an outcome favored in solvents whose dielectric constants, ϵ_{solv} , are high
 168 (Kronberg et al., 2014). HSP characterization is a thermodynamic approach
 169 and a RST of $1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$ was selected following a calibration aimed at
 170 minimizing the influence of such kinetic effects on the sedimentation results.

171 At low RST , sedimentation results were strongly correlated with the di-
 172 electric constants of the solvents (Table A.1). Quickly, a discrimination how-
 173 ever appears among highly dielectric solvents and, at a RST of $5.9 \cdot 10^{10} \text{ s}^2\text{m}^{-2}$,
 174 we were already able to hint “good” solvents from “poor” ones independently
 175 of their dielectric constant. At $\text{RST} = 1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$, results are no

longer correlated with the dielectric constants. Highly dielectric solvents like methanol ($\epsilon_{\text{solv}}=33.0$), ethylene glycol (41.4), DMF (38.3), or propylene carbonate (66.1) received the grade 0, while DMSO (47.2) or ethanolamine (31.9) are at 2. The state of sedimentation at $RST = 1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$ was found to be meta-stable as increasing RST beyond $1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$ no longer affects the results. Vials were kept for months and in volatile media such as chloroform and dichloromethane, the solvent was fully evaporated before any significant change in the suspension turbidity could be observed. It does not mean that the electrostatic stabilizing effect is no longer felt at $RST = 1.18 \cdot 10^{11} \text{ s}^2\text{m}^{-2}$, but that electrostatic stabilization alone is no longer sufficient to prevent sedimentation at this point. For particles to remain in suspension at high RST , and whatever the level of electrostatic stabilization, there has to be a certain level of chemical affinity. It is this chemical affinity that the HSP analysis seeks to capture.

2.3. Thermodynamic approach - Hansen solubility parameters

2.3.1. Background

Initially developed to address the issue of the dispersibility of the various components of paints, solubility -or cohesion- parameters theory aims at quantifying the cohesive energy density (taken equal to χ^2 , MPa) between a chemical and its neighboring media (Hildebrand & Scott, 1950, 1962; Hansen, 2007). Hansen proposed to split the total cohesion parameter, χ , into its three main components resulting from the London dispersion forces, χ_D , the dipole-dipole interactions (χ_P), and hydrogen bonding interactions (χ_H) (Hansen 1967a,b, 2007; Hansen & Skaarup, 1967). The linearity of the decomposition in terms of energies means that χ^2 square may then be written as the sum of the squared HSP (Eq. 2). In the HSP theory, every chemical may be represented by a triplet (χ_D , χ_P , χ_H), and then be plotted in a 3 dimensional graph (Hansen, 2007). HSP values of solvents may be determined directly experimentally or estimated by group contribution methods and are now tabulated, alongside those of many commodity polymers (Hansen, 1967b, 2007; Abbott et al., 2018). Gardebjer et al. (2016) used one of these group contribution methods to estimate the HSP of cellulose's repeating unit, cellobiose. They computed a value of $(\chi_D, \chi_P, \chi_H) = (16.3; 16.2; 20.7) \text{ MPa}^{1/2}$ and assumed it to be the HSP values of CNCs (Gardebjer et al., 2016). Although it provided a quick and easy estimate, the method is unsatisfactory as it does not take into account the fact that polymer HSP are almost systematically greater than those of their repeating units, nor the

fact that crystallinity may greatly affect HSP values (Hansen, 2007; Abbott et al., 2018). Unknown HSP may be determined more accurately through an indirect approach. Affinity tests between the material and various solvents are conducted with the idea that, “like seeking like”, the stronger are the interactions the shorter is the distance, R_a ($\text{MPa}^{1/2}$, Eq. 3), between their respective Hansen solubility parameters (Hansen, 2007). “Good” solvents, where the “goodness” may be assigned quantitatively (e.g. maximum solubility) or qualitatively (e.g. suspension turbidity or swelling behavior), thus describe a sphere of radius R_0 ($\text{MPa}^{1/2}$), whose center corresponds to the unknown’s HSP (Hansen, 2007). The set of solvents may be completed by mixtures (Machui et al., 2012), Their HSP (D_{mix} ; P_{mix} ; H_{mix}) were calculated through Eq. 4 (Hansen, 2007), in which (D_i ; P_i ; H_i) are the HSP values of the constituent i and ϕ_i its volume fraction; n is the total number of solvents in the mixture.

$$\frac{R_a^2}{T} = \frac{R_a^2}{D} + \frac{R_a^2}{P} + \frac{R_a^2}{H} \quad (2)$$

$$R_a^2 = 4 \left(\frac{D_{\text{mix}} - D_i}{n} \right)^2 + \left(\frac{P_{\text{mix}} - P_i}{n} \right)^2 + \left(\frac{H_{\text{mix}} - H_i}{n} \right)^2 \quad (3)$$

$$D_{\text{mix}} = \sum_{i=1}^n \phi_i D_i ; P_{\text{mix}} = \sum_{i=1}^n \phi_i P_i ; H_{\text{mix}} = \sum_{i=1}^n \phi_i H_i \quad (4)$$

Our set of solvents was selected based on their position in the HSP graph to maximize the coverage and based on the uncertainty of the solvents’ HSP coordinates. Indeed, the indirect method of HSP determination for an unknown compound is no more precise than that of the solvents that are employed to perform the characterization. Historically, HSP coordinates were determined experimentally for a set of 90 common solvents, from which group contribution models have been derived (Hansen, 2007). Nowadays, and based on these group contribution methods, HSP of thousands of solvents have been calculated (Hansen, 2007; Abbott et al., 2018). When we selected our 27 pure solvents, we aimed at picking them from the list of the 90 experimentally confirmed solvents. Exceptions to the list are ethyl benzoate, heptane, d-limonene, triethanolamine, and water. Water, with its three sets of HSP, is a special case (see Hansen 2007). Heptane, being purely dispersive, has a low uncertainty (uncertainty arises mostly from the calculation of the polar and hydrogen-bonding components: P and H , respectively) (Abbott et al., 2018). Ethyl benzoate, d-limonene, and triethanolamine HSP values have

243 been calculated, rather than empirically determined, inducing a greater un-
 244 certainty. They were nonetheless selected for their interesting position in the
 245 HSP graph.

246 2.3.2. HSP analysis

247 HSP analysis was performed with the software HSPiP (Abbott et al.,
 248 2018). HSP values of pure solvents, binary mixtures, and polymers, were
 249 extracted from the HSPiP database (Abbott et al., 2018) and are respectively
 250 provided in Tables A.1, A.2, and A.3.

251 For the sphere fitting, we considered both grade 1 and grade 2-solvents
 252 (and mixtures) to be “good” and grade 0-ones to be “poor”. The algorithm of
 253 the software maximizes the function FIT described below (Eq. 6) (Hansen,
 254 2007; Abbott et al., 2018). The ideal result is a sphere of center $(D_s; P_s$
 255 $; H_s)$ and of radius R_0 that contains all the “good” solvents and mixtures
 256 while excluding any “poor” ones. A solvent/mixture is located in the sphere
 257 if its distance to the sphere’s center, R_a (Eq. 2), is smaller than or equal to
 258 R_0 . It corresponds to a reduced energy difference $RED \leq 1$ (Eq. 5).

$$RED = R_a/R_0 \quad (5)$$

259 The quality of the fitting may be assessed through the FIT value and
 260 through the uncertainty on the $(D_s; P_s; H_s)$ coordinates (Hansen, 2007;
 261 Abbott et al., 2018). FIT (Eq. 6) is a desirability function (Hansen, 2007)
 262 that provides information about the quality of the fit on the m solvents tested
 263 : indeed, a “poor” solvent/mixture located inside a sphere ($RED \leq 1$) or a
 264 “good” one located outside ($RED > 1$) induces a penalty on the FIT coeffi-
 265 cient. The better the fit, the closest FIT will be from 1.0 ($FIT \leq 1.0$). The
 266 uncertainty “ $(D_s; P_s; H_s)$ ” provides information on the tightness
 267 of the HSP sphere core’s position. Values in the range of $0.25\text{-}0.50 \text{ MPa}^{1/2}$
 268 are indicative of a very good fit and of a tight core, while a poor fit will
 269 result in uncertainties in the range of $> 1 \text{ MPa}^{1/2}$ (Abbott et al., 2018). It is
 270 possible to have a tight core for two parameters and a loose one for the last,
 271 meaning that there is a lack of data points in that direction (Abbott et al.,
 272 2018). It has to be noted that fitting a sphere on less than 4-5 good solvents
 273 necessarily leads to an uncertainty that may not be reflected in the FIT
 274 value nor in the “ $(D_s; P_s; H_s)$ ”. The existence of an uncertainty
 275 means that results obtained in running several times the algorithm on the
 276 same data differ slightly. Results reported here are those corresponding to

the highest FIT value and the lowest uncertainty over at least 10 runs of the fitting algorithm. The values were overall very stable between the different tests with variations in the range of 0.001 for FIT and of 0.05 MPa^{1/2} for the different uncertainties: (D_{i,s}; P_{i,s}; H_{i,s}).

$$FIT = \sum_{i=1}^m A_i^{1/m}$$

For "good" solvents inside a sphere : $A_i = 1$ (6)

For "poor" solvents outside a sphere : $A_i = 1$

For "good" solvents outside a sphere : $A_i = e^{+(R_0 - R_a)}$

For "poor" solvents inside a sphere : $A_i = e^{+(R_a - R_0)}$

3. Results and discussion

Considering both grade 2 and 1 as good solvents, two distinct regions of preferential dispersibility may clearly be distinguished. The first is in the polar region of the graph (high ρ and H , Fig. 2.c) and contains all of the grade 2 solvents: dimethylsulfoxide (DMSO), formamide, water, and ethanolamine. The area delimited by these solvents is bordered by 0-grade ones like triethanolamine, propylene carbonate, N,N-dimethylformamide, or acetone. A second distinct region may then be distinguished in the mildly non-polar region (intermediate ρ and H) where chloroform and dichloromethane are classified as grade 1 and stand alone surrounded by poor solvents. This behavior, with two distinct regions, is expected in the HSP theory for amphiphilic species such as particles or block copolymers for instances (Hansen, 2007). In this configuration, two HSP spheres, which correspond to the different affinities of the chemical, may be drawn.

For a better HSP test, sedimentation tests were performed for binary mixtures of DMSO + acetone, toluene, and methanol, and binary mixtures of formamide + methanol and 1-propanol. Results obtained with binary mixtures validate our scale of dispersibility as the goodness of a grade 2 solvent like DMSO decreases to grade 1 once 40 vol% of methanol, a grade 0 solvent, is added and then to 0 beyond 60 vol% (Fig. A.2.b&e). DMSO is known to be one of the best solvent for CNCs dispersion as it enables strong gel formation upon heating (Sojoudiasli et al., 2017).

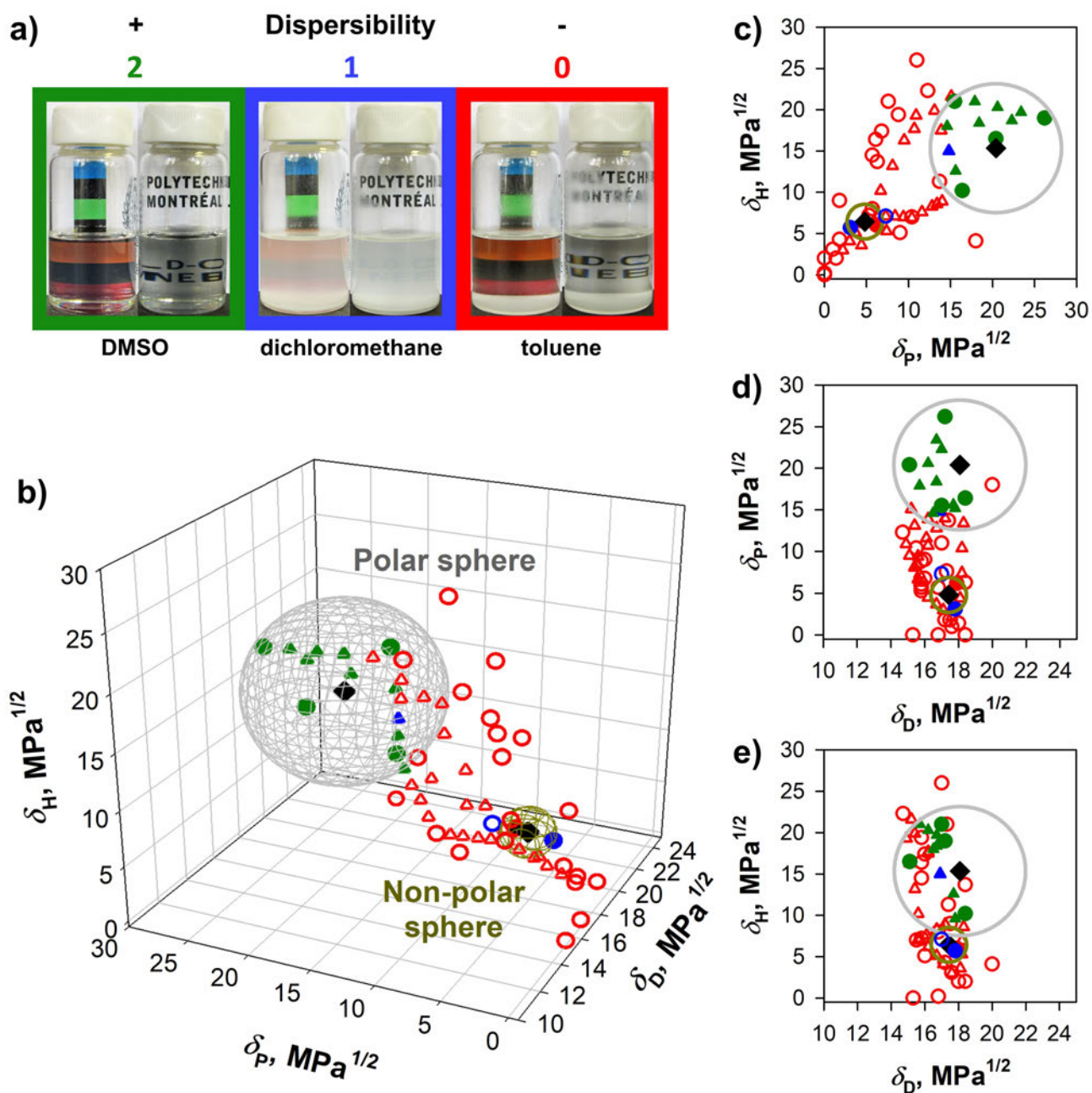


Figure 2: HSP graph of wood-based sulfuric acid-hydrolyzed CNCs. (a) CNC scale of dispersibility. Three different grades were attributed to the CNC state of dispersion, from best to worst: 2-in green-No sediment at the bottom of the vial, 1-in blue-Presence of a sediment, the suspension is too turbid to be able to read a text through, 0-in red-Presence of a sediment, the suspension is less turbid/clear. Pure solvents are represented by circles, binary mixtures by triangles, sphere centers by black diamonds. Two different spheres may be plotted: a large polar sphere (δ_D ; δ_P ; δ_H) = (18.1; 20.4; 15.3) (0.5; 0.5; 0.4) $\text{MPa}^{1/2}$ and another smaller sphere in the mildly non-polar region (δ_D ; δ_P ; δ_H) = (17.4; 4.8; 6.5) (0.3; 0.5; 0.6) $\text{MPa}^{1/2}$. Symbols located inside a sphere are full and symbols outside are empty. The HSP graph is represented in a 3-dimensional view (b), and in 2-dimensional views alongside the planes δ_H - δ_P (c), δ_P - δ_D (d), and δ_H - δ_D (e).

Using HSPiP (Hansen Solubility Parameters in Practice) software (Abbott et al., 2018), it was possible to obtain a well defined sphere ($FIT = 1.0$, see Eq. 6) of radius $R_{0,P}=7.8 \text{ MPa}^{1/2}$ in the polar region. It includes 13 good solvents and mixtures while excluding any poor ones. Its center's coordinates ($\delta_D; \delta_P; \delta_H$) are $(18.1; 20.4; 15.3) - (0.5; 0.5; 0.4) \text{ MPa}^{1/2}$ for a τ of $31.3 - 1.6 \text{ MPa}^{1/2}$. Having defined with precision what stands clearly for the dominant affinity of CNCs, the case of chloroform and dichloromethane may be addressed. These results are concordant with reports by Yu et al. of stable suspensions of sulfuric acid hydrolyzed CNCs in chloroform (Yu & Qin, 2012; Yu et al., 2012). A fitting in this area of the graph yields a FIT of 0.974 with a sphere of radius $R_{0,P}=2.1 \text{ MPa}^{1/2}$ and centered about $(\delta_D; \delta_P; \delta_H) = (17.4; 4.8; 6.5) - (0.3; 0.5; 0.6) \text{ MPa}^{1/2}$. It corresponds to a τ of $19.2 - 2.7 \text{ MPa}^{1/2}$. Here, the FIT value is lowered by ethyl benzoate, which is a 0-grade solvent despite having HSP close to that of dichloromethane and chloroform. It is not clear whether it highlights a limitation of the HSP method itself –as we know that conformation effects for instance are not accounted for in HSP theory– or a limitation of the HSP group contribution models. Ethyl benzoate is indeed among the few solvents we employed whose HSP were calculated without any experimental confirmation (Hansen, 2007). It may thus be that the FIT value is only lowered by imprecise solvent coordinates: ethyl benzoate while being plotted as inside of the non-polar sphere (Fig. 2) may actually be out of it. From the 90 solvents experimentally proofed by Hansen and co-workers (1967; 1967a; 1967b), and aside from chloroform and dichloromethane, none is located in the area of interest. This issue cannot be settled easily with the current experimental method. Fitted using only two good solvents, the position of the non-polar sphere thus has to be considered with caution. It however provides the first experimental estimates of CNC hydrophobic surface HSP.

The polar sphere is considered to correspond to the HSP of the hydroxyl rich (110) and $(1\bar{1}0)$ surfaces. Computer simulations indeed predicts that (110) and $(1\bar{1}0)$ surfaces have similar surface energies (Yamane et al., 2006) and hydrophilicity (Heiner et al., 1998; Matthews et al., 2006), which means that they are expected to be represented by a single HSP sphere (Table 1). Meanwhile, the mildly non-polar sphere is attributed to the display of (200) surfaces by the nanocrystals. Their lower simulated surface energy (Yamane et al., 2006) and higher modeled water contact angle (Mazeau & Rivet, 2008) are indeed expected to result into a distinct HSP sphere.

The contrast between the better fit and wider radius of the polar sphere

341 and the lesser ones of the non-polar sphere is coherent with the fact that
 342 sulfuric acid hydrolyzed CNCs have been reported to exhibit experimentally
 343 a predominant polar and hydrophilic behavior. HSP of the polar sphere are
 344 furthermore very close to those obtained for the chemical accessibility of cel-
 345 lulose : $(\delta_D; \delta_P; \delta_H) = (19.09; 15.77; 15.29) \quad (0.15; 0.25; 0.30) \text{ MPa}^{1/2}$
 346 (Hansen & Björkman, 1998; Larsson & Johns, 1988; Minhas & Robertson,
 347 1967). These are calculated from the ability of different solvents to swell
 348 cotton-based I cellulose pulp. Swelling increases the active surface area of
 349 the pulp by increasing hydroxyl group accessibility, the amount of which is
 350 quantified chemically through a thallation of the -OH functions (Minhas &
 351 Robertson, 1967). The only significant deviation lies in δ_P , the polar compo-
 352 nent, that is increased by $+4.6 \text{ MPa}^{1/2}$ from the chemical accessibility of cellu-
 353 lose HSP to our polar sphere's results. Slight variations in δ_D and δ_H , coupled
 354 to a sharp increase in δ_P are coherent with the effect of surface sulfatation
 355 based on the predictions of HSP group contributions (Stefanis & Panayiotou,
 356 2008). The δ_P increase for CNCs with respect to the cotton-based pulp is
 357 thus attributed to the introduction of sulfate groups on the hydroxyl groups
 358 of the nanocrystal surfaces during the sulfuric acid hydrolysis (Hamad &
 359 Hu, 2010; Hamad, 2017). Part of this variation is also probably imputable
 360 to the difference in wettability between I and I hydroxyl-rich surfaces, al-
 361 though simulations predict very similar surface energies with 154 mN m^{-1}
 362 and 155 mN m^{-1} , respectively (Yamane et al., 2006).

363 It is worth noting that this shift of $+4.6 \text{ MPa}^{1/2}$ in δ_P reduces the HSP
 364 distance of CNCs with water from $9.3 \text{ MPa}^{1/2}$ to $6.1 \text{ MPa}^{1/2}$, which may
 365 be able to partly explain the increased affinity of sulfated CNCs for water.
 366 As contact angles have usually been found experimentally to be positively
 367 correlated with HSP distance (Hansen, 2007), this finding is also coherent
 368 with the water contact angle value obtained by simulation by Mazeau &
 369 Rivet (2008). The 43° of the (110) surface corresponds to a HSP distance
 370 of $6.1 \text{ MPa}^{1/2}$, while the 95° of the (200) surface corresponds, based on our
 371 results, to a HSP distance of $19.1 \text{ MPa}^{1/2}$.

372 From our knowledge of the CNC structure, it is thus possible to assign
 373 each of the spheres to a lattice plane, which enables us for the first time to
 374 estimate the amphiphilicity of wood-based sulfated CNCs. Our results also
 375 highlight the limitations of group contribution methods to estimate cellulose
 376 nanocrystal HSP. Given that they do not take into account conformation
 377 effects, computations by Gardebjer et al. (2016) were not able to predict
 378 a second non-polar sphere for CNCs. If we compare their results to those

379 of our polar sphere, they also underestimate δ_D and δ_P by 1.7 MPa^{1/2} and
 380 4.2 MPa^{1/2}, respectively, which is not unexpected when HSP of a polymer
 381 are compared to those of its repeating unit (Hansen, 2007). The hydrogen
 382 bonding component, δ_H , was underestimated by 5.4 MPa^{1/2} (Gardebjer et al.,
 383 2016). It may probably be attributed to the fact that the influence of the
 384 -OH groups of cellulose is hindered by their involvement in the crystalline
 385 network of CNCs (Jarvis, 2003; Djahedi et al., 2016).

386 The amphiphilicity of cellulose chains has recently been advanced as a
 387 key-factor to explain the low solubility of cellulose chains in polar solvents
 388 (Medronho et al., 2012). This parameter was not considered by Hansen &
 389 Björkman (1998) when they worked on wood ultrastructure and cellulose
 390 affinity. While Fig. 2 provides experimental evidence for this amphiphilic-
 391 ity, we believe that due to the high dependency of HSP with conformation
 392 effects, such as those induced by crystallinity (Hansen, 2007; Abbott et al.,
 393 2018), any extrapolation from crystalline to amorphous cellulose has to be
 394 considered with great caution. Our interest in HSP instead lies in their abil-
 395 ity to represent in a same graph –thus enabling comparisons– chemicals of
 396 very different scales, from solvents to polymers, (nano)particles, and macro-
 397 scale surfaces. Determining HSP of cellulose nanocrystals, based on their
 398 behavior in a set of solvents, may thus provide information about their affin-
 399 ity for polymer matrices. HSP of some common polymer matrices, such
 400 as poly(vinyl alcohol) (PVOH), poly(lactic acid) (PLA), poly(ethylene gly-
 401 col) (PEG), poly(methyl methacrylate) (PMMA), poly(ethylene) (PE), and
 402 poly(propylene) (PP), are available (Abbott et al., 2018) and are plotted
 403 in the Fig. 3. It is worth pointing out that the HSP values of polymers
 404 are notably functions of their molecular weight and degree of crystallinity
 405 (Hansen, 2007; Abbott et al., 2018) and the parameters employed here are
 406 average values as provided in the HSPiP polymer dataset (Abbott et al.,
 407 2018). These polymers may be split into 3 groups based on their HSP: I-in
 408 the polar sphere (PVOH), II-in between the spheres (PEG, PLA, PMMA)
 409 and III-in the non-polar region (PE and PP). CNC-polymer affinity is not
 410 the only factor at play for CNC dispersion in polymer matrices.

411 The protocol employed (melt mixing or solvent casting) has, for instance,
 412 a major influence (Bagheriasl et al., 2016, 2017). Assuming that the quality
 413 of CNC dispersion in the solvent is important for solvent casting, then other
 414 parameters such as the "goodness" of the solvent (Fig. 2), the initial state of
 415 CNCs (Beuguel et al., 2018b; Peng et al., 2016) –the use of never-dried, freeze-
 416 dried, or spray-dried–, and the protocol employed for the dispersion –such as

417 ultrasonication conditions (Beuguel et al., 2018a)– are also relevant. Keeping
 418 these points in mind, it is striking how these polymer-categories (I, II, and
 419 III), based solely on HSP, match with the experimental quality reported
 420 for the dispersion of sulfuric acid-hydrolyzed CNCs in the aforementioned
 421 matrices: PVOH has been reported to be one of the best matrices for CNC
 422 dispersion both in solvent casting and melt mixing (Hamad, 2017), which
 423 is coherent with it being in the dominant polar sphere of CNCs. A good
 424 dispersion of CNCs is also achievable in PLA (Zhang et al., 2015; Bagheriasl
 425 et al., 2016, 2017), PEG (Beuguel et al., 2018a; Yao et al., 2017; Zhou et al.,
 426 2011; Xu et al., 2013, 2014), and PMMA (Yin et al., 2016) through a solvent
 427 casting. Direct melt mixing may however remain difficult for this group II-
 428 polymers as in the case of PLA (Raquez et al., 2013; Khoshkava & Kamal,
 429 2013; Dhar et al., 2016; Bagheriasl et al., 2017).

430 Dhar et al. (2016) demonstrated that the sulfatation of CNC surfaces
 431 lessens their dispersibility in PLA matrices, which is consistent with our
 432 HSP results: the shift of $+4.6 \text{ MPa}^{1/2}$ in the ρ of the polar sphere between
 433 sulfated CNCs and chemically accessible cellulose increases the distance be-
 434 tween the PLA matrices and the (110) and (1 $\bar{1}$ 0) surfaces' sphere from 11.4
 435 to $15.0 \text{ MPa}^{1/2}$. Based on the HSP theory, the absence of any adsorption
 436 of PEG on CNC surfaces (Beuguel et al., 2018a; Reid et al., 2017) is also
 437 coherent with this polymer being out of any sphere, adsorption being only
 438 expected for compounds of very similar HSP (Hansen, 1997). Modification
 439 of the nanocrystal OH groups, which is expected to result in a shift of the
 440 corresponding surfaces HSP sphere (Peng et al., 2016; Yoo & Youngblood,
 441 2016), may significantly improve the CNC dispersion and the reinforcing ef-
 442 fect in group II-matrices (Raquez et al., 2013; Yin et al., 2016; Zhang et al.,
 443 2015; Khoshkava & Kamal, 2013). It is likely that a systematic HSP char-
 444 acterization of the modified CNCs would have concluded that any chemical
 445 modification that improves the CNC dispersion in a matrix also reduces
 446 the HSP distance between the polar sphere and this matrix, as in the case
 447 of Peng et al. (2017). In group III-matrices such as PP (Bagheriasl et al.,
 448 2015; Khoshkava & Kamal, 2014) and PE (Lewandowska & Eichhorn, 2016;
 449 Inai et al., 2018), nanoscale dispersion in melt compounding seems to be
 450 impossible without the use of a compatibilizer. While unmodified nanocrys-
 451 tals have an interfacial tension with PP more than fourfold that with PLA,
 452 surface modification may, here again, shift the relative affinity of CNCs and
 453 make dispersion more favorable in PP with a slightly lower interfacial ten-
 454 sion (Khoshkava & Kamal, 2014). Probably due to the low solubility of

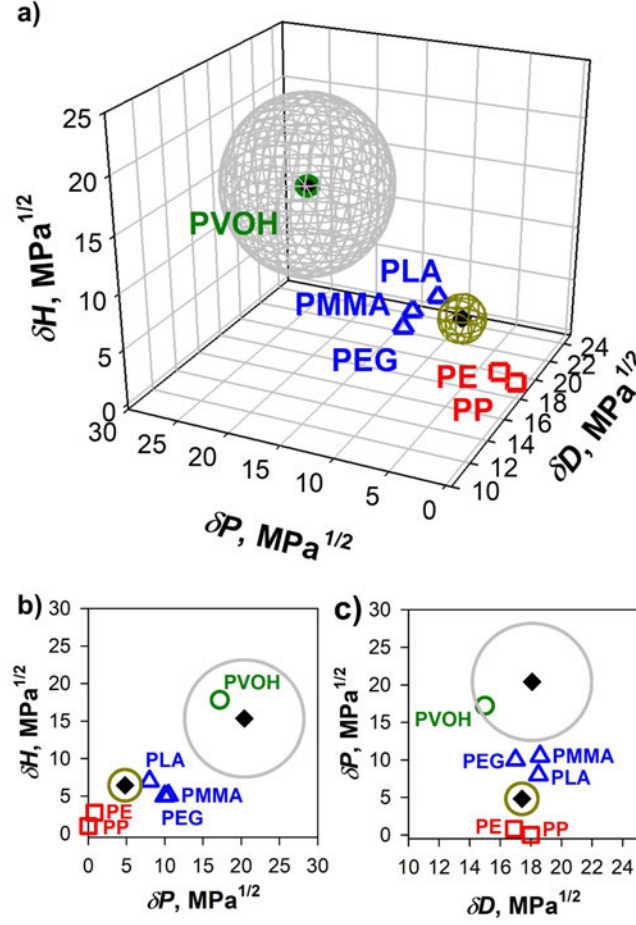


Figure 3: HSP graph of wood-based sulfuric acid hydrolyzed CNCs (see Fig. 2) compared to some commodity polymers. These polymers may be split into 3 groups based on their HSP (Abbott et al., 2018): I-green circles-in the polar sphere for poly(vinyl alcohol) (PVOH); II-blue triangles-in between the spheres for poly(lactic acid) (PLA), poly(ethylene glycol) (PEG), and poly(methyl methacrylate) (PMMA); and III-red squares-in the non-polar region for poly(ethylene) (PE), and poly(propylene) (PP). Categories I, II, and III match, from best to worst, with experimental reports for the dispersibility of CNCs in these matrices. The HSP graph is represented in a 3-dimensional view (a), and in 2-dimensional views alongside the planes H - P (b), and P - D (c).

these polymers in common solvents (Hansen, 2007), no experimental data
are available for the solvent casting of these PP and PE nanocomposites.

457 4. Concluding remarks

458 In conclusion, we linked CNC dispersibility in a large set of solvents and
459 binary mixtures to the anisotropy of the nanocrystal structure. Wood-based
460 sulfuric acid-hydrolyzed CNCs were found to be predominantly polar par-
461 ticles with a main HSP sphere of radius $7.8 \text{ MPa}^{1/2}$ and of center $(D; P$
462 $; H) = (18.1; 20.4; 15.3) (0.5; 0.5; 0.4) \text{ MPa}^{1/2}$. This main behavior is
463 thought to reflect the influence of their hydroxyl-rich (110) and (1 $\bar{1}$ 0) surfaces
464 and is coherent with their behavior described in the literature. While pre-
465 dicted years ago through simulations and expected based on cross-sectional
466 structure analysis of the nanocrystals through X-ray scattering and AFM
467 techniques, this study is the first to experimentally confirm the contribution
468 of **hydrophobic surfaces** to the behavior of CNCs in suspensions. We pro-
469 vide an approximation of their chemical influence through the determination
470 of their Hansen solubility parameters (HSP). Although refinements are still
471 necessary, as based only on two good solvents, the non-polar sphere location
472 is estimated in the range of $(17.4; 4.8; 6.5) (0.3; 0.5; 0.6) \text{ MPa}^{1/2}$ with a
473 radius of $2.1 \text{ MPa}^{1/2}$. This position, relatively to that of the polar sphere, is
474 coherent with results from computer simulations **for the display of (200) lat-**
475 **tice planes by the CNC particles.** Further work is required to determine the
476 influence of the feedstock, of the hydrolysis conditions, and of the dispersion
477 protocol on the display of an amphiphilic behavior by CNCs.

478 HSP graphs are a useful tool to predict the CNC dispersion in polymer
479 matrices and allow us a better understanding of results already published in
480 the literature. Such characterization could be carried out on functionalized
481 particles to understand the effect of the chemical modification on the surface
482 properties of the nanocrystals (Yoo & Youngblood, 2016; Peng et al., 2016)
483 and on their dispersibility (Peng et al., 2017) in non-polar media.

484 Conflicts of interest

485 There are no conflicts to declare

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498 References

- 499 Abbott, S. J., Hansen, C. M., & Yamamoto, H. (2018). Hansen solubility
 500 parameters in practice software, ebook, datasets. Url: [http://www.hansen-](http://www.hansen-solubility.com)
 501 [solubility.com](http://www.hansen-solubility.com), accessed on 2018/07/03.
- 502 Atalla, R. H., & Vanderhart, D. L. (1999). The role of solid state ^{13}C NMR
 503 spectroscopy in studies of the nature of native celluloses. *Solid State Nucl.*
 504 *Magn. Reson.*, *15*, 1–19.
- 505 Bagheriasl, D., Carreau, P. J., Dubois, C., & Riedl, B. (2015). Proper-
 506 ties of polypropylene and polypropylene/poly(ethylene-co-vinyl alcohol)
 507 blend/CNC nanocomposites. *Compos. Sci. Technol.*, *117*, 357–363.
- 508 Bagheriasl, D., Carreau, P. J., Riedl, B., Dubois, C., & Hamad, W. Y.
 509 (2016). Shear rheology of polylactide (PLA)–cellulose nanocrystal
 510 (CNC) nanocomposites. *Cellulose*, *23*, 1885–1897.
- 511 Bagheriasl, D., Safdari, F., Carreau, P. J., Dubois, C., & Riedl, B. (2017).
 512 Development of cellulose nanocrystal-reinforced polylactide: A compara-
 513 tive study on different preparation methods. *Polym. Compos.*, . DOI:
 514 10.1002/pc.24676.
- 515 Beuguel, Q., Tavares, J. R., Carreau, P. J., & Heuzey, M.-C. (2018a). Rheo-
 516 logical behavior of cellulose nanocrystal suspensions in polyethylene glycol.
 517 *J. Rheol.*, *62*, 607–618.
- 518 Beuguel, Q., Tavares, J. R., Carreau, P. J., & Heuzey, M.-C. (2018b). Ul-
 519 trasonication of spray- and freeze-dried cellulose nanocrystals in water. *J.*
 520 *Colloid Interface Sci.*, *516*, 23–33.

- 521 Brown, R. M. (1996). The biosynthesis of cellulose. **J. Macromol. Sci., Part**
522 **A: Pure Appl. Chem., A33**, 1345–1373.
- 523 Chaturvedi, K., Ganguly, K., Kulkarni, A. R., Kulkarni, V. H., Nadagouda,
524 M. N., Rudzinski, W. E., & Aminabhavi, T. M. (2011). Cyclodextrin-based
525 siRNA delivery nanocarriers: a state-of-the-art review. **Expert Opin. Drug**
526 **Del., 8**, 1455–1468.
- 527 Conley, K. M., Godbout, L., Whitehead, M. A., & van de Ven, T. G. M.
528 (2017a). Reversing the structural chirality of cellulosic nanomaterials. **Cel-**
529 **lulose 24**, 5455–5462.
- 530 Conley, K. M., Whitehead, M. A., & van de Ven, T. G. M. (2017b). Prob-
531 ing the structural chirality of crystalline cellulose with induced circular
532 dichroism. **Cellulose 24**, 479–486.
- 533 Cousins, S. K., & Brown, R. M. (1995). Cellulose I microfibril assembly:
534 computational molecular mechanics energy analysis favours bonding by
535 van der Waals forces as the initial step in crystallization. **Polymer, 36**,
536 3885–3888.
- 537 Dhar, P., Bhasney, S. M., Kumar, A., & Katiyar, V. (2016). Acid function-
538 alized cellulose nanocrystals and its effect on mechanical, thermal, crys-
539 tallization and surfaces properties of poly (lactic acid) bionanocomposites
540 films: A comprehensive study. **Polymer, 101**, 75–92.
- 541 Ding, S.-Y., & Himmel, M. E. (2006). The Maize Primary Cell Wall Mi-
542 crofibril: A New Model Derived from Direct Visualization. **J. Agric. Food**
543 **Chem., 54**, 597–606.
- 544 Ding, S.-Y., Liu, Y.-S., Zeng, Y., Himmel, M. E., Baker, J. O., & Bayer,
545 E. A. (2012). How Does Plant Cell Wall Nanoscale Architecture Correlate
546 with Enzymatic Digestibility? **Science 338**, 1055–1060.
- 547 Ding, S.-Y., Zhao, S., & Zeng, Y. (2014). Size, shape, and arrangement of
548 native cellulose fibrils in maize cell walls. **Cellulose 21**, 863–871.
- 549 Djahedi, C., hle Wohlert, M. B., Berglund, L. A., & Wohlert, J. (2016). Role
550 of hydrogen bonding in cellulose deformation-the leverage effect analyzed
551 by molecular modeling. **Cellulose 23**, 2315–2323.

- 552 Dufresne, A. (2017). *Nanocellulose. From Nature to High Performance Tai-*
553 *lored Materials*. (2nd ed.). Berlin/Boston: Walter de Gruyter GmbH.
- 554 Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J.-L., Heux, L., Dubreuil,
555 F., & Rochas, C. (2008). The shape and size distribution of crystalline
556 nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacro-*
557 *molecules*, *9*, 57–65.
- 558 Eyley, S., & Thielemans, W. (2014). Surface modification of cellulose
559 nanocrystals. *Nanoscale*, *6*, 7764–7779.
- 560 French, A. D. (2017). Glucose, not cellobiose, is the repeating unit of cellulose
561 and why that is important. *Cellulose*, *24*, 4605–4609.
- 562 Gardebjer, S., Andersson, M., Engström, J., Restorp, P., Persson, M., &
563 Larsson, A. (2016). Using Hansen solubility parameters to predict the
564 dispersion of nano-particles in polymeric films. *Polym. Chem.*, *7*, 1756–
565 1764.
- 566 Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose Nanocrystals:
567 Chemistry, Self-Assembly, and Applications. *Chem. Rev.*, *110*, 3479–3500.
- 568 Hamad, W. Y. (2017). *Cellulose Nanocrystals Properties, Production and*
569 *Applications*. Chichester, U. K.: Wiley.
- 570 Hamad, W. Y., & Hu, T. Q. (2010). Structure-process-yield interrelation in
571 nanocrystalline cellulose extraction. *Can. J. Chem. Eng.*, *88*, 392–402.
- 572 Hansen, C. M. (1967a). The Three Dimensional Solubility Parameter - Key
573 to Paint Component Affinities I. - Solvents, Plasticizers, Polymers, and
574 Resins. *J. Paint Techn.*, *39*, 104–117.
- 575 Hansen, C. M. (1967b). *The Three Dimensional Solubility Parameter and*
576 *Solvent Diffusion Coefficient, Their Importance in Surface Coating For-*
577 *mulation*. Ph.D. thesis Technical University of Denmark Copenhagen,
578 Denmark.
- 579 Hansen, C. M. (1997). Cohesion Parameters for Surfaces, Pigments, and
580 Fillers. *Surf. Coat. Int.*, *8*, 386–391.
- 581 Hansen, C. M. (2007). *Hansen Solubility Parameters A User's Handbook*.
582 Boca Raton, FL, U. S. A.: CRC Press.

583

584

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585

586

587

J. Paint Techn. 39

588

589

590

Carbohydr. Res. 306

591

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592

593

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594

595

596

597

Science 315

598

599

600

Compos. Sci. Technol. 154

601

Nature 426

602

603

604

Biomacromolecules 14

605

606

607

Powder Technol. 261

608

609

Surfactants and Polymers

Surface Chemistry of

610

611

612

J. Microsc.-Oxford 178

- 613 Larsson, A., & Johns, W. E. (1988). Acid-base interactions between cell-
614 lose/lignocellulose and organic molecules. *J. Adhesion*, *25*, 121–131.
- 615 Lewandowska, A. E., & Eichhorn, S. J. (2016). Raman imaging as a tool for
616 assessing the degree of mixing and the interface between polyethylene and
617 cellulose nanocrystals. *IOP Conf. Ser. Mater. Sci. Eng.*, *139*, 012030.
- 618 Li, Q., & Renneckar, S. (2011). Supramolecular Structure Characterization
619 of Molecularly Thin Cellulose I Nanoparticles. *Biomacromolecules*, *12*,
620 650–659.
- 621 Liu, D., Chen, X., Y.Yue, Chen, M., & Wu, Q. (2011). Structure and rheology
622 of nanocrystalline cellulose. *Carbohydr. Polym.*, *84*, 311–322.
- 623 Machui, F., Langner, S., Zhu, X., Abbott, S., & Brabec, C. J. (2012). *Sol.*
624 *Energ. Mat. Sol. C.*, *100*, 138–146.
- 625 Marques, H. M. C. (2010). A review on cyclodextrin encapsulation of essential
626 oils and volatiles. *Flavour Frag. J.*, *25*, 313–326.
- 627 Matthews, J. F., Skopec, C. E., Mason, P. E., Zuccato, P., Torget, R. W.,
628 Sugiyama, J., Himmel, H. E., & Brady, J. W. (2006). Computer simulation
629 studies of microcrystalline cellulose I . *Carbohydr. Res.*, *341*, 138–152.
- 630 Mazeau, K., & Rivet, A. (2008). Wetting the (110) and (100) Surfaces of I
631 Cellulose Studied by Molecular Dynamics. *Biomacromolecules*, *9*, 1352–
632 1354.
- 633 Mazeau, K., & Wyszomirski, M. (2012). Modelling of Congo red adsorption
634 on the hydrophobic surface of cellulose using molecular dynamics. *Cellu-*
635 *lose*, *19*, 1495–1506.
- 636 Medronho, B., Romano, A., Miguel, M. G., Stigsson, L., & Lindman, B.
637 (2012). Rationalizing cellulose (in)solubility: reviewing basic physicochem-
638 ical aspects and role of hydrophobic interactions. *Cellulose*, *19*, 581–587.
- 639 Minhas, P. S., & Robertson, A. A. (1967). Accessibility of Cellulose by the
640 Thallous Ethylate Method-Application to the Measurement of Cellulose
641 Liquid Interactions 1. *Textile Res. J.*, *37*, 400–408.

- 642 Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011).
 643 Cellulose nanomaterials review: structure, properties and nanocomposites.
 644 **Chem. Soc. Rev.** **40**, 3941–3994.
- 645 Nishiyama, Y. (2017). Molecular interactions in nanocellulose assembly. **Phil.**
 646 **Trans. R. Soc. A.**, **376**, 20170047.
- 647 Nishiyama, Y., Langan, P., & Chanzy, H. (2002). Crystal Structure and
 648 Hydrogen-Bonding System in Cellulose I from Synchrotron X-ray and
 649 Neutron Fiber Diffraction. **J. Am. Chem. Soc.**, **124**, 9074–9082.
- 650 Nishiyama, Y., Sugiyama, J., Chanzy, H., & Langan, P. (2003). Crystal
 651 Structure and Hydrogen Bonding System in Cellulose I from Synchrotron
 652 X-ray and Neutron Fiber Diffraction. **J. Am. Chem. Soc.**, **125**, 14300–
 653 14306.
- 654 Peng, S. X., Chang, H., Kumar, S., Moon, R. J., & Youngblood, J. P. (2016).
 655 A comparative guide to controlled hydrophobization of cellulose nanocrys-
 656 tals via surface esterification. **Cellulose** **23**, 1825–1846.
- 657 Peng, S. X., Shrestha, S., Yoo, Y., & Youngblood, J. P. (2017). Enhanced
 658 dispersion and properties of a two-component epoxy nanocomposite using
 659 surface modified cellulose nanocrystals. **Polymer**, **112**, 359–368.
- 660 Petersson, L., Kvien, I., & Oksman, K. (2007). Structure and thermal proper-
 661 ties of poly(lactic acid)/cellulose whiskers nanocomposite materials. **Com-**
 662 **pos. Sci. Technol.** **67**, 2535–2544.
- 663 Raquez, J.-M., Habibi, Y., Murariu, M., & Dubois, P. (2013). Polylactide
 664 (PLA)-based nanocomposites. **Prog. Polym. Sci.**, **38**, 1504–1542.
- 665 Reid, M. S., Villalobos, M., & Cranston, E. D. (2017). The role of hydro-
 666 gen bonding in non-ionic polymer adsorption to cellulose nanocrystals and
 667 silica colloids. **Curr. Opin. Colloid In.**, **29**, 76–82.
- 668 Sèbe, G., Ham-Pichavant, F., Ibarboure, E., Koffi, A. L. C., & Tingaut,
 669 P. (2012). Supramolecular Structure Characterization of Cellulose II
 670 Nanowhiskers Produced by Acid Hydrolysis of Cellulose I Substrates.
 671 **Biomacromolecules** **13**, 570–578.

- 672 Segal, L., Creely, J. J., Martin, Jr, A. E., & Conrad, C. M. (1959). An
673 Empirical Method for Estimating the Degree of Crystallinity of Native
674 Cellulose Using the X-Ray Diffractometer. *Text. Res.*, *29*, 786–794.
- 675 Siqueira, G., Bras, J., & Dufresne, A. (2010). New Process of Chemical Graft-
676 ing of Cellulose Nanoparticles with a Long Chain Isocyanate. *Langmuir*,
677 *26*, 402–411.
- 678 Sojoudiasli, H., Heuzey, M.-C., Carreau, P. J., & Riedl, B. (2017). Rheologi-
679 cal behavior of suspensions of modified and unmodified cellulose nanocrys-
680 tals in dimethyl sulfoxide. *Rheol. Acta*, *56*, 673–682.
- 681 Stefanis, E., & Panayiotou, C. (2008). Prediction of Hansen Solubility Pa-
682 rameters with a New Group-Contribution Method. *Int. J. Thermophys.*,
683 *29*, 568–585.
- 684 Uhlig, M., Fall, A., Wellert, S., Lehmann, M., Prévost, S., Wågberg, L.,
685 von Klitzing, R., & Nyström, G. (2016). Two-dimensional aggregation and
686 semidilute ordering in cellulose nanocrystals. *Langmuir*, *32*, 442–450.
- 687 Usov, I., Nyström, G., Adamcik, J., Handschin, S., Schütz, C., Fall, A.,
688 Bergström, L., & Mezzenga, R. (2015). Understanding nanocellulose chi-
689 rality and structure–properties relationship at the single fibril level. *Nat.*
690 *Commun.*, *6*, 7564.
- 691 Wade, R. H., & Creely, J. J. (1974). Structure and Stability of Chloroform-
692 Included Cotton Cellulose1. *Text. Res. J.*, *44*, 941–945.
- 693 Xu, X., Liu, F., Jiang, L., Zhu, J. Y., Haagensohn, D., & Wiesenborn, D. P.
694 (2013). Cellulose Nanocrystals vs. Cellulose Nanofibrils: A Compara-
695 tive Study on Their Microstructures and Effects as Polymer Reinforcing
696 Agents. *ACS Appl. Mater. Inter.*, *5*, 2999–3009.
- 697 Xu, X., Wang, H., Jiang, L., Wang, X., Payne, S. A., Zhu, J. Y., & Li, R.
698 (2014). Comparison between Cellulose Nanocrystal and Cellulose Nanofib-
699 ril Reinforced Poly(ethylene oxide) Nanofibers and Their Novel Shish-
700 Kebab-Like Crystalline Structures. *Macromolecules*, *47*, 3409–3416.
- 701 Yamane, C., Aoyagi, T., Ago, M., Sato, K., Okajima, K., & Takahashi, T.
702 (2006). Two different surface properties of regenerated cellulose due to
703 structural anisotropy. *Polym. J.*, *38*, 819–826.

- 704 Yao, K., Meng, Q., Bulone, V., & Zhou, Q. (2017). Flexible and Respon-
 705 sive Chiral Nematic Cellulose Nanocrystal/Poly(ethylene glycol) Compos-
 706 ite Films with Uniform and Tunable Structural Color. *Adv. Mater.*, 29,
 707 1701323.
- 708 Yin, Y., Tian, X., Jiang, X., Wang, H., & Gao, W. (2016). Modi cation
 709 of cellulose nanocrystal via SI-ATRP of styrene and the mechanism of its
 710 reinforcement of polymethylmethacrylate. *Carbohydr. Polym.*, 142, 206
 711 212.
- 712 Yoo, Y., & Youngblood, J. P. (2016). Green One-Pot Synthesis of Surface
 713 Hydrophobized Cellulose Nanocrystals in Aqueous Medium. *ACS Sustain-
 714 able Chem. Eng.*, 4, 3927-3938.
- 715 Yu, H., & Qin, Z. (2012). E ect of Cellulose nanocrystal on Crystallization
 716 Behavior of Poly(3-â€hydroxybutyrate-â€co-â€3-â€hydroxyvalerate).
 717 *Adv. Mat. Res.*, 430-432, 20-23.
- 718 Yu, H.-Y., Qin, Z.-Y., Liu, Y.-N., Chen, L., Liu, N., & Zhou, Z. (2012).
 719 Simultaneous improvement of mechanical properties and thermal stability
 720 of bacterial polyester by cellulose nanocrystals. *Carbohydr. Polym.*, 89,
 721 971-978.
- 722 Zhang, C., Salick, M. R., Cordie, T. M., Ellingham, T., Dan, Y., & Turng, L.-
 723 S. (2015). Incorporation of poly(ethylene glycol) grafted cellulose nanocrys-
 724 tals in poly(lactic acid) electrospun nanocomposite bers as potential scaf-
 725 folds for bone tissue engineering. *Mater. Sci. Eng. C Mater. Biol. Appl.*,
 726 49, 463-471.
- 727 Zhou, C., Chu, R., Wu, R., & Wu, Q. (2011). Electrospun polyethylene
 728 oxide/cellulose nanocrystal composite nano brous mats with homogeneous
 729 and heterogeneous microstructures. *Biomacromolecules*, 12, 2617-2625.