Functionalization of Cellulose Nanocrystals Powder by Non-Thermal Atmospheric-Pressure Plasmas

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Functionalization of cellulose nanocrystal powder by non-thermal atmospheric-pressure plasmas

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Abstract Despite promising characteristics such as the biodegradability and the environmentally-benign nature of cellulose nanocrystal (CNC) based composites, their poor dispersion and agglomeration in thermoplastic matrix during the melting process is a “bottleneck” in the development of these composites. In this work, a cylindrical atmospheric pressure dielectric barrier discharge (AP-DBD) was employed to functionalize CNCs to reduce their surface hydrophilicity and improve their dispersion in polar organic solvents. Three different gas mixtures were used for plasma treatment, argon/methane, argon/silane and an argon/methane followed by argon/silane. In all cases, the plasma treatment was conducted below 90°C as determined from optical emission spectroscopy (OES) analysis. The x-ray diffraction (XRD) analysis of both raw and plasma treated CNC powders confirms that the CNC crystallographic properties remain unchanged after plasma treatment. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis reveal the presence of hydrophobic C-H_x moieties on the CNC granular surface after argon/methane plasma treatment whereas SiH_x, Si-O-Si, SiC bonds were formed after argon/silane plasma treatment. Under these experimental conditions, water wettability tests reveal some significant water repellency of the naturally hydrophilic cellulosic raw material. Moreover, the formation the SiH_x moieties in silane-treated CNCs clearly enhances the hydrophobicity of the CNC powder in contrast to the sole C-H_x moieties synthesized by argon/methane plasma. High-resolution SEM images indicate the presence of agglomerated granules with 5-10 µm diameters in size. The surface functionalities of CNC powder enhance its dispersibility in polar solvents. Overall, this study emphasizes that AP-DBDs are suitable to process thermo-sensitive CNCs.

Keywords: CNC powder, hydrophobic, hydrophilic, surface treatment, AP-DBD

Conflicts of interest: There are no conflicts of interest to declare.

38 Introduction

39 In recent years, earth-abundant resources have attracted worldwide attention for the development of
40 high-performance environmentally benign polymeric materials based on green and sustainable
41 materials as a substitute to petroleum resources. Unfortunately, the performance of renewable
42 polymers is often inferior to traditional petroleum-based ones. The fabrication of composite
43 materials by embedding bio-fibers with renewable bio-based polymers could reduce the gap between
44 renewable and petroleum-based polymers and satisfy sustainable development needs (Abdul Khalil
45 et al. 2012; Ghasemlou et al. 2019; Koronis et al. 2013). In this context, nanostructured cellulose in
46 the form of nanocrystals (CNCs) has often been regarded as the next generation of renewable
47 reinforcement for the production of high performance biocomposites due to their excellent properties
48 such as a high tensile strength and low thermal expansion coefficient (Benítez and Walther 2017;
49 Ching et al. 2016; Ferreira et al. 2019). CNC-based nanocomposite materials could open new fields
50 of applications in various sectors including automotive, aerospace and packaging (Lourenço et al.
51 2020; Ventura et al. 2020; Wang et al. 2019; Wei et al. 2020).

52 The behavior of cellulose surfaces in different media as well as their interaction and compatibility
53 with different chemicals are of great importance for engineering new CNC-based composites. More
54 importantly, poor dispersibility of CNCs (strongly hydrophilic) in organic solvents is a serious
55 limitation that should be solved for any composite material development (Boluk et al. 2012; Bullard
56 et al. 2020; Fall et al. 2011; Mariano et al. 2014; Oguzlu et al. 2017). To overcome this shortcoming,
57 intense research was carried out for functionalizing the CNC surface in order to favor its dispersion
58 in these solvents. The effectiveness of some chemical modification techniques for CNC
59 functionalization has been demonstrated (Bullard et al. 2020; Habibi et al. 2013; Kaboorani and
60 Riedl 2015; Khanjanzadeh et al. 2018). However, such chemical techniques are complex and costly.
61 Furthermore, waste disposal, residual contamination and costly chemical storage are problematic,
62 which limits the efficient industrial implementation of the process. Another issue is the difficulty of
63 designing a single-step roll-on process to functionalize raw CNC powders. The use of non-thermal
64 plasmas can be considered as an innovative solution to meet these challenges and address the above-
65 mentioned shortcomings. This kind of plasma can be proposed as an efficient, green and scalable
66 alternative for the functionalization of CNCs. Non-thermal plasmas are exceptional reactive media
67 mainly composed of electrons, ions, atoms, radicals and molecules where some chemical reactions
68 can occur without using harmful catalyzers or chemicals. Of noteworthy interest is the atmospheric
69 pressure dielectric barrier discharge (AP-DBD) able to provide high densities of active species at
70 moderate gas temperature with a relatively low operating cost.

71 DBDs have proved their efficiency for functionalizing polymers by altering their outermost layer
72 without affecting their bulk properties. Actually, depending on the plasma interaction with polymer
73 surfaces, new functionalities can arise from various mechanisms including: (Arpagaus et al. 2018)
74 (i) surface etching or cleaning (the polymer surface being exposed to positive ions, UV radiation,
75 and reactive neutrals, this results in clean, decontaminated, or sterilized surfaces); (ii) formation of

functional groups on the polymer surface by either breaking the bonds of polymer chains or allowing the insertion of functional bonds; (iii) deposition of a surface layer by plasma polymerization of a precursor; and (iv) formation of nanoparticles from monomers and reactive gases followed by their attachment on the surface. Furthermore, it is possible to operate with different gases, which allows achieving various functionalization properties. For instance, modifying the gas environment enables controlling the reactive species in the plasma to induce several functional groups on the polymer surface. This provides a way of changing the wettability properties to improve hydrophilicity (Dimic-Misic et al. 2019; Dumitrascu et al. 2005; Pejić et al. 2020) or hydrophobicity (Chan et al. 2020). Another advantage of AP-DBDs is the possibility of treating polymers in the form of powders, (Arpagaus et al. 2018; Pichal et al. 2009) which makes this technology suitable for its implementation up to industrial scales.

Despite the promising properties of AP-DBDs for functionalizing cellulose-based materials, only a few works can be found in the literature concerning their use to modify the affinity of cellulose with polar and non-polar solvents. Abenojar et al. (2014) successfully improved the wettability of hydrophobic natural cork by using an air plasma keeping its exceptional properties as insulating material. Poaty et al. (2013) enhanced water repellency of black spruce wood surfaces by means of an Ar plasma with CF₄ gas as precursor of hydrophobic CF, CF₂ and CF₃ groups. The hydrophobicity of cellulose-based materials was also enhanced by producing superhydrophobic cellulose (Balu et al. 2008; Li et al. 2007) and hydrophobic nanofibrillated cellulose films (Kusano et al. 2018; Siró et al. 2013). Cho et al. (2009) also reported a dramatic decrease of the wettability of filter paper surface after its exposure to low pressure HMDSO and toluene plasmas whereas Dimitrakellis et al. (2017) obtained superhydrophobic paper by a double-step treatment consisting in surface etching followed by deposition of a thin fluorocarbon film. In addition, hydrophilic cellulose nanocrystals films were functionalized by appropriate plasma treatment to promote superhydrophilicity, hydrophobicity and superhydrophobicity surfaces by altering the plasma chemistry using different gaseous precursors (Matouk et al. 2020). Natural lycopodium powder was exposed to plasma for changing its intrinsic wettability properties from hydrophobic to hydrophilic, thus allowing to obtain stable water suspension (Bormashenko and Grynyov 2012).

In this work, an AP-DBD is used to functionalize a CNC powder to further improve its dispersability in non-polar solvents by altering its surface energy. Emitting plasma species (*i.e.* plasma precursors) were identified by optical emission spectroscopy (OES) to examine the influence of the CNC powder on the plasma behaviour. Besides, the temperature of the neutral plasma species was measured to make sure that its value remains sufficiently low to prevent any thermal damage of CNCs. Afterwards, the chemical modifications induced by the plasma on the CNC powder was evaluated using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). In addition, the wettability of the treated powder was also studied by water contact angle (WCA). The morphological properties were also assessed by scanning electron microscopy (SEM) and by high resolution transmission electron microscopy (HR-TEM). Finally, the raw and plasma exposed powders were dispersed in solvents widely used in polymer industries to examine the potential interest of new polymeric composites.

116 Experimental Setup and Methodology

117 Material

118 The pristine CNC powder was supplied by FPIInnovations (Pointe-Claire, QC, Canada). Different
119 solvents including water, dichloromethane (DCM) and dimethylsulfoxide (DMSO) were selected to
120 form 1% wt. suspension. Water was used as a solvent only for the dispersion test of untreated CNCs.
121 Dichloromethane was selected because it is a suitable solvent for polypropylene that could be
122 considered as the target matrix to synthesize the composites. Dichloromethane (99.9%) and
123 dimethylsulfoxide (99.9%) were purchased from Sigma Aldrich. The CNC powder was treated in
124 Ar/CH₄ (0.4 %) or Ar/SiH₄ (0.09 %). The argon flow was kept constant at 0.5 L/min. It was also
125 treated with a sequence consisting of Ar/CH₄ (0.4%) plasma followed by Ar/SiH₄ (0.09%) plasma.
126 Furthermore, untreated CNCs were considered as the reference.

127 Plasma Processing and Characterization

128 The DBD setup, depicted in Fig. 1, was developed exclusively for the treatment of CNC powder.

129

130 **Fig. 1** Scheme of the experimental set up.

131 As shown in Fig. 1, a quartz tube with inner and outer diameters of 11 and 13 mm was used as DBD
132 reactor, the tube forming the dielectric part. The two electrodes consist of 3 layers of thin films (5
133 nm of chromium, 1 μ m of copper and 10 nm of gold) deposited by low-pressure e-beam evaporation
134 on the external surface of the tube and facing each other. The effective area per electrode is $6.3 \times$
135 520 mm^2 . The gap between the dielectrics is about 10 mm. All experiments were conducted at
136 atmospheric pressure. One of the electrodes was grounded and the high voltage was applied to the
137 other electrode from a sine-wave generator (TREK, model 20/20C-HS, high voltage amplifier)
138 operating at 3.5 kHz. The applied high voltage was maintained to 7.2 kV. The electrical
139 characteristics of the discharge were monitored with a high voltage probe (Tektronix P6015A 75
140 MHz) and a current probe (Lilco LTD 13W5000 400Hz-100MHz) connected to a digital
141 oscilloscope (Tektronix wavejet).

142 The spectral emission of the DBD was collected by an optical set up and focused on the entrance
143 slit of a 500-mm focal length Andor Shamrock 500i monochromator with 600 grooves/mm
144 holographic diffraction grating. A CCD iStar camera (Andor technology, 1024 x 256) was used as
145 a detector.

146 CNC powder was introduced into the plasma by a system specifically designed and developed for
147 this purpose. The powder was placed in a container and introduced in the plasma reactor by means
148 of mechanical and periodic tapping on the container produced by a solenoid actuator at a frequency
149 of 10 Hz. This introduction system allows continuous CNCs introduction with a rate of ~100 mg/h
150 without forming large aggregates. Plasma-treated CNC powder was collected by a circular filter
151 formed of a 200 μm grid and placed downstream at the extremity of the dielectric tube.

152 **Materials characterization**

153 X-ray measurements were performed to verify whether or not the treated CNC powder keeps its
154 original crystalline structure. The powder was analyzed by grazing incidence X-ray diffraction
155 (GIXRD, $\omega=2^\circ$) by XRD (Bruker D8 Advance) diffractometer with $\text{CuK}\alpha$ radiation operated at 45
156 kV and 40 mA. sm transform infrared (FTIR) was also used to determine the nature of the functional
157 groups on the treated CNCs. Powder samples of reference and functionalized cellulose (2 mg) were
158 mixed with a matrix of KBr (200 mg) and further compressed to form pellets. The data acquisition
159 was achieved from 32 scans, in the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . The chemical
160 composition of the treated powders was analyzed by X-ray photoelectron spectroscopy (XPS, VG
161 Escalab 220I XL) using an $\text{AlK}\alpha$ X-ray source at 1486.6 eV. Quantitative information on the
162 wettability of the powder was obtained from water contact angle (WCA) measurements. It was
163 determined by using a 5 μL deionized-water droplet deposited manually with a micropipette on a
164 CNC powder bed. The images of the droplets were taken by using a Dino-Lite optical digital
165 microscope 10x-220x and the droplet contact angles were measured using the Canevas 11 free
166 software. The particle size (granulometry) and shape (morphology) of the CNC powder was
167 investigated by scanning electron microscopy (SEM Tescan Vega3 LMH). A droplet of the
168 suspension (1% CNCs in water) was deposited on a Cu-grid and coated with a thin film of lacy
169 carbon. To improve the contrast, the cellulose nanocrystals were stained with a 1 wt.% solution of
170 uranyl acetate for 30s. The sample was then immersed in distilled water to remove the excess of
171 chemicals, before drying at ambient temperature. The plasma treated CNCs were dispersed in the
172 previously-mentioned solvents in order to assess their compatibility with non-polar solvents.
173 Accordingly, 200 mg of powder (before and after treatment) was dispersed separately into 10 mL of
174 the selected solvents and sonicated at 2000 J (10 kJ/g) for one minute. In order to investigate the
175 plasma effect on the CNCs and evaluate the effectiveness of the treatment, the powders were
176 analyzed by different techniques.

Results and Discussion

Physicochemical properties of AP-DBD: effect of CNC introduction

OES analysis of the plasma emission was performed to examine the effect of introducing CNC powder on the plasma behavior.

Fig. 2 shows optical emission spectra of Ar/CH₄ and Ar/SiH₄ plasmas in the presence or absence of CNC powder. The Ar/CH₄ (Fig. 2a) plasma spectrum shows the presence of CH ($A^2\Delta \rightarrow X^2\Pi$ at 431.4 nm) emission which is suggested to be the plasma precursor for the formation of hydrophobic alkyl groups (Dimitrakellis and Gogolides 2018). On the other hand, in Ar/SiH₄ (Fig. 2b), the presence of a weak SiH molecular band ($A^2\Delta \rightarrow X^2\Pi$ at 414.2 nm) is observed. Such Si-based species are considered to be the plasma precursors for the formation of superhydrophobic CNC films (Matouk *et al.* 2020).

Furthermore, both plasma spectra exhibit the OH ($A^2\Sigma \rightarrow X^2\Pi$ at 306.4 nm) molecular band that is likely due to the presence of water impurities. When introducing CNCs in the plasma, its intensity increases (Fig. 2a and 2b). This might be understood as resulting from CNC powder outgassing as also suggested in ³².

Fig. 2 Emission spectra of **a** Ar/CH₄ and **b** Ar/SiH₄ plasmas in the presence and absence of CNCs.

196 The plasma treatment time together with the tight control of the gas temperature are key issues to
 197 prevent thermal damage. On the one hand, at atmospheric pressure, the number of collisions between
 198 heavy molecules is large enough to assume that the rotational temperature of probe molecules such
 199 as OH is in equilibrium with the gas temperature. Therefore, measuring the rotational temperature
 200 of OH provides a reliable value of the gas temperature. It was estimated by fitting the experimental
 201 spectra with theoretical simulations of OH spectra obtained by the LIFBASE software developed by
 202 Luque and Crosley (1999). According to these fits, the gas temperature was found equal to 350 and
 203 360 K in Ar/CH₄ and Ar/SiH₄ plasmas, respectively. On the other hand, the treatment time is
 204 calculated as the residence time of CNC powders in the plasma and it can be assessed as a function
 205 of the experimental conditions such as the gas flow rate ($\phi = 0.5$ L/min) and the geometry of the
 206 plasma region where the gas flows in the reactor, *i.e.* the length of the electrodes ($l = 520$ mm) and
 207 the section of the quartz tube ($S \sim 95$ mm²) as (Eq. 1): (Brunet et al. 2017)

$$208 \quad t = \frac{l \cdot S}{\phi} \quad (\text{Eq. 1})$$

209 Therefore, CNC treatment time was equal to ~ 6 s in all plasma conditions since none of the
 210 aforementioned experimental conditions were changed. It is worth mentioning that the double
 211 plasma treatment (methane and silane) makes the CNC powders be in contact with the plasma during
 212 ~ 12 s that is sufficiently short to make the intrinsic properties of the thermosensitive CNC powder
 213 unchanged.

214 **Modification of CNC powders by the AP-DBD process, CNC** 215 **characterization**

216 From here, CNC powders treated by Ar/CH₄, Ar/SiH₄ and Ar/CH₄ followed by Ar/SiH₄ plasmas
 217 will be denoted as CNC-methane, CNC-silane and CNC-methane/silane, respectively whereas the
 218 untreated reference sample is referred as untreated CNCs.

219 The treated powders were physically and chemically characterized to identify the parameters that
 220 could explain the affinity of CNC powder with different solvents (see below). Changing the CNC
 221 properties to favour their dispersion in non-polar solvents may be the key to eventually synthesize a
 222 composite.

223 *X-ray diffraction:*

224 Fig. 3 illustrates XRD patterns for pristine powder and for CNC-methane, CNC-silane and CNC-
 225 methane/silane. As shown in Fig. 3, no obvious difference between untreated and treated CNCs
 226 occurs. Indeed, the characteristic diffraction peaks remain at about the same 2θ angles around 14.9° ,
 227 16.7° , 22.5° and 34.5° corresponding to the (1 $\bar{1}$ 0), (110) and (200) crystallographic planes (French
 228 2014).

Fig. 3 XRD patterns of the reference and treated plasma CNCs.

The shoulder at about 20.5° (2θ) can be attributed to the (012) and (102) reflections in agreement with the characteristic diffraction peaks of cellulose I_α (French 2014). The crystallinity index (CrI) was calculated according to the Segal method (Segal et al. 1959) using (Eq. 2) (Ju et al. 2015) where I_{200} is the height of the (200) peak whereas I_{am} is the minimum intensity between the (200) and (110) peaks. I_{200} represents both the crystalline and amorphous material, while I_{am} is related to the amorphous material.

$$CrI = \left(\frac{I_{200} - I_{am}}{I_{200}} \right) \cdot 100 \quad (\text{Eq. 2})$$

The crystallite size is given by the Scherrer equation (Eq. 3).

$$\tau = \frac{K\lambda}{\beta \cos \theta} = \frac{0.145}{\beta \cos \theta} \quad (\text{Eq. 3})$$

where τ is the size perpendicular to the lattice plane represented by the main peak, in our case peak (200); K is a constant that depends on the crystal shape, 0.94 (Maiti et al. 2013), λ is the wavelength of the incident beam in the diffraction experiment, 0.1542 nm; β is the FWHM in radians and θ is the position of the peak (half of the plotted 2θ value). The values of the crystallinity index and crystallite size for each sample are summarized in Table 1.

Table 1 Crystallinity index and crystallite size for untreated and treated CNC powder.

Powder	CrI (%)	Size (nm)
Untreated	74.5	3.9
CNC-methane	74.1	4.1
CNC-silane	73.9	3.9
CNC-methane/silane	74.2	4.0

The CNC crystallinity index of about 74% obtained for each condition shows that the intrinsic crystalline structure of CNCs is not modified by the plasma treatment. This suggests that CNC

modification is mainly localized on its surface and does not affect the bulk. Similar results were reported for CNC films treated in AP-DBD (Matouk et al. 2020).

Fourier-transform infrared spectroscopy:

FTIR measurements were performed on both untreated and plasma treated CNC powder. The results are shown in Fig. 4. All spectra exhibit almost similar profiles, confirming that plasma treatment mainly yields chemical changes on the CNC surface without altering the bulk.

All spectra show the band at 3348 cm^{-1} associated to O-H band stretch (Altaner et al. 2014), while the bands at 2975 and 2902 cm^{-1} are attributed to symmetric C-H stretching (Aguayo et al. 2018; Yu et al. 2014). The wide band observed in the range of $3700\text{--}3000\text{ cm}^{-1}$ is related to hydrogen bonding (Hishikawa et al. 2017). More specifically, hydroxyl groups are bonded to numerous intra and intermolecular hydrogen bonds that build the cellulose structure. The band at 1644 cm^{-1} originates from the CNC absorbed moisture (Liu et al. 2006; Wang et al. 2013). The bands around 1430 cm^{-1} are related to the symmetrical C-H bending of CH_2 group (Liu et al. 2006). The band at 1038 cm^{-1} corresponds to O-H bending vibration of hydroxyl group (Celebi and Kurt 2015). The band corresponding to methylene group (CH_2) asymmetric stretching vibration occurs at about 2987 cm^{-1} (Lu et al. 2005). Finally, the band at about 1124 cm^{-1} corresponds to C-O stretching, and that at about 1780 cm^{-1} to C=O stretching of an hydrolyzed ester functional group present on the CNCs (Alemdar and Sain 2008).

Fig. 4 FTIR signal of reference CNCs, CNC-methane, CNC-silane and CNC-methane/silane treated powder.

The FTIR spectra of all plasma treated CNCs differ only slightly from the untreated one. Si and CH related bands lie in the range between 1000 cm^{-1} to 1250 cm^{-1} . However, their signature overlaps with the Si-O-Si and C-O-C vibrations peaks in all cases. Two new bands at 1032 cm^{-1} and 2280 cm^{-1} can be distinguished in the CNC-silane spectrum. The band at 1032 cm^{-1} results from Si-O vibrations (overlapping C-O vibrations) (Yin et al. 2019). Its presence suggests that a salinization reaction occurs. On the other hand, the 2280 cm^{-1} band may correspond to the decomposition of the

279 SiH₄ precursor as confirmed by the presence of the Si-H stretching mode. The occurrence of Si-O-
 280 Si, Si-O-C and Si-C components may be due to the interaction of SiH_x plasma species with O
 281 stemming from water outgassing and with C from the CNC surface. Finally, no significant changes
 282 are observed for the position of the characteristic bands, indicating that the cellulose backbone is not
 283 significantly disturbed, in agreement with the X-ray diffraction results (Fig. 3).

284 *Photoelectron spectroscopy:*

285 The chemical composition of the untreated and treated CNCs was analyzed using XPS analysis.

286
 287 **Fig. 5** XPS survey of reference CNCs, CNC-methane, CNC-silane and CNC-methane/silane
 288 treated CNC powder.

289
 290 In Fig. 5, all XPS survey spectra display two expected peaks in the regions of 531 and 285 eV
 291 corresponding to oxygen (O 1s) and carbon (C 1s) atoms, respectively. However, the XPS spectra
 292 of CNC-silane and CNC-methane/silane show the presence of an additional peak at 102 eV which
 293 is attributed to Si 2p. The occurrence of this peak undoubtedly proves that Si-based plasma
 294 effectively incorporates Si-based species on the CNC surface.

Powder	Untreated CNCs	CNC-methane	CNC-silane	CNC-methane/silane
C	60	62.2	47.1	38.1
O	40	37.8	36.7	41.7
Si	-	-	16.2	20.2
O/C	0.7	0.6	0.9	1.1

295
 296 **Table 2** Percentage of C, O, and Si in untreated CNC powder and in CNCs treated in methane,
 297 silane and methane/silane

298
 299 The oxygen to carbon ratio ([O]/[C]) is commonly considered to evaluate the amount of lignin in
 300 lignocellulosic materials. The results shown in Table 2 indicate that [O]/[C] is ~0.7 for untreated
 301 samples, a value close to the theoretical ratio (0.8). In the case of CNC-methane, this ratio decreases

to 0.6 indicating the decay of oxygen from the CNC surface due to outgassing and/or the increase of carbon concentration because of the presence of CH_x moieties on the surface (Matouk et al. 2020), resulting from CH_4 decomposition in the plasma as suggested by OES. On the other hand, in silane (*i.e.* for CNC-silane and CNC-methane-silane), the $[\text{O}]/[\text{C}]$ ratio reaches 0.9 and 1.1 respectively. Similar values were found by Alexander et al. (1999) in organosilicon films deposited in low pressure plasmas. Conversely, it should be highlighted that the chemical composition is strongly influenced by the nature of the organosilicon precursor and by the specific plasma conditions as noted by Twomey et al. (2008). The carbon-based species on the CNC surface were identified by performing a deep analysis of C 1s high resolution-XPS scan (Fig. 6).

Fig. 6 XPS fitted spectra of C(1s) peak of **a** reference CNCs and **b** CNC-methane **c** CNC-silane and **d** CNC-methane/silane treated powder.

The (C 1s) peak of untreated (Fig. 6a) and methane treated CNC powder (Fig. 6b) were deconvoluted into three sub-peaks at 285.0, 286.4 and 287.8 eV ascribed to C-C/C-H, C-O, C=O/O-C-O bonds, respectively. In addition, the CNC-methane C 1s peak has one extra small contribution of adventitious carbon at 283 eV. Comparing Fig. 6a and Fig. 6b, it can be clearly concluded that Ar/CH_4 plasma favors the formation of C-H bonds, which can be understood as resulting from the formation of CH species in Ar/CH_4 plasma.

Fig. 6 (c and d) presents the deconvolution of the C 1s peak for CNC-silane and CNC-methane/silane. In addition to the three peaks observed for untreated CNCs, a new peak at 283.3 eV appears which is attributed to Si-C bonds (Kusunoki and Igari 1992). Therefore, the major contribution to the C1s peak is due to Si-C groups as also confirmed by FTIR. Other minor contributions to the C1s peak include O-C=O (288eV) and $\pi-\pi^*$ (291.eV) components. In this work, the chemical shift between each contribution is of the order of the instrument resolution (0.2 eV). Therefore, based on the data presented in Table 2, the surface composition of the CNC-methane and

CNC-methane/silane treated powders is polymer-like as $\text{Si}_x\text{O}_y\text{C}_z\text{H}$. This result agrees with the FTIR analysis described in the previous section as it reveals (i) plasma assisted fragmentation of the gas precursor that yields C-H_x and SiH_x species and (ii) partial oxidation of the gas precursor fragments during the plasma process to form the Si-O-Si network.

Water Contact Angle:

The efficiency of plasma treatment to modify CNC powder affinity to water was assessed by performing static water contact angle measurements on a CNC powder bed. Fig. 7 exhibits the results for untreated CNCs, CNC-methane, CNC-silane and CNC-methane/silane.

Fig. 7 WCA measurements on a powder bed formed with the untreated, and CNC-methane, CNC-silane and CNC-methane/silane treated powder.

The WCA values for all plasma exposed CNCs exceed 80° in contrast with the 30° value measured for untreated CNCs which are naturally hydrophilic. These findings on the hydrophobic behaviour are in agreement with the conclusions of FTIR and XPS results (confirmed by the presence of C-O and C=O components). The WCA increase for the plasma exposed CNCs could be ascribed to the presence of low-surface energy components coatings. For CNC-methane, XPS measurements reveal that the chemical composition of the top layer is controlled by CH_x hydrophobic functional groups, which makes the treated CNC powder exhibiting a hydrophobic feature with $\text{WCA} = 80^\circ$. Similar results are reported in (Matouk et al. 2020; Rincón et al. 2016). Regardless of some significant differences observed in the FTIR and XPS analysis, the average static contact angle lies within 10 degrees for CNC-silane and CNC-methane/silane (150° vs 140° , respectively). In the previous section, it was mentioned that the chemical composition is slightly different between these two treated CNCs. The CNC-silane surface is composed of 67.5% of hydrophobic components (Si-C and C-C/C-H) as compared to 53.9% for CNC-methane/silane. This could explain the slight difference in the WCA for these two treatments. Similar results concerning the increase of WCA of CNC films treated by Ar/CH_4 and Ar/SiH_4 plasmas were reported in a previous work (Matouk et al. 2020). Comparable results were also observed for hydrophobic coatings on paper-based substrates. Mukhopadhyay et al. (2002) achieved a WCA value of 140° using fluorocarbon precursor (perfluoro-methylcyclohexane) on cellulose filter paper. Furthermore, by using fluorocarbon (CF_4) and organosilicon (HMDSO) precursors at atmospheric pressure DBD, Wolf (2012) obtained similar values of WCA, namely 100° (for CF_4) and 140° (for HMDSO).

Dispersion Tests:

The dispersion test of the CNCs in different solvents is a key feature to assess the dispersion of CNCs to form new nanocomposites. Cellulose nanocrystals are known to show poor dispersion because of intermolecular interactions via the van der Waals forces in the nanomaterials. Hence, the

363 CNC dispersion depends on its surface functionalization, the surface/volume aspect ratio and the
 364 surface charges. Qualitative information concerning the affinity of the treated and untreated CNCs
 365 with water, DMSO and DCM were obtained by observing their dispersion in these solvents after 1h
 366 (Fig. 8). More specifically, the amount of material deposited by sedimentation and the turbidity of
 367 the solvent after 1 hour were examined. For the untreated CNC powder as well as for CNC-methane
 368 and CNC-methane/silane, the dispersibility in water, DCM and DMSO (henceforth, $d(water)$,
 369 $d(DCM)$ and $d(DMSO)$, respectively) can be sorted in the ascending order as
 370 $d(water) > d(DCM) > d(DMSO)$; for CNC-silane, we obtained $d(DCM) > d(water) > d(DMSO)$.
 371 A simple visual comparison shows that the liquid phases of the dispersed untreated CNCs and CNC-
 372 methane powder behave similarly when using the same solvent (water, DCM or DMSO). Untreated
 373 CNCs form a transparent stable suspension with water and DCM while a turbid solution is observed
 374 in DMSO. In the case of CNC-methane sample, its dispersion in water is also possible while it is
 375 limited or incomplete in DCM. Concerning its dispersibility in DMSO, it produces a turbid solution.
 376 These results indicate that the Ar-CH₄ plasma has partially modified the CNC surface.
 377 Both CNC-silane and CNC-methane/silane show a similar behavior in the various solvents. The
 378 liquid phases with the dispersed samples are turbid for the three solutions, indicating the
 379 effectiveness of the plasma treatment. The result obtained with DMSO is in agreement with that
 380 found by Jiang et al. (2019). As it can be seen in Fig. 7, the wetting property of the CNC-
 381 methane/silane sample is similar to that of CNC-silane even though the final treated powder exhibits
 382 differences in colour. The solution containing CNC-silane tends to be yellow in contrast to the one
 383 with CNC-methane/silane that is colorless. This is due to the silane treatment that make the CNC
 384 powder yellow. Our result indicates that combining two plasma treatments (Ar/CH₄ followed by
 385 Ar/SiH₄) yields a higher efficiency than each treatment separately.

Fig. 8 Dispersion tests of the untreated and plasma treated CNC–methane, -silane in **a** water, **b** DMSO and **c** DCM.

Scanning Electron Microscopy:

The morphology of the untreated powder can be observed in the SEM image shown in Fig. 9. The powder is formed of granules of 10 μm diameter. Each granule (of microscopic level) is formed of numerous individual cellulose crystals (of nanometer size).

Fig. 9 SEM image of untreated CNCs.

Dense granules can be seen on the SEM image, which may reduce the plasma treatment to the outermost layer of the CNC powder, thus preventing in-depth modification of all CNC granules. Consequently, the dispersion of modified CNCs in non-polar solvents could be limited, which may explain the similar dispersion results obtained for untreated CNCs and CNC-methane powder. From this analysis it could be understood that the effectiveness of plasma treatment is only limited by the initial size and shape of CNC powder granules.

Conclusion

The present work uncovered an effective technique for modifying the surface of cellulose nanocrystals by non-thermal plasmas. Using a specifically-designed cylindrical DBD reactor, three different plasmas were employed. Accordingly, mixtures of argon with methane (Ar/CH₄) or silane (Ar/SiH₄) and a successive combination of these two mixtures (Ar/CH₄ followed by Ar/SiH₄) were used in order to promote the dispersibility of CNC powder in organic solvents. The results show that depending on the gas composition, different functionalized CNCs could be obtained. All treatments led to a hydrophobic behavior of the CNC powder, although the highest hydrophobicity is achieved with Ar/SiH₄ and Ar/CH₄-SiH₄. It is noteworthy that the crystalline composition of pristine nanocellulose remains unaffected during all treatments. This is likely due to the short plasma treatment time and to the fact that the gas temperature was always below 360 K. XPS results show that Ar/CH₄ plasma exposure produces CH_x functional groups on the CNC film surface that is responsible for hydrophobic functionalities. Concerning silane-based treatment (SiH₄ and CH₄-SiH₄), one can conclude that the CH_x and/or SiH_x species react with the water adsorbed at the surface of the CNC powder granules from ambient humidity for producing different hydrophobic groups. Finally, the proposed plasma treatment opens a new way to modify the wettability of the CNCs without impacting their intrinsic properties.

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563

Figures

Figure 1

Scheme of the experimental set up.

Figure 2

Emission spectra of a Ar/CH₄ and b Ar/SiH₄ plasmas in the presence and absence of CNCs.

Figure 3

XRD patterns of the reference and treated plasma CNCs.

Figure 4

FTIR signal of reference CNCs, CNC-methane, CNC-silane and CNC-methane/silane treated powder.

Figure 5

XPS survey of reference CNCs, CNC-methane, CNC-silane and CNC-methane/silane treated CNC powder.

Figure 6

XPS fitted spectra of C(1s) peak of a reference CNCs and b CNC-methane c CNC-silane and d CNC-methane/silane treated powder.

$$\theta = 30^\circ \pm 2^\circ$$

CNC-Reference

$$\theta = 80^\circ \pm 1^\circ$$

CNC-Methane

$$\theta = 150^\circ \pm 1^\circ$$

CNC-Silane

$$\theta = 140^\circ \pm 1^\circ$$

CNC-Methane-Silane

Figure 7

WCA measurements on a powder bed formed with the untreated, and CNC-methane, CNC-silane and CNC-methane/silane treated powder.

Figure 8

Dispersion tests of the untreated and plasma treated CNC–methane, -silane in a water, b DMSO and c DCM.

Figure 9

SEM image of untreated CNCs.