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1 INFLUENCE OF HEMICELLULOSE CONTENT AND CELLULOSE CRYSTAL 2 CHANGE ON CELLULOSE NANOFIBERS PROPERTIES

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17

18**Abstract:** This study aimed to evaluate the properties of cellulose nanofibers (CNFs) with different
19hemicellulose contents and cellulose II polymorphs. A link was found between these
20polysaccharides and the properties of CNFs. A decrease in crystallinity (from 69 to 63%) and
21changes in the crystalline structure of cellulose subjected to an alkaline environment were observed,
22promoting the partial conversion of cellulose I to cellulose II (from 2 to 42%) and preventing CNFs
23production at NaOH concentrations higher than 5%. Most treatments showed pseudoplastic fluid
24behavior, except for the 10% NaOH treatment over 2 hours, which showed Newtonian fluid
25behavior. The quality index of the reference CNFs (TEMPO-oxidized) was the highest (80 ± 3),
26followed by that of the 5% NaOH-treated (68 ± 3 and 22% energy savings compared to the
27untreated sample), and the untreated (63 ± 3) samples; and the 10% NaOH treatments had quality
28indices of 51 ± 3 and 32 ± 1 , respectively.

29

30**Keywords:** Cellulose nanofibers; Cellulose polymorphs; Nanocellulose; Polyose; Shear rheology.

31

32 1. Introduction

33 In recent years, there has been growing interest the production and application of
34 cellulose nanofibers (CNFs). CNFs are usually obtained from fibers that have native cellulose
35 polymorphs, known as cellulose I. There are three other types of cellulose polymorphs,
36 cellulose II, III, and IV. Cellulose I and II are the most studied and most used in industrial
37 applications. Some works in the literature report that the conversion of cellulose I to cellulose II
38 hinders the nanofibrillation process [1,2].

39 Cellulose II can be obtained from native cellulose by mercerization and regeneration
40 processes because it has a more stable structure. However, crystalline structure conversion
41 through these processes results in materials with inferior mechanical properties [2].

42 One of the essential characteristics of nanocellulose-based materials is their complex
43 rheology. Because of this characteristic, processing is challenging, especially finding the most
44 suitable application according to its produced characteristics, which can vary [3] due to the
45 source of the materials and the method by which the materials were obtained. The deformation
46 of these suspensions at different shear rates is essential in various potential applications [3].

47 The rheology of an aqueous suspension of nanocellulose is influenced by hydrogen
48 bonding between nanofibrils and water molecules [4], which is directly related to the efficiency
49 and quality of nanofibrillation, where suspensions with high nanocellulose content have a gel-
50 like appearance and consequently a higher viscosity. In comparison, less nanofibrillated
51 materials have a more aqueous appearance and a lower viscosity. The viscosity of nanocellulose
52 materials is an important factor that must be optimized to be low enough to enable the
53 material's processing and high enough to improve the dispersion [5].

54 The morphological and chemical composition of the raw material affects the rheological
55 and mechanical properties of the obtained cellulose nanomaterial and the quality of the final
56 product [6–8]. The morphological properties of CNFs are dependent on the source and
57 production process. However, CNFs has re-active surfaces, low densities (1.54 g/cm^3) when
58 compared to other materials, and a high number of free hydroxyl groups that contribute to the
59 grafting of various chemicals to reach specific properties [9].

60 Lignocellulosic biomass is formed by cellulose, hemicellulose, lignin, and other minor
61 components that create a complex matrix structure with natural recalcitrance, resulting from
62 both the intrinsic molecules' nature and their interactions [10]. These components do not occur
63 individually in the cell wall structure but are linked together in the Lignin-Carbohydrate
64 Complex through stable chemical bonds [11].

65 Hemicellulose is the second most abundant class of hydrophilic polysaccharides found
66 in nature and in the plant cell wall, closely associated with cellulose and lignin in all higher

67 plants, where they represent 20 - 30% of the plant dry mass [12]. These polymers has much
68 lower molar weight when compared to cellulose, and contains a considerable degree of
69 ramifications between its chains, possessing a highly amorphous nature, unlike cellulose, and is
70 more susceptible to chemical hydrolysis under milder conditions [13]. Hemicellulose has a large
71 proportion of hydroxyl groups that are bound in intra- and intermolecular hydrogen bonds,
72 making it more hygroscopic than cellulose, and some of these bonds naturally bind water to
73 cellulose molecules [14].

74 Due the higher number of free hydroxyl groups, hemicellulose presents a highly
75 hydrophilic nature, and together with its amorphous nature and ramified structure, causes it to
76 swell greatly when in contact with water molecules [15]. The swelling of the hemicellulose also
77 has a strong impact on the cellulose crystal structure, due to a strong bond with the cellulose
78 surfaces [16]. These polysaccharides may have an important role to play in the production of
79 CNFs, for example, Iwamoto et al. [17] demonstrated that hemicellulose acts as an inhibitor of
80 the cellulose microfibrils coalescence, thus contributing to the ease of the nanofibrillation
81 process.

82 The number of studies regarding CNFs production and applications has increased
83 progressively; hence, it is essential to extend the knowledge of its behavior and the relations
84 between its chemical composition and the performance of derived materials. Therefore, this
85 study aimed to evaluate the effects of the modifications on the properties of eucalyptus CNFs,
86 especially the rheology of those containing different hemicellulose levels and cellulose
87 I/cellulose II polymorph ratios.

88 **2. Experimental**

89 **2.1 Materials**

90 Once-dried BHKP (Bleached eucalyptus kraft pulp) donated by Klabin S.A.
91 (Paraná/Brazil), was used throughout this work. All the materials and chemicals were used as
92 received from the manufacturers: deionized water; sodium hydroxide (NaOH) (ACS reagent,
93 $\geq 98\%$, Sigma–Aldrich, Brazil); TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical -
94 $C_9H_{18}NO$) (ACS reagent, $\geq 98\%$, Alfa Aesar, Germany); hydrochloric acid (HCl) (ACS reagent,

95 37%, Neon, Brazil); sodium bromide (NaBr) (ACS reagent, 99%, Synth, Brazil); sodium
96 hypochlorite (NaClO) (ACS reagent, $\geq 10\%$, Dinâmica, Brazil); absolute ethyl alcohol (C₂H₆O)
97 (ACS reagent, 99%, Sigma–Aldrich, Brazil); 0.5 M cupriethylenediamine solution (ACS
98 reagent, Dinâmica, Brazil) and sulfuric acid (H₂SO₄) (ACS reagent, 99%, Sigma–Aldrich,
99 Brazil).

100 **2.2 Alkaline treatment of cellulose kraft pulp**

101 The alkaline treatment was performed under different concentration conditions and
102 reaction times to achieve fibers with different hemicellulose contents. This step was carried out
103 according to Dias et al. [18]. The pulp was treated with 5 and 10 wt% aqueous NaOH solution
104 at 80 °C for 1 and 2 h under continuous stirring (800 rpm). After treatment, the fibers were
105 filtered and repeatedly washed with deionized water until the pH reached neutrality. They were
106 then dried in an air-circulating oven at 50 °C for 24 h.

107 **2.3 TEMPO-mediated oxidation treatment of cellulose kraft pulp**

108 This treatment was also performed as a quality reference to compare the CNFs
109 properties obtained after the alkaline treatments. This step was based on the methodology of
110 Fukuzumi et al. [19]. The fibers (1 g) were suspended in water (40 mL) containing TEMPO
111 (0.016 g) and sodium bromide (0.1 g). The NaClO solution (10 mmol) was added to the slurry,
112 and the mixture was stirred at room temperature for three hours, and a pH of 10 was maintained
113 by adding drops of 0.5 M NaOH. Afterward, 100 mL of ethanol was added to quench the
114 reaction, and the system pH was corrected to 7 by the addition of drops of 0.5 M hydrochloric
115 acid (HCl).

116 **2.4 Fourier Transformed Infrared Spectroscopy (FTIR)**

117 To investigate the changes in functional groups of CNFs that the treatments may have
118 caused, FTIR analyses were performed employing an Attenuated Total Reflectance (ATR) FTIR
119 Spectrometer Varian 600-IR Series equipped with a GladiATR from Pike Technologies. The
120 samples were scanned from 4000 to 600 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹.

121 **2.5 Monosaccharide's quantification**

122 Monosaccharides (glucan, xylan, mannan and galactan) were determined after acid
123 hydrolysis. The samples were hydrolyzed by adding 50 mg of fibers to 0.5 mL of 72 wt%
124 sulfuric acid. The mixture was heated in a water bath at 30 °C for 1 h and then diluted to 4 wt%
125 sulfuric acid concentrations with deionized water. The diluted mixture was then heated at 105
126 °C for 150 min before cooling on ice. An ion chromatography system (Dionex ICS 5000, USA)
127 with a Dionex CarboPac PA1 column at 25 °C with a flow rate of 1 mL min⁻¹ of MQ-water. The
128 detector sensitivity was optimized by post column addition of 200 mM NaOH at a flow rate of
129 0.5 mL min⁻¹ to perform the analysis.

130 **2.6 Cellulose nanofibers (CNFs) production**

131 Eucalyptus cellulose fibers were immersed in distilled water at 2 wt% consistency for
132 three days to guarantee fiber swelling. Then, they were nanofibrillated by passing the pulp
133 through an ultrafine grinder Supermasscolloider (model MKCA6-2, stone model MKGA6-80,
134 Masuko Sangyo Co., Ltd., Japan). The stone speed was fixed at 1,500 rpm [18]. Five passes
135 through the equipment were necessary to obtain cellulose nanofibers.

136 **2.7 Turbidity, visual inspection, and stability of the suspensions**

137
138 The turbidity, measured in Nephelometric Turbidity Units (NTU), of the CNFs
139 suspensions was measured with a portable turbidimeter (Aqualytic, AL-250, wavelength 860
140 nm) on a CNFs suspension that was diluted to 0.1 wt% and stirred for 1 min with Ultra Turrax
141 (IKA T-25) at 10,000 rpm. The suspensions were placed in the test locations for photo
142 acquisition. Images were acquired at 0, 10, 30 min and 1, 2, 3, 4, 5, 6, 7, 8, and 24 h. Fiji
143 software was used to estimate the CNFs decantation in the suspensions, and then stability was
144 calculated according to Eq. 1 proposed by Silva et al. [20]:

145
$$\text{Stability} = \left(\frac{\text{Dispersed}}{\text{Total}} \right) \times 100\% \quad (1)$$

146 where “Dispersed” is the height corresponding to suspended particles, and “Total” is the height
147 of all the liquid in the recipient location.

148 **2.7 Micro size area (μm^2)**

149 The CNFs suspensions were characterized using a light microscope (Zeiss Axio AX10,
150 Germany). The suspensions were previously diluted to 0.1 wt%, stirred for 1 min with Ultra
151 Turrax (IKA T-25) at 10,000 rpm, and sonicated for five minutes in an ultrasonic bath to obtain
152 a better dispersion. Photographs were taken at 10x magnification and analyzed using Fiji
153 software. The micro sized area was obtained by following the methodology described elsewhere
154 [21].

155 **2.8 Transmission Electron Microscopy (TEM)**

156 The morphology of the CNFs was investigated using a Tecnai G2-12 (FEI company,
157 USA) instrument with an accelerated voltage of 80 kV. Sample preparation and TEM
158 configurations followed recommendations described elsewhere [22]. Diameter measurements of
159 CNFs were performed for at least 300 individual structures per image using open-source
160 software biological image analysis Fiji [23].

161 **2.9 X-ray diffraction (XRD)**

162 XRD analyses were performed using a PANalytical X'Pert PRO MPD X-ray
163 diffractometer (Malvern Panalytical, UK) equipped with an X'celerator detector with a Cu-K α
164 source ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 10-40°, with a 0.066° interval at 4°/min step rate. The
165 equipment was operated at a tension of 45 kV and a current of 40 mA.

166 The theoretical coordinates of native cellulose I β (full width at half maximum (FWHM)
167 = 0.1) and cellulose II (FWHM = 0.1) were extracted from crystallography information data
168 (.cif) using the software Mercury 2020.2.0 (CCDC, UK) obtained from the Supplementary
169 Information accompanying the original work Nishiyama et al. [24].

170 The patterns were deconvoluted using the Gaussian function with Magic Plot 2.9
171 (Magicplot Systems, Russia). For the amorphous halo, the cellulose II pattern with full
172 width at half maximum (FWHM = 9), only varying its intensity, was used, as suggested
173 in the literature [25]. After deconvolution, the crystalline fraction (CF) was calculated from the

174 ratio between the area below all the crystalline peaks and the total area below the curve,
175 determined after deconvolution from Eq. 2:

$$176 \quad CF(\%) = \frac{\sum \text{Area}_{\text{Crystalline Peaks}}}{\sum \text{Area}_{\text{Crystalline Peaks}} + \text{Area}_{\text{Amorphous Halo}}} \times 100 \quad (2)$$

177 For each NaOH-treated sample, the cellulose I (CI) and cellulose II (CII) contents were
178 determined. From the sum of the peak area of the same crystal system (\sum area for cellulose I and
179 \sum area for cellulose II), the CI and CII percentages were calculated using Eq. 3 and 4, which
180 were proposed in a study by Oudiani et al. [26].

$$181 \quad CI(\%) = \frac{\sum \text{Area}_{\text{CI}}}{\sum \text{Area}_{\text{CI}} + \text{Area}_{\text{CII}}} \times 100 \quad (3)$$

$$182 \quad CII(\%) = \frac{\sum \text{Area}_{\text{CII}}}{\sum \text{Area}_{\text{CI}} + \text{Area}_{\text{CII}}} \times 100 \quad (4)$$

183 The crystallite size (CS) of the (200) plane peak was calculated according to Scherrer's
184 equation (Eq. 5):

$$185 \quad D = \frac{K \times \lambda}{\beta \times \cos\theta} \quad (5)$$

186 where D is crystallite size (Å), K (0.9) is a constant that refers to crystal shape, λ is the
187 wavelength of the ray used (copper), β is the FWHM of the peak, in radians, and θ is Bragg's
188 angle of (200) plane diffraction.

189 **2.10 Rheological behavior**

190 The rheological behavior of CNFs suspensions at a 1% wt concentration at 25 °C was
191 studied on a HAAKE ReoStress 6000 (Thermo Scientific, Karlsruhe, Germany) rheometer
192 coupled to a HAAKE A10 (Thermo Scientific) thermostatic bath and a universal temperature
193 control system HAAKE UTM Controller (Thermo Scientific brand, Karlsruhe, Germany) using
194 a CC25 DIN Ti concentric cylinder sensor (D = 25.0 mm; Gap = 5.3 mm). The Newton law (Eq.
195 6), Power-law (Eq. 7), and Herschel-Bulkley (Eq. 8) models were adjusted to the data of the
196 second increasing curve to determine the fluid flow profile and obtain the viscosity. The
197 adjustment of the models was performed by the Statistical Analysis System 9.1.2 statistical
198 package (SAS Institute Inc, USA) using three repetitions:

199 $\tau = \mu \times \dot{\gamma}$ (6)

200 where τ is the shear stress in (Pa), μ is the dynamic viscosity (Pa.s), and $\dot{\gamma}$ is the shear rate (s^{-1}).

201 $\tau = K \times \dot{\gamma}^n$ (7)

202 where τ is the shear stress in (Pa), K is the consistency index ($Pa\ s^n$), $\dot{\gamma}$ is the deformation rate
203 (s^{-1}), and n is the flow behavior index (dimensionless).

204 $\tau = \tau_0 + K \times \dot{\gamma}^n$ (8)

205 where τ is the shear stress in (Pa), τ_0 is the yield stress in (Pa), K is the consistency index ($Pa\ s^n$), $\dot{\gamma}$ is the deformation rate (s^{-1}), and n is the flow behavior index (dimensionless).

207 The apparent viscosity values were evaluated at a shear rate of $100\ s^{-1}$, which,
208 according to Souza et al. [27], corresponds to a deformation commonly suffered by fluids in
209 industrial pipes due to processes such as pumping and agitation.

210 **2.11 CNFs films casting**

211 Films were formed by casting, in which 60 mL of samples (1 wt%) was sonicated
212 (Sonifier model QR500, Ecosonics, Brazil) at 40% power of the ultrasound for homogenization
213 and later poured onto 15 cm diameter acrylic Petri dishes. The samples were kept in an
214 acclimatized room at $23 \pm 2\ ^\circ C$ and a relative humidity of 50% until water evaporation. CNFs
215 films were formed after approximately seven days under those conditions.

216 **2.12 Transparency at 550 nm (%)**

217 The transmittance of the CNFs films was measured at a wavelength of 550 nm using a
218 UV spectrophotometer (SP 2000 UV, Bel photonics, Italy) in photometric mode. For each
219 sample, five measurements were performed for samples from at least three different films. The
220 transparency (T_{550}) of the film samples was calculated according to Eq. adapted from the work
221 of Sothornvit et al. [28]:

222 $T_{550} = \frac{(\log \%T)}{b}$ (9)

223 where $\%T$ is the percent transmittance and b are the film thickness (mm).

250 **3. Results and discussion**

251 To better communicate the results and facilitate the reading of the text, Table S1
 252 summarizes each treatment carried out in this study, the materials, and their respective
 253 identification codes.

254 **3.1 Hemicellulose quantification**

255 Table 1 gives the chemical composition of the eucalyptus fibers before and after the
 256 TEMPO and alkaline treatments. All treatments involved removing the hemicellulose from the
 257 pulp, although the alkaline treatment was more efficient than the TEMPO treatment.

258

259 **Table 1:** Average and standard deviation of the cellulose and hemicellulose contents of Eucalyptus fibers
 260 (F) before and after TEMPO and alkaline treatments. * Different letters in the same column indicate
 261 significant ($p \leq 0.05$) differences between the samples for Tukey's test. ND = Not detected.

Samples	Cellulose (%)	Xylan (%)	Mannan (%)	Galactan (%)	Total hemicellulose (%)
Untreated_F	83.52 ± 0.44 ^c	16.14 ± 0.20 ^a	0.10 ± 0.14 ^a	0.04 ± 0.06 ^a	16.28 ± 0.40 ^a
TOF	84.83 ± 0.45 ^c	14.85 ± 0.01 ^b	0.22 ± 0.30 ^a	ND	15.17 ± 0.45 ^b
Na5_2_F	89.82 ± 0.77 ^b	9.84 ± 0.52 ^c	0.11 ± 0.16 ^a	0.03 ± 0.04 ^a	9.98 ± 0.72 ^c
Na10_1_F	95.77 ± 1.35 ^a	4.06 ± 0.26 ^d	ND	ND	4.06 ± 0.26 ^d
Na10_2_F	96.58 ± 1.13 ^a	3.30 ± 0.11 ^e	ND	ND	3.30 ± 0.11 ^e

262

263 The hemicellulose content decreased from 16.28 ± 0.39 in Untreated_F to 3.30 ± 0.11 in
 264 Na10_2_F. Higher NaOH concentrations and longer reaction times led to lower hemicellulose
 265 contents. Xylan was the major hemicellulosic compound in the fibers, despite treatment.
 266 Mannan and galactan were also found in the hemicellulosic fraction, but at extremely low
 267 proportions, lower than 0.22%. In fact, neither was detected in Na10_1_F and Na10_2_F, and
 268 galactan was not found in TOF. Hardwood pulp fibers such as those from Eucalyptus contain
 269 xylan, which is mainly located on the fiber surface, however, the mannan located between the
 270 dense structure of the elementary fibrils is difficult to contact directly in the alkaline solution
 271 [29]. The relative xylan content is higher than that in the corresponding inner layers after the
 272 kraft cooking process [30], where chemical attack is most efficient, which explains the effect of
 273 the treatments.

274 Hemicellulose presents a higher affinity for water than cellulose. Reducing the xylan
275 content in the CNFs modifies the rheological behavior of the suspension, resulting in a weaker
276 gel structure [31], which may affect the nanofibrillation efficiency.

277 **3.2 Fourier Transform Infrared Spectroscopy (FTIR) analysis**

278 The spectra of CNFs treatments ATR-FTIR analyses are shown in Figure 1. The band
279 representing the O-H stretch band assignment differs between the treatments. In the NA 10_2_N
280 and TONFC treatments peaks in this band occur. This indicates the presence of free hydroxyl
281 (OH) in these samples.

282 **[Figure 1 here]**

283 **Fig. 1.** FTIR analysis of treatments and untreated CNFs.

284 The band at 2889 cm^{-1} present in the spectrum of TONFC, NA5_2_N, and NA10_2_N
285 corresponds to the stretching vibration of CH [32,33]. Just the NA10_1_N treatment had the
286 same behavior in this peak as the untreated one, so this treatment has no CH bonds in this band.
287 Indicating the influence of the treatment on the nanofibrillation process.

288 The TEMPO-mediated oxidation treatment influences the chemical bonds of the CNFs
289 the most, and it is possible to see the 1600 cm^{-1} peak present only in it. The absorption band due
290 to C=O stretching of sodium carboxyl (CooNa) groups at 1600 cm^{-1} , was formed during the
291 selective oxidation process of the C6 hydroxyl groups [34]. The treatment of CNFs with
292 TEMPO-mediated oxidation differed in other results as well. The presence of this peak shows
293 that the CNFs are indeed directly influenced by this treatment due to their chemical
294 composition.

295 The peaks from 1154 to 897 cm^{-1} are characteristic when analyzing cellulose
296 compounds [35–38]. The peak 1154 cm^{-1} is referring to C–O stretching. While the peak 1104
297 cm^{-1} represents the C–H bend. The chemical bond C–O stretching is represented at the peak of
298 1027 cm^{-1} of the graph. Both peaks 1027 cm^{-1} and 1154 cm^{-1} also represent the presence of
299 xylan [39]. And the peak of 897 cm^{-1} corresponds to the C–H bend, which represents a type of
300 cellulose I [39,40].

3.3 Turbidity, visual inspection, and stability of the CNFs suspensions

As expected, TOCNF showed the lowest turbidity (83 ± 5 NTU). The Na5_2_N treatment promoted less turbidity (359 ± 4 NTU) than the Untreated_N treatment (377 ± 3 NTU), suggesting that treatment with a solution of 5% NaOH can increase the degree of nanofibrillation of the material, while Na10_1_N and Na10_2_N showed the highest values (706 ± 8 and 912 ± 1 NTU, respectively), indicating less nanofibrillation and aggregation of these CNFs. The turbidity is linked to the material's size; if the suspension is only composed of nanoscale materials, the turbidity value is close to zero. However, the presence of non-nanofibrillated material in the suspension tends to increase the turbidity. These results demonstrate the importance of maintaining certain hemicellulose levels to avoid coalescence between the cellulose micro/nanofibrils.

The sedimentation analysis and the percentage stability over time allowed evaluation of the general stability of the aqueous CNFs suspensions (Fig. 2).

[Figure 2 here]

Fig. 2. A) Dispersion states of the 0.1 wt.% CNFs suspensions at 0, 10, 30 min, 1, 2, 3, 4, 5, 6, 7, 8, and 24 h. Influence of time on CNFs suspension stability in water.

TOCNF showed the most stable behavior (97% after 24 h compared to 74% Untreated_N) among all the samples, corroborating the previous results. Nanoscale cellulose particles are stable due to Brownian motion, which maintains the suspended particles through the interaction of repelling forces, according to Silva et al. [41].

The sedimentation results show a tendency of NaOH to strongly affect the stability of the suspension. After 24 h, the CNFs Na5_2_N showed a stability of approximately 62%, followed by Na10_1_N and Na10_2_N with 38% and 22% stability, respectively. The stability decrease may be related to two factors: (i) the removal of hemicellulose with the increase in alkali concentration and (ii) partial conversion of cellulose I to cellulose II. Hemicellulose acts as an inhibitor of cellulose coalescence. Therefore, as the removal of hemicellulose increases, the cellulose fibrils tend to agglomerate more, consequently decreasing the suspension stability.

329 During alkali treatment, cellulose microfibrils agglomerate via interdigitation.
330 According to Lee et al. [42], the polarities of the cellulose II nanofibrils are the opposites of
331 those of the adjacent nanofibrils; thus, neighboring nanofibrils intermingle into irregular
332 aggregates.

333 3.4 CNFs morphology

334 Fig. 3 shows the CNFs networks of Untreated_N (Fig. 3a), TOCNF (Fig. 3b), Na5_2_N
335 (Fig. 3c), Na10_1_N (Fig. 3d) and Na10_2_N (Fig. 3e).

336 **[Figure 3 here]**

337 **Fig. 3.** Typical transmission electron microscopy (TEM) and diameter distribution of CNFs and images
338 from (A and F) Untreated_N; (B and G) TOCNF; (C and H) Na5_2_N; (D and H) Na10_1_N; and (E and
339 J) Na10_2_N. The green arrows indicate more individualized CNFs, while purple arrows indicate more
340 electrodense regions and consequently less individualized CNFs.

341 Note that as expected, TOCNF produced more individualized CNFs (indicated by green
342 arrows) with smaller diameters (26 ± 20 nm), followed by Na5_2_N with an average diameter
343 of approximately 34 ± 22 nm, while Untreated_N led to CNFs with an average diameter of
344 approximately 45 ± 23 nm. Na10_1_N showed nanofibril structures with an average diameter of
345 77 ± 48 nm, and Na10_2_N showed structures with an average diameter greater than 100 nm
346 (approximately 194 ± 171 nm). Taking into consideration the relationship between
347 hemicellulose content and diameter of CNFs subjected to alkaline treatment, the results of this
348 study showed similar trends with the results of the Lu et al. [39] study, where hemicellulose
349 levels near 10% generated the smallest average diameters. These results are associated with the
350 results obtained in the turbidity analysis, in which the treatments with smaller diameters were
351 also those with lower turbidity values (Table 2).

352 With the excessive decrease in the hemicellulose content before the CNFs is obtained
353 (Figs. 3d and 3e), the products have larger diameters, indicating less fibril individualization,
354 evidencing, once again, the role of these noncellulosic polysaccharides as regulators of the
355 morphological properties of the CNFs.

356 More intense alkaline treatments led to a higher degradation of hemicellulose (xylan)
357 from the fiber structure, forming aggregates of cellulose fibrils and affecting the CNFs network
358

359 structure (Figs. 3d and 3e). Furthermore, surface xylan played a significant role as an
360 electrostatic stabilizer in the CNFs dispersions by reducing the cohesion energy between the
361 fibrils, whereas the removal of xylan drastically changed the CNFs dispersion properties
362 [43,44].

363 Fig. 3 also shows the diameter distribution of CNFs produced under different
364 conditions. With average diameters lower than 30 nm, which make the CNFs potentially useful
365 as reinforcing agents in composites [45], the content of CNFs was approximately 33%, 72%,
366 and 62% for Untreated_N, TOCNF, and Na5_2_N, respectively, and approximately 12% and
367 0% for Na10_1_N and Na10_2_N, respectively. These results indicate that the alkali-treated
368 sample containing approximately 10% hemicellulose (Na5_2) was the only one that led to better
369 nanofibrillation and individualization of the fibrils. This treatment presented more homogeneous
370 nanofibrils, with 62% of the elements measured within the class of diameter of 15-30 nm,
371 surpassing even the TOCNF treatment that presented 41% of the elements measured within the
372 same class. Dias et al. [18] stated that hemicellulose content in the range of approximately 9 to
373 12% facilitates cell wall deconstruction.

374 TOCNF showed a slight reduction in hemicellulose content (from ~16% to ~15%), and
375 it was the treatment with the best level of nanofibrillation. However, it is essential to note that,
376 unlike other treatments, TEMPO-mediated oxidation promotes cellulose chemical modification
377 through the selective oxidation of C6 hydroxyl groups by inserting carboxyl and aldehyde
378 groups [19].

379 The darker regions in Figs 2d and 2e overlap, showing less individualization in these
380 samples. The darker color (purple arrows) indicates a more electrodense region. The beam
381 electrons cannot be transmitted in these regions, meaning that they are thicker than in Figs. 3a,
382 3b, and 3c.

383 Figs. 3a (Untreated_N), 3b (TOCNF), and 3c (Na5_2_N) more prominently show that
384 these samples had better-structured CNFs networks (mainly in Figs. 3b and 3c) compared to the
385 others. The more efficient the fibrils' individualization was, the greater the surface area of the
386 material, allowing it to have more sites available to bind with water molecules improving the

387 CNFs network's swelling, contributing to its final gel consistency. According to Pääkkönen et
388 al. [31], the swelling level has a considerable contribution to the gel network's quality,
389 rheological behavior, and dewatering behavior of CNFs suspensions.

390 **3.5 X-ray diffraction (XRD)**

391 Fig. 4 shows that samples Untreated_N and TOCNF present the typical parallel
392 crystalline structure of cellulose I β with peaks at $2\theta = 14.9^\circ$, 16.4° , 20.5° , 22.6° and 34.7° ,
393 corresponding to lattice planes (1-10), (110), (102), (200) and (004), respectively [46]. Sample
394 Na5_2_N presents all the mentioned peaks related to cellulose I β . However, a displacement of
395 the peak at $2\theta = 22.6^\circ$ can be attributed to the beginning of the formation of an additional peak
396 at $2\theta = 22^\circ$. It corresponds to the lattice plane (020) of cellulose II, which may indicate the
397 beginning of cellulose mercerization [26].

398

399

400 **[Figure 4 here]**

401 **Fig. 4.** Typical X-ray patterns of Eucalyptus CNFs samples obtained from fiber pulps before and after
402 TEMPO and alkaline treatments. Characteristic peaks and the associated lattice planes are indicated for
403 Cellulose I β (black dashed lines) and Cellulose II (red dashed lines), respectively. An amorphous halo of
404 cellulose II with an FWHM of 9 is used as a reference for crystalline fraction calculation.
405

406 Fig. 4 also shows the partial conversion from native cellulose I β to cellulose II on fibers
407 treated with an alkali concentration of 10% (Na10_1_N and Na10_2_N). The diffraction peaks
408 observed at $2\theta = 12.2^\circ$, 20.1° and 22.1° correspond to the (1-1 0), (110) and (020) lattice planes
409 of cellulose II, respectively [46].

410 The crystalline fractions (CFs) were calculated using peak deconvolution and an area-
411 based method because the amorphous component used in the Segal method is substantially
412 influenced by the overlap of crystalline peaks [25]. Table 2 shows the modifications that
413 occurred in the samples after the respective treatments. A higher CF average was found in
414 Untreated_N, followed by TOCNF and the alkaline treatments Na5_2_N, Na10_1_N and
415 Na10_2_N.

416

417 **Table 2:** Average and standard deviation values of the crystalline fraction (CF) and crystallite size (CS)
 418 for Eucalyptus CNFs produced under different conditions. Different letters in the same column indicate
 419 significant ($\rho \leq 0.05$) differences between the samples for Tukey's test.

Samples	Crystalline fraction (CF%)	Cellulose I (%)	Cellulose II (%)	Crystallite size (CS nm)
Untreated_N	69 ± 1^a	100	0	3.23 ± 0.02^c
TOCNF	67 ± 1^a	100	0	3.63 ± 0.03^a
Na5_2_N	67 ± 1^a	98	2	3.49 ± 0.04^b
Na10_1_N	63 ± 2^b	73	23	2.78 ± 0.01^d
Na10_2_N	63 ± 1^b	58	42	2.31 ± 0.01^e

420

421 All the treatments impacted the crystallinity of the cellulose. TEMPO-mediated
 422 oxidation preserved the native cellulose I structure of the sample. A slight (nonsignificant)
 423 decrease in TOCNF crystallinity was observed. This decrease in crystallinity may indicate that
 424 decrystallization of crystalline cellulose presumably occurred to some extent under oxidation
 425 [47].

426 The NaOH concentration also influenced the CF of the samples. As the NaOH
 427 concentration increased, CF decreased, probably due to the beginning of cellulose
 428 mercerization, inducing irreversible transformation of the native crystalline structure into
 429 cellulose II. According to Banvillet et al. [48], the formation of the cellulose II crystalline
 430 structure was globally less organized, leading to a decrease in crystallinity.

431 In Na10_1_N and Na10_2_N, cellulose II formation with antiparallel chains (Fig. 4)
 432 resulted in a gradual decrease in the cellulose I crystalline regions to soda cellulose I crystallites
 433 (Table 3). Cellulose I with antiparallel chains could absorb more alkaline solution, and then it
 434 was converted into cellulose II [26]. Furthermore, the conversion to cellulose II by the alkaline
 435 solution made fibrillation more complicated because of the aggregation via the interdigitation of
 436 micro/nanofibrils in the fiber's secondary cell wall [1].

437 The untreated sample had a crystallite size of 3.23 ± 0.05 nm (Table 3). The following
 438 TEMPO treatment led to an increase in CS (3.63 ± 0.03 nm). The explanation for this increase is
 439 that during TEMPO-mediated oxidation, the intra- and intermolecular repulsion increases with
 440 the selective oxidation of hydroxyl groups at C6, leading to an increase in crystallite size.

441 TEMPO-mediated oxidation is known to insert negative charges to form strong electrostatic
 442 repulsion between cellulose chains in water [49].

443 Na5_2_N also led to an increase in the CS (3.49 ± 0.04 nm). This increase may be due
 444 to the rearrangement in the crystal orientation and formation of some interstitial coalescence
 445 during the conversion of the (200) plane to the (020) plane [50]. In contrast, Na10_1_N and
 446 Na10_2_N showed decreased CS, 2.78 ± 0.01 nm, and 2.31 ± 0.01 nm, respectively. The
 447 stronger alkali solution could penetrate the crystalline regions, resulting in a disorder in the fiber
 448 crystallites, leading to decreased sizes [26].

449 3.6 Rheological behavior

450 The rheological behavior of the Eucalyptus CNFs suspensions was investigated at 25
 451 °C. The curves of apparent viscosity as a function of shear rate are shown in Fig. 5.

452 [Figure 5 here]

453 **Fig. 5.** Apparent viscosity vs. shear rate for the CNFs suspensions under different conditions.
 454

455 In Table 3, Newton's Law was adequately adjusted for Na10_2_N ($R^2 \geq 0.9544$), while
 456 the Power law and Herschel-Bulkley models were adjusted for Untreated ($R^2 \geq 0.9963$ and
 457 0.9984 , respectively), TOCNF ($R^2 \geq 0.9975$ and 0.9983 , respectively), Na5_2_N ($R^2 \geq 0.9941$
 458 and 0.9957 , respectively) and Na10_1_N ($R^2 \geq 0.9883$ and 0.9963 , respectively). All the samples
 459 presented low square root mean square error (RMSE) values (≤ 0.17).

460 **Table 3:** Parameters of the Newton model for EUC10% 2H and power law and Herschel-Bulkley models
 461 for Untreated_N, TOCNF_N, Na5_2_N, and N10_1_N.

Newton's Law							
Sample	μ	Pr > t	R^2	RMSE	$\eta_{initial}$ (mPa.s)	η_{100} (mPa.s)	
Na10_2_N	0.0024	<.0001	0.9544	0.05	6.0 ± 2	2.0 ± 0.1	

Power law							
Sample	k (Pa.s ⁿ)	n (-)	Pr > t	R^2	RMSE	$\eta_{initial}$ (mPa.s)	η_{100} (mPa.s)
Untreated_N	2.08	0.34	<.0001	0.9963	0.17	1265 ± 26	99.0 ± 1.0
TOCNF_N	11.65	0.26	<.0001	0.9975	0.11	4450 ± 131	307.0 ± 5.0
Na5_2_N	1.01	0.34	<.0001	0.9941	0.10	635 ± 34	48.0 ± 0.7
Na10_1_N	0.08	0.52	<.0001	0.9883	0.04	70 ± 4	8.0 ± 0.1

Herschel-Bulkley							
------------------	--	--	--	--	--	--	--

Sample	t	k (Pa.s ⁿ)	n (-)	Pr > t	R ²	RMSE	η_{initial} (mPa.s)	η_{100} (mPa.s)
Untreated_N	1.95	1.10	0.43	<.0001	0.9984	0.11	1265 ± 26	99.0 ± 1.0
TOCNF_N	3.89	9.10	0.29	<.0001	0.9983	0.10	4450 ± 131	307.0 ± 5.0
Na5_2_N	0.81	0.59	0.41	<.0001	0.9957	0.09	635 ± 34	48.0 ± 0.7
Na10_1_N	0.24	0.02	0.73	<.0001	0.9963	0.02	70 ± 4	8.0 ± 0.1

464

465 It was observed that the consistency index (K) was higher for TOCNF. A higher value
466 of the (K) factor may indicate suspensions containing CNFs with a higher aspect ratio, which is
467 expected for TEMPO-oxidized CNFs. The (K) and apparent viscosity seem to be strongly
468 influenced by the hemicellulose content. It can be observed that the value decreases clearly from
469 Untreated_N to Na5_2_N and almost reaches zero to Na10_1_N. According to Pääkkönen et al.
470 [31], hemicellulose (especially xylan) is responsible for linking a significant amount of water to
471 the fiber/CNFs structure, conferring higher viscosity to the suspensions, thereby increasing the
472 (K) value.

473 The morphology of the material (each fibril) may be related to the (K) value. Poor
474 nanofibrillated material (Na10_1_N and Na10_2_N) containing particles with larger dimensions
475 leads to a weak fiber network with lower stiffness, facilitating its breaking and ordering when
476 subjected to shear, thereby decreasing the viscosity [27].

477 Untreated_N presented flow index values of 0.34 (Power law) and 0.43 (Herschel-
478 Bulkley), while TOCNF presented the lowest values (0.26 and 0.29 for Power Law and
479 Herschel-Bulkley, respectively). Na5_2_N presented flow index values of 0.34 and 0.41 (Power
480 Law and Herschel-Bulkley, respectively), and Na10_1_N presented (n) values of 0.52 and 0.73
481 (Power Law and Herschel-Bulkley, respectively).

482 The flow index (n) depends on the structural properties of the entire suspension [51] and
483 indicates the degree of non-Newtonian characteristics of the material. The values for all CNFs
484 samples (except Na10_2_N) in the Power law and Hershel-Bulkley models point to
485 pseudoplastic fluid behavior, presenting values lower than 1. Similar behavior was reported by
486 Naderi et al. [52] when investigating the viscosity of softwood pulp and reported by Souza et al.
487 [27] when studying the rheological behavior of Pinus, Eucalyptus, and cocoa shell CNFs. The
488 decrease in viscosity is characteristic of pseudoplastic fluids as the shear rate applied to the fluid

489 increases (Fig. 5). This phenomenon is due to the state of order of the material present in the
490 stable solution, which is disordered, and, as shear is applied, it starts to become organized,
491 decreasing the viscosity.

492 The (K) values can also be linked as an indicator of the viscosity of the suspension,
493 while the (n) values can be related to the shear-thinning behavior of the suspension. Thus,
494 highly viscous suspensions would yield larger (K) values, while (n) values would decrease as
495 the suspensions become more thinning [53].

496 The rheology of nanocellulose suspensions is dependent on the structure, degree of
497 dispersion, degree of nanofibrillation, and interactions between the nanocellulose and the
498 solvent or matrix material [54]. The presence of a significant amount of surface hydroxyl groups
499 makes them easily dispersed in water and provides fluids with shear-thinning rheology and
500 thixotropy, even at low concentrations [55]. Rheological behavior characterization is essential
501 for understanding nanocellulose applicability to the use of nanocellulose-containing products
502 and processing issues related to coating, extrusion, molding, etc. [6].

503 Na10_2_N presented almost Newtonian flow, and the difference from the other
504 treatments may be due to the low efficiency of nanofibrillation. Fig. 3 shows that there was no
505 good deconstruction of the fiber cell wall in Na10_2_N, so there was no efficient
506 individualization of nanoscale fibrils, leading to the absence of a gel-like aspect. Geng et al. [56]
507 found that without reaching the gel-like point, the behavior of CNFs suspensions is almost
508 Newtonian.

509 The majoritarian presence of large particles may have contributed to this behavior, as
510 observed by Marchessault et al. [57], who studied the viscosity of cellulose microcrystal
511 suspensions and found that particle size influenced the rheological behavior of suspensions,
512 showing Newtonian behavior. The low concentration (1%) of this suspension (Na10_2_N) also
513 contributed to this behavior.

514 Due to its gel-like behavior, CNFs can be applied in the paper industry as a coating
515 layer on paper and paperboards. Coating processes such as bars and extrusion have the

516 advantages of high flexibility, absence of adhesive, and low production cost compared to a
517 laminated system [58].

518 The rheological behavior of the CNFs may be correlated to the efficiency of
519 nanofibrillation and the morphology of the material, which explains the lower viscosity of the
520 CNFs of Na10_2_N; they have more non-nanofibrillated fibers than other CNFs. This
521 discrepancy may result in the lack of a web-like network, which could facilitate breaking and
522 ordering when the CNFs are exposed to shear force [27]. When nanofibrillation is effective, the
523 surface area increases, and therefore, more interactions between fibril aggregates occur, leading
524 to higher flow resistance of the suspension [59,60].

525 Two different types of behaviors can be observed in cellulose fiber suspensions: at
526 lower shear rates, the pulp suspension is a Newtonian fluid, and at higher shear rates, pulp
527 behavior is a non-Newtonian fluid [61].

528 Fig. 6 shows the apparent viscosity of CNFs at 100 s^{-1} under different conditions as a
529 function of hemicellulose content. When the hemicellulose content in the CNFs increased, the
530 apparent viscosity also increased, demonstrating a direct correlation ($R^2 = 0.9966$) between
531 these two parameters. The hemicellulose content of Na5_2_N decreased by approximately 39%
532 compared with that of Untreated_N, and the apparent viscosity decreased by approximately
533 52% at a shear rate of 100 s^{-1} . The hemicellulose content of Na10_1_N and Na10_2_N
534 decreased by 75% and 80%, respectively, whereas the apparent viscosity at shear rate at 100 s^{-1}
535 decreased 92% and 98%, respectively.

536 **[Figure 6 here]**

537 **Fig. 6.** The relationship between apparent viscosity and hemicellulose contents in the different CNFs after
538 nanofibrillation. * EUC TEMPO was not considered in the correlation because, unlike the other fibers, it
539 was a chemically modified fiber. Schematic representation showing how hemicellulose influences the
540 separation of cellulose microfibrils. A) Representation of cellulose nanofibrils composed of crystalline
541 and amorphous domains, both formed by ordered and disordered regions of cellulose chains; B) fibers
542 with higher hemicellulose content being cut during nanofibrillation and being easily individualized; and
543 C) nanofibrils from fibers with a low hemicellulose content are more difficult to individualize due to the
544 coalescence between microfibrils.

545
546 However, in TOCNF, substitution by aldehyde and carboxyl groups in C6 caused the
547 nanofibrils to create strong electrostatic repulsions with each other, allowing a greater number

548 of bonds with water molecules. This bonding resulted in a significant increase in the viscosity of
549 the suspension (210%), despite the slight loss of hemicellulose (~7%) due to oxidation in an
550 alkaline environment.

551 Hemicellulose plays an essential role in the nanofibrillation of wood pulp because its
552 presence impedes microfibril coalescence due to its ability to bind directly to cellulose
553 microfibrils through hydrogen bonds [62]. These results indicate that a higher hemicellulose
554 content supports CNFs individualization (as shown in Fig. 6) because of the increase in
555 viscosity, implying the formation of a complex network of CNFs. In contrast to cellulose, which
556 is more rigid than the other cell wall components, the behavior of hemicellulose is more plastic,
557 and hemicellulose can be plasticized, reducing the cohesion forces between the microfibrils
558 [63].

559 The viscosity of polymers and their solutions and suspensions is an essential transport
560 property that involves their process and applications. The rheological behavior of Untreated_N,
561 TOCNF, and Na5_2_N suspensions indicates that these can be applied in processes where
562 viscosity is a determinant, such as coating on the paper surface.

563 During the coating process, the viscosity of the paper coating is relatively low at high
564 shear rates. After being transferred to the paper surface, CNFs in the coating form a highly
565 viscous layer when the shear force ends [64]. Na10_1_N and Na10_2_N, due to their low
566 viscosity, may be applied as reinforcement agents, where the viscosity is not a limiting factor.

567 The viscosities of the Na10_1_N and Na10_2_N samples at a shear rate of 100 s^{-1} are
568 extremely low (8 mPa.s and 2 mPa.s, respectively), indicating that they have more free water in
569 the suspension and would not be effective as rheological modifiers in the present conditions.
570 This free water in greater quantities can harm the healing process of a cement system.

571 **3.7 Mechanical performance of the CNFs films**

572 Table 4 shows the average and standard deviation values of the mechanical properties of
573 different CNFs films.

574 **Table 4:** Average and standard deviation values of tensile strength, Young's modulus, and elongation at
575 break of the nanostructured films from CNFs under different conditions. *It was impossible to perform

576 the test on EUC10% 2H because it was not possible to form films for this treatment. Different letters in
 577 the same column indicate significant ($p \leq 0.05$) differences between the samples for Tukey's test.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Untreated_N	41.5 ± 5.5^b	3.8 ± 0.8^{bc}	1.8 ± 0.4^a
TOCNF	54.5 ± 5.5^a	8.5 ± 0.9^a	1.2 ± 0.3^b
Na5_2_N	45.9 ± 6.5^{ab}	4.2 ± 0.5^b	1.7 ± 0.3^a
Na10_1_N	24.9 ± 6.4^c	3.0 ± 0.6^c	1.1 ± 0.2^b
Na10_2_N*	-	-	-

578

579 TOCNF had higher averages of tensile strength and Young's modulus, whereas
 580 Na10_1_N had lower averages. Untreated_N and Na5_2_N presented intermediate averages and
 581 did not differ from each other. This result can be attributed to the reduction of empty spaces in
 582 the interfaces between nanofibrils, promoted by the increase in the highly individualized
 583 nanofibril surface area. However, CNFs Na10_1_N (24.9 ± 6.4 MPa) exhibited lower
 584 nanofibrillation efficiency. A higher free volume between fibrils may have resulted in a
 585 reduction in the crystallinity index, thereby decreasing the tensile strength and Young's modulus
 586 (3.0 GPa) of fibrils themselves [65].

587 Another factor that explains the decrease in the mechanical properties of the CNFs
 588 Na10_1_N films is the partial conversion of cellulose I to cellulose II. In the literature, cellulose
 589 II has a lower Young's modulus than cellulose I [66].

590 The hemicellulose content can also influence the mechanical properties of films, as
 591 shown in the previous section. Na10_1 demonstrated a lower hemicellulose content ($\sim 4\%$) than
 592 Untreated ($\sim 16\%$), TOCNF ($\sim 15\%$), and Na5_2 ($\sim 10\%$). When the hemicellulose content
 593 declined drastically, the mechanical properties of the Na10_1 sample film may have decreased.
 594 The superiority of samples with a higher hemicellulose content on mechanical properties may
 595 be due to many hydroxyl groups that increase the hydrogen bond energy density [67].
 596 Furthermore, the presence of more xylan contributes to the adhesion between CNFs in the dried
 597 state, leading to an improvement in the strength of the CNFs films [68].

598 The elongation at break averages of Untreated_N and Na5_2_N were similar.
 599 Na10_1_N presented a lower average, although it was similar to TOCNF. In the case of

600 Na10_1_N ($1.1 \pm 0.2\%$), the decrease may indicate that hemicellulose is essential for plastic
 601 deformation of CNFs films because of their amorphous nature [69].

602 Excessive removal of hemicellulose caused coalescence between fibrils, impeding the
 603 formation of an interconnected network resulting in low nanofibrillation (Fig. 3D). As already
 604 reported, these polymers inhibit the coalescence between microfibrils, facilitating cell wall
 605 delamination.

606 3.8 Effect of modifications on quality of cellulose nanofibers

607 The CNFs produced after the different treatments were evaluated by the simplified
 608 quality index (*Q.I.) proposed by Desmaisons et al. [21], obtaining the values shown in Table 5.

609 **Table 5:** Simplified quality indices of CNFs produced by different treatments. Different letters in the
 610 same column indicate significant ($\rho \leq 0.05$) differences between the samples for Tukey's test.

Sample	Turbidity (NTU)	Transparency (%)	Young's modulus (GPa)	Microsize area (μm^2)	*Q.I.
Untreated_N	377 ± 3^c	29 ± 4^c	3.8 ± 0.8^{bc}	32.8 ± 1^{bc}	63 ± 3^b
TOCNF	83 ± 5^e	77 ± 9^a	8.5 ± 0.9^a	22.8 ± 1^c	80 ± 3^a
Na5_2_N	359 ± 4^d	51 ± 4^b	4.2 ± 0.5^b	28.7 ± 7^c	68 ± 3^b
Na10_1_N	706 ± 8^b	46 ± 8^b	3.0 ± 0.6^c	52.5 ± 13^b	51 ± 3^c
Na10_2_N	912 ± 1^a	43 ± 1^{bc}	-	121.2 ± 22^a	32 ± 1^d

611

612 The TOCNF treatment obtained the highest score in the quality index. It was observed
 613 that the Na5_2_N treatment obtained a quality index score statistically equal to that of the
 614 Untreated_N sample. However, it promoted economical energy consumption during
 615 nanofibrillation, reflecting the efficiency of this treatment in reducing the recalcitrance of the
 616 fibers, facilitating its deconstruction into smaller structures. The quality index score for the
 617 Untreated_N sample was similar to those obtained by Espinosa et al. [70] (59.5 ± 5.5), while
 618 the Na10_1_N treatment obtained a lower value than that found by Banvillet et al. [48] ($54.0 \pm$
 619 2.8)).

620 The Na10_2_N treatment resulted in the lowest score, demonstrating the influence of
 621 the reaction time of the alkaline treatment. As already discussed in previous sections, this
 622 behavior may be associated with the hemicellulose content in the samples, which facilitates the

623 deconstruction of the fiber cell wall, as shown in the results of the micro-sized area, where the
624 treatment with less hemicellulose showed a larger area of non-nanofibrillated particles.

625 The NaOH treatments, in general, promoted increased transparency of the samples
626 compared to Untreated_N, which can be attributed to the disorder caused by the alkaline
627 treatment in the cellulose structure during the conversion from the native form to cellulose II
628 and to the increased presence of amorphous structures [71].

629 **4 Conclusions**

630 NaOH treatments under different conditions promoted changes in fiber properties and
631 the crystalline structure of cellulose. The partial removal of hemicellulose to a range close to
632 10% and the coexistence of cellulose I and cellulose II polymorphs (in low quantity) facilitated
633 the production of CNFs. Hemicellulose influenced the rheological behavior of the CNFs
634 because its removal reduced the formation of complex networks between nanofibrils because it
635 has free hydrogen bonding sites that allow for cross-linking between cellulose chains. It also
636 influenced their mechanical performance; the higher removal impaired the entanglement of the
637 nanofibrils, weakening the structure of the films.

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649 **Conflict of interest**

650 The authors declare that they have no conflicts of interest.

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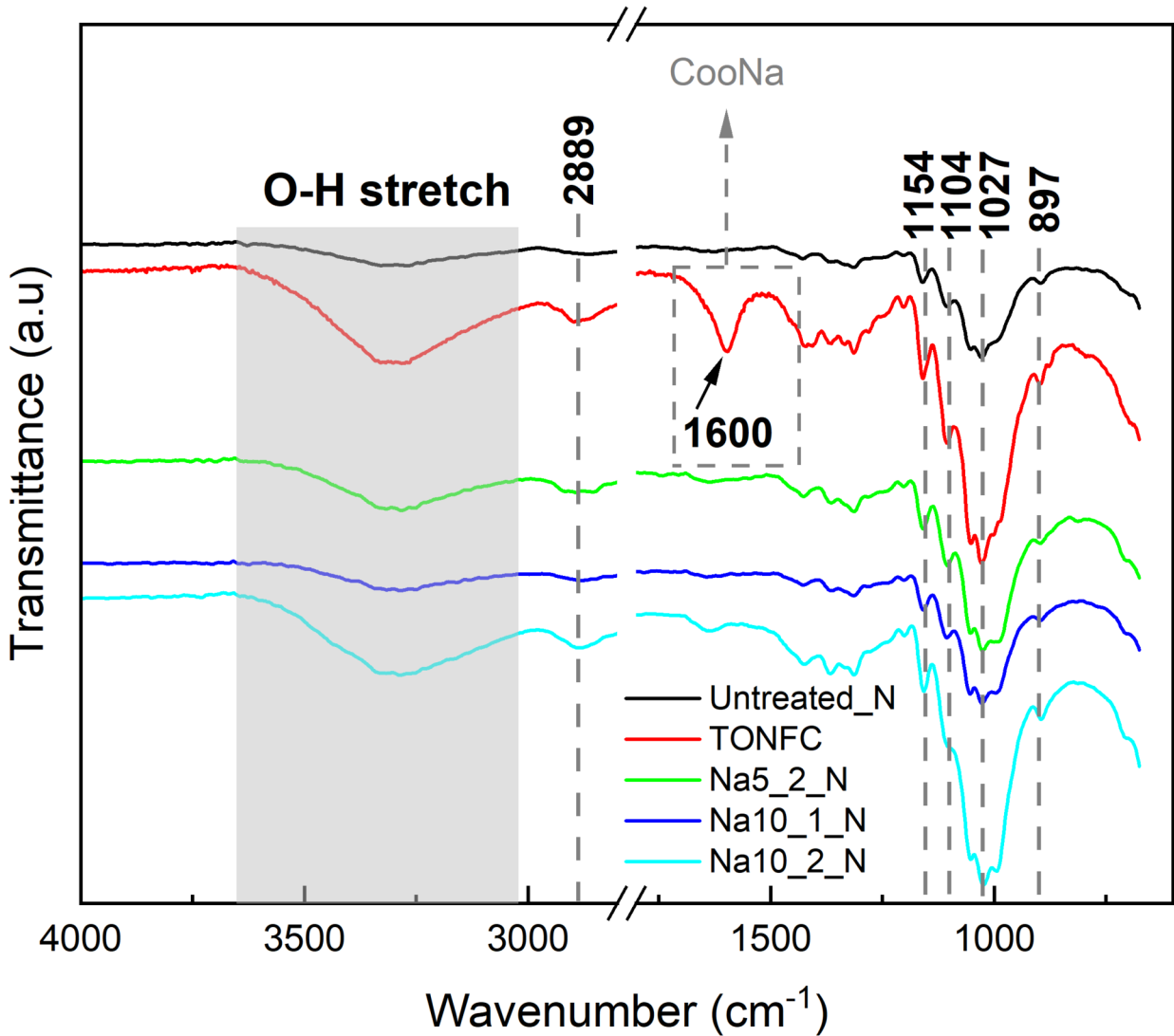
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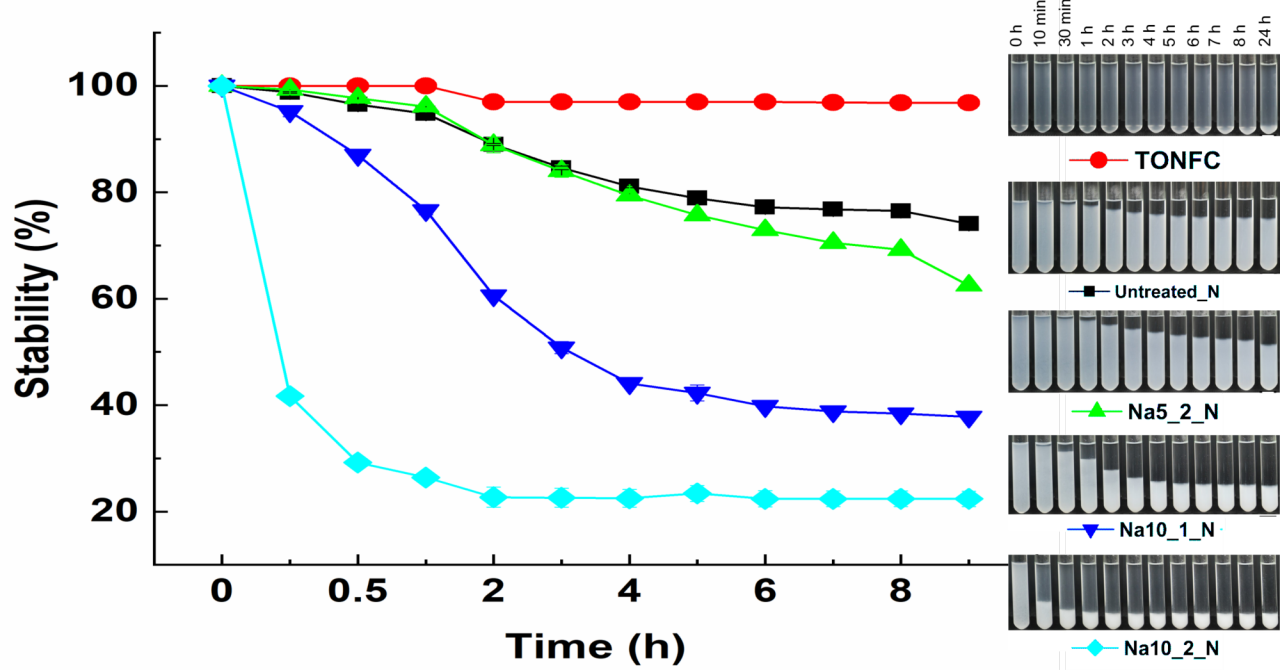
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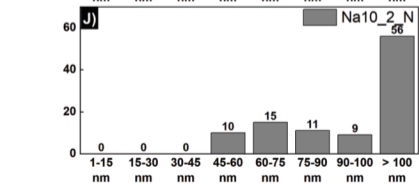
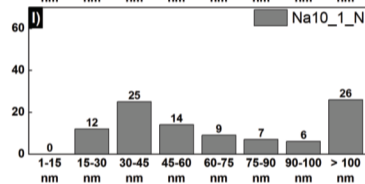
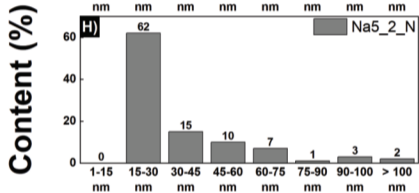
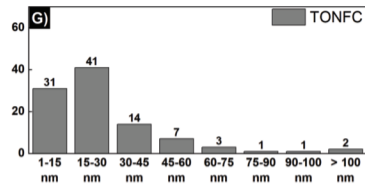
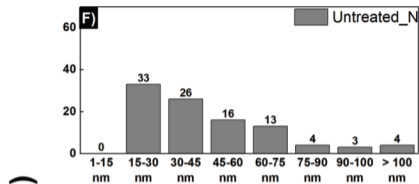
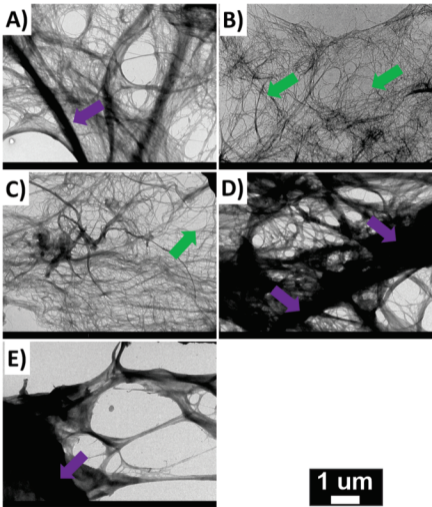
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Diameter range (nm)

