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5 **Gelation of cellulose-NaOH solutions in the presence of cellulose fibers**

6

7

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23 **Highlights**

- 24 • Gelation of cellulose-NaOH solutions in the presence of fibers was studied
- 25 • Added cellulose fibers and non-dissolved cellulose fraction accelerate gelation
- 26 • Modulus at gel point is higher for solutions with cellulose fibers
- 27 • Interactions between dissolved and non-dissolved cellulose were suggested
- 28 • Inert fibers do not influence gelation of cellulose solutions

29

30 **Abstract**

31 It is well known that when cellulose is dissolved in aqueous NaOH-based solvent, solutions  
32 are gelling with increasing time and temperature. The goal of this work was to understand if  
33 the presence of non-dissolved cellulose fibers influences gelation behavior of the whole  
34 system. One of the motivations is to control gelation when making all-cellulose composites  
35 with short fibers dispersed in cellulose-NaOH-water solutions. Gelation kinetics of  
36 cellulose(dissolving pulp)-NaOH-water solutions with added softwood kraft fibers were  
37 investigated using dynamic rheology. Fiber concentration, dissolving pulp degree of  
38 polymerization and solution temperature were varied. In all cases the addition of kraft fibers  
39 accelerate gelation and increase modulus at gel point while the presence of “inert” carbon  
40 fibers does not influence solution gelation kinetics. It was suggested that acceleration of  
41 gelation and reinforcement of cellulose gels is due to the interactions between dissolved and  
42 non-dissolved cellulose.

43

44 **Key words:**

45 All-cellulose composites; solutions; fibers; suspensions; rheology

## 46 **1. Introduction**

47 Cellulose is a natural polymer extracted mainly from plants and wood and it is renewable and  
48 biodegradable. There are different ways to make cellulose-based materials: either to use  
49 natural fibers as is, or dissolve cellulose, or derivatise it prior to processing. Common organic  
50 solvents cannot dissolve cellulose and thus specific solvents must be utilized. Mostly used are  
51 N-methylmorpholine-N-oxide (NMMO) monohydrate (Fink, Weigel, Purz & Ganster, 2001),  
52 LiCl/dimethylacetamide (McCormick & Lichatowich, 1979) or ionic liquids (Cao et al.,  
53 2009) of which only NMMO monohydrate is currently applied for the commercial production  
54 of cellulose fibers.

55 Cellulose can also be dissolved in aqueous 6-9 wt% NaOH (Davidson, 1934; Budtova &  
56 Navard, 2016), which provides a commercially available low cost solvent, with existing  
57 recycling methods used by pulping industry. However, this solvent has several drawbacks as  
58 cellulose dissolution must be performed at subzero temperatures, it has low dissolution  
59 capacity limited by cellulose degree of polymerization (DP) and concentration (Kamide, K.,  
60 Okajima, K., & Kowsaka, K. 1992; Egal, Budtova & Navard, 2007), and irreversible gelation  
61 of cellulose-NaOH solutions occurs with time and temperature increase (Roy, Budtova &  
62 Navard, 2003). Gelation can be slowed down by utilizing additives such as urea, thiourea or  
63 ZnO (Cai & Zhang, 2006; Liu, Budtova & Navard, 2011; Ruan, Lue & Zhang, 2008; Weng,  
64 Zhang, Ruan, Shi & Xu, 2004; Zhou & Zhang, 2000). In all cases gelation is affected by  
65 multiple parameters including time, temperature and cellulose concentration in the solution  
66 (Budtova & Navard, 2016).

67 Limited dissolution capacity (theoretical maximum of 8 wt% cellulose in 8 wt% NaOH-  
68 solution) (Egal, Budtova & Navard, 2007) and solution gelation are the major issues  
69 preventing using 6-9 wt% NaOH-water for classical cellulose processing, i.e. making films or

70 textile fibers. However, these drawbacks are not causing problems when making all-cellulose  
71 composites as in this case complete cellulose dissolution is not required (Yang et al. 2010;  
72 Nadhan et al. 2012; Korhonen, Sawada & Budtova, 2019; Labidi, Korhonen, Zrida,  
73 Hamzaoui & Budtova, 2019). All-cellulose composites are based on the principle of single-  
74 polymer composites, where the matrix and the reinforcing fibers are made of the same matter,  
75 thus avoiding using compatibilizers and simplifying recycling (Capiati & Porter, 1975; Ward  
76 & Hine, 1997). All-cellulose composites can be produced from different raw materials via  
77 dissolution-coagulation-drying route (Nishino, Matsuda & Hirao, 2004; Huber et al., 2012).  
78 Processing can be divided into two main approaches: *i*) “long-fiber” approach consisting of  
79 long fibers making a continuous phase, aligned or assembled into a fabric or pulp sheet and  
80 “glued together” due to the partial dissolution of fiber surfaces (Abbot & Bismarck 2010;  
81 Duchemin, Newman, & Staiger, 2009; Gindl & Keckes, 2005; Hildebrandt, Piltonen,  
82 Valkama & Illikainen, 2017; Piltonen et al. 2016; Sirviö, Visanko & Hildebrandt, 2017) and  
83 *ii*) “short-fiber” approach based on dispersing short fibers in cellulose solution (Ouajai &  
84 Shanks, 2009; Yang, Le & Zhang, 2010; Nadhan, Rajulu, Li, Jie & Zhang, 2012; Korhonen,  
85 Sawada & Budtova, 2019; Labidi, Korhonen, Zrida, Hamzaoui & Budtova, 2019).

86 Aqueous NaOH solvent can be easily used for making all-cellulose composites (Yang et al.  
87 2010; Nadhan et al. 2012; Korhonen et al. 2019; Labidi et al. 2019). If using short-fiber  
88 dispersion approach, the system is no longer cellulose-NaOH solution, but a suspension of  
89 non-dissolved fibers dispersed in such solution. How the presence of non-dissolved fibers  
90 influence suspension gelation? It is known that the addition of natural fibers to thermoplastic  
91 polymers strongly modify the rheological properties of molten composites (Sojoudiasli,  
92 Heuzey & Carreau, 2014; Abdennadher, Vincent & Budtova, 2016). However, nothing is  
93 known on how non-dissolved fibers are affecting gelation of cellulose-NaOH-water solutions,  
94 which is crucial for the production of all-cellulose composites.

95 The goal of our work is to understand if the presence of non-dissolved cellulose fibers  
96 influences gelation behavior of a suspension of short cellulose fibers dispersed in cellulose-  
97 NaOH solution. Dynamic rheology was used to trace gelation time and modulus at gel point.  
98 Dissolving pulp of DP 320 and 640 was used to make solutions, and kraft fibers were added  
99 at different concentrations. A special care was taken to ensure that kraft fiber concentration  
100 remained below the percolation concentration, which was determined from fiber size  
101 distribution. Similar to our previous work on all-cellulose composites (Korhonen et al. 2019),  
102 we considered the dissolution power of the solvent, i.e. the presence of non-dissolved fraction  
103 in solution of cellulose of higher DP. As a proof of concept, we used inert carbon fibers  
104 dispersed in cellulose solution to demonstrate that it is the interactions between dissolved  
105 cellulose and non-dissolved cellulose fibers which accelerate gelation and lead to a formation  
106 of a strong network.

107

## 108 **2. Materials and Methods**

### 109 **2.1. Materials**

110 Bleached birch dissolving pulp and softwood kraft fibers (crystallinity of kraft fibers is 42%,  
111 see Korhonen et al. 2019 for details) were kindly provided by Stora Enso Oyj as air-dry  
112 sheets and were disintegrated by a laboratory mill. NaOH flakes (analytical grade, purchased  
113 from Fischer Scientific) was dissolved in distilled water (8 wt%) and used as cellulose  
114 solvent. Commercial carbon fibers from pyrolysed polyacrylonitrile fibers were kindly  
115 donated by Deakin University, Australia, as continuous filament, and they were cut to match  
116 the size of the kraft fibers. Sulphuric acid (95-97%, EMSURE<sup>®</sup> ISO) was purchased from  
117 Merck and diluted with distilled water.

118

119 **2.2. Methods**

120 2.2.1. Pulp characterization and acid hydrolysis

121 The composition of all pulps was determined according to the analytical method NREL/TP-  
122 510-42618. Monosaccharides were analyzed via high-performance anion exchange  
123 chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000  
124 column and carbohydrates were determined according to Janson (1970). Acid soluble lignin  
125 content was analyzed via UV-VIS spectrophotometer (UV-2550, Shimadzu) and no traces of  
126 non-soluble lignin were detected.

127 The degree of polymerization (DP) of all pulps was determined via intrinsic viscosity based  
128 on cellulose dissolution in cupriethylenediamine (CED), according to the standard SCAN-  
129 CM 15:88.

130 Since the solubility of high DP cellulose in NaOH-water is low (Kamide, Okajima &  
131 Kowsaka, 1992; Budtova & Navard, 2016; Korhonen et al. 2019), the dissolving pulp was  
132 hydrolyzed to decrease the initial DP of 1100 to DP 640 and 320. Acid hydrolysis was  
133 conducted at 3% consistency for 60 minutes via sulphuric acid with concentrations 0.1 M and  
134 0.6 M at controlled temperature of 82 °C and 88 °C, respectively. Hydrolysis occurred under  
135 overhead mixing (125 rpm) and samples were washed with deionized water until neutral pH  
136 was reached. Samples were air-dried and the gravimetric yield for both DPs was  $98 \pm 1 \%$ .

137

138 2.2.2. Determination of size distributions of kraft fibers, carbon fibers and non-dissolved  
139 solids

140 Fiber size distribution of softwood kraft fibers was determined in triplicate via FiberLab™  
141 (Metso Automatization) device.



142 The size distribution of carbon fibers was determined by dispersing them in acetone; their  
143 length and width were obtained from optical microscopy images (Olympus SZX10 equipped  
144 with Olympus DP74 camera, magnification  $\times 0.8$ , software Olympus CellSens and LEICA  
145 DM 750 with camera LEICA ICC550 HD, magnification  $\times 20$ , software LAS EZ,  
146 respectively). The reason of using different microscopes was very different magnifications  
147 needed to capture dimensions of fibers of very high aspect ratio. The mean values were  
148 calculated as arithmetic averages.

149 Cellulose solution of DP 640 in 8 wt% NaOH-water contained non-dissolved solids, and their  
150 size distribution was determined from optical microscopy images as described in Korhonen et  
151 al. (2019). Briefly, the solution was diluted with 8 wt% NaOH-water and at least 80  
152 fragments per solution were analyzed; their mean sizes were calculated as arithmetic  
153 averages.

154

### 155 2.2.3. Determination of the fraction of non-dissolved solids in cellulose-NaOH-solutions

156 The amount of non-dissolved solids in the solution was determined as follows (for more  
157 details see Korhonen et al., 2019). 5 wt% of pulp with DP 320 or 640 was dissolved in 8 wt%  
158 NaOH in the same way as for making samples for the rheological study, i.e. at  $-7\text{ }^{\circ}\text{C}$  for 2 h  
159 under overhead mixing (300 rpm). The non-dissolved fraction was separated from the  
160 dissolved phase via centrifugation (15 minutes, 11 000 rpm, Eppendorf Centrifuge 5804R),  
161 washed and dried. The fraction of non-dissolved solids in the solution was calculated with  
162 equation 1, where  $m(\textit{dissolving pulp})$  is the oven-dried weight of the pulp prior to dissolution  
163 and  $m(\textit{non-dissolved})$  is oven-dried weight of the separated non-dissolved solids:

$$164 \quad \textit{Solid fraction, \%} = \frac{m(\textit{non-dissolved})}{m(\textit{dissolving pulp})} \times 100\% \quad (1)$$

165 Solid fraction is 0 % when there is no residue (implying complete dissolution) and 100 % is  
166 the case of no dissolution.

167

#### 168 2.2.4. Sample preparation for the rheological study

169 5 wt% of acid hydrolyzed pulp of DP 320 or DP 640 was dissolved in 8 wt% NaOH at – 7 °C  
170 with overhead mixer (300 rpm). After 2 h of mixing, 0%, 0.25%, 0.5% or 1% of kraft fibers  
171 or 0%, 0.25% or 0.5% of carbon fibers were added; mixing rate was reduced to 125 rpm to  
172 minimize the amount of air bubbles. Fibers and cellulose solutions were mixed together for  
173 15 min and then stored at 5 °C for 30 min prior to rheological measurement. Additionally,  
174 solutions of pulp DP 320 with cellulose concentrations 5 wt%, 5.25 wt%, 5.5 wt% and 6 wt%  
175 were prepared without any added fibers. We will call “cellulose solutions” the systems when  
176 dissolving pulp of DP 320 or 640 is dissolved in NaOH-water in order to distinguish them  
177 from the cases of “cellulose suspensions” when kraft or carbon fibers are added.

178

#### 179 2.2.5. Concentrations of cellulose in solutions and suspensions

180 Because of the presence of non-dissolved fractions in cellulose solutions, several  
181 concentrations of cellulose and of “solids” in suspensions have to be considered in order to  
182 understand their rheological properties. First, total cellulose concentration describes the  
183 overall concentration of all cellulose in the system and is calculated according to the equation  
184 2, where  $m(kraft)$  is the oven-dry weight of added kraft fibers and  $m(NaOH)$  is the weight of  
185 solvent.

$$186 \quad Total\ cellulose\ \% = \frac{m(dissolving\ pulp)+m(kraft)}{m(dissolving\ pulp)+m(kraft)+m(NaOH)} \times 100\% \quad (2)$$

187 The second concentration to consider is total solids concentration (eq.3), which shows the  
188 amount of all matter dispersed in cellulose solution, i.e. non-dissolved fraction and added  
189 fibers  $m(\text{added fibers})$  (kraft or carbon):

$$190 \quad \text{Total solids \%} = \frac{m(\text{non-dissolved})+m(\text{added fibers})}{m(\text{dissolving pulp})+m(\text{added fibers})+m(\text{NaOH})} \times 100\% \quad (3)$$

191 The third concentration is simply the amount of added fibers, either kraft or carbon. It is  
192 calculated according to the equation 4:

$$193 \quad \text{Added fibers \%} = \frac{m(\text{added fibers})}{m(\text{dissolving pulp})+m(\text{added fibers})+m(\text{NaOH})} \times 100\% \quad (4)$$

194 Table 1 shows these concentrations in all samples studied. The nomenclature is as follows:  
195 first, dissolving pulp DP, then the type of fiber added (“K” and “C” stand for added kraft and  
196 carbon fibers, respectively) and finally, the concentration of added fibers.

197 Table 1. List of samples studied

Sample set	Sample ID	Dissolving pulp DP	Total cellulose, wt %	Total solids, wt %	Added fibers, wt %	Solution temperature, °C	
<b>Kraft fibers added</b>	DP(320)K0.00%	320	5	0.20	0.00	5	
						10	
						15	
	DP(320)K0.25%		5.25	0.45	0.25	5	
						10	
						15	
	DP(320)K0.50%		5.5	0.70	0.50	5	
						10	
						15	
	DP(320)K1.00%		6.0	1.20	1.00	5	
	DP(640)K0.00%		640	5	1.70	0.00	5
							10

						15	198
	DP(640)K0.25%		5.25	1.94	0.25	5	199
10						200	
15						201	
	DP(640)K0.50%		5.5	2.19	0.50	5	202
10						203	
15							
	DP(640)K1.00%		6.0	2.66	1.00	10	204
<b>Cellulose solutions of various concentrations</b>	DP(320)5.25%	320	5.25	0.21	0	5	205
	DP(320)5.5%		5.5	0.22	0	5	206
	DP(320)6%		6	0.24	0	5	207
<b>Carbon fibers added</b>	DP(320)C0.25%	320	5	0.44	0.25	5	
	DP(320)C0.5%		5	0.70	0.5	5	208

## 210 2.2.6. Rheological measurements

211 The rheological properties of solutions and suspensions were measured with GEMINI  
212 Advanced rheometer (Bohlin instrument) using Bohlin software. Rheometer was equipped  
213 with plate-plate geometry and Peltier temperature control system. The gap was set to 1.5 mm  
214 to take into account the presence of added fibers. Strain and frequency were set for all  
215 measurements at 5% and 2 Hz, respectively, to ensure the linear visco-elastic regime. Storage  
216 ( $G'$ ) and loss ( $G''$ ) moduli were studied at 5 °C, 10 °C and 15 °C. The experimental errors in  
217 determination of gel point were less than 10%.

218

## 219 **3. Results**

### 220 **3.1. Characterization of pulps and cellulose solutions**

221 All pulps consisted mostly of cellulose and hemicelluloses. Acid hydrolysis did not affect the  
222 composition and all dissolving pulps (including the initial pulp with DP 1100) contained 92%  
223 cellulose, 7% hemicelluloses and < 1% acid soluble lignin. Kraft fibers were of DP 2550 and  
224 contained 80% cellulose, 19% hemicelluloses and < 1% acid soluble lignin.

225 The fraction of solids present in 5 wt% solutions of dissolving pulps of DP 320 and 640 was  
226 determined according to eq.1 (see section 2.2.3). The results are shown in Table 1. In the case  
227 of DP 320, practically all of the 5 wt% cellulose was dissolved and very few non-dissolved  
228 fragments remained. However, the solution with DP 640 contains a significant amount of  
229 non-dissolved solids, since only 3.3 wt% of pulp is actually dissolved (Table 2).

230

231 Table 2. Characteristics of neat 5 wt% cellulose-NaOH solutions for DP 320 and 640: solid  
232 fraction (eq. 1) and concentration of dissolved and non-dissolved cellulose.

	DP 320	DP 640
Solid fraction, wt%	4	34
Concentration of dissolved cellulose in solution, wt %	4.8	3.3
Concentration of non-dissolved cellulose in solution, wt%	0.2	1.7

233

### 234 **3.2. Analysis of fiber sizes: non-dissolved fragments, kraft fibers and carbon fibers**

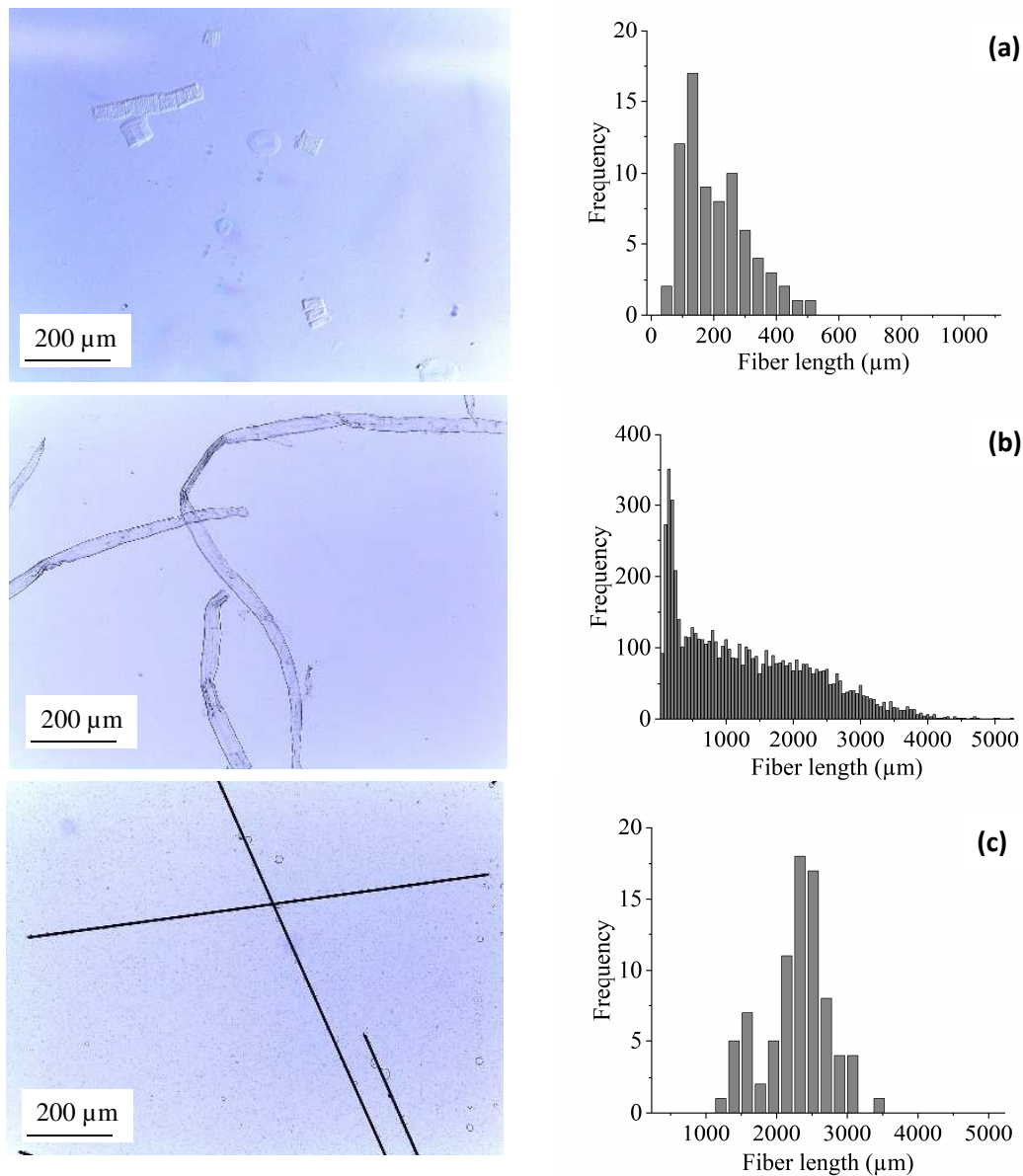
235 Figure 1 illustrates all solids in cellulose solutions and suspensions and shows their length  
236 distributions, the mean values are summarized in Table S1. Width and aspect ratio  
237 distributions are shown in the Supporting information (Fig. S1). Non-dissolved fraction in  
238 solutions of DP 640 contains swollen particle-like fibers and their fragments, with low aspect  
239 ratio around 4. Man-made carbon fibers are straight, rigid, have uniform width and high  
240 aspect ratio around 270, whereas kraft fibers are long and flexible with aspect ratio around  
241 50.

242

243

244

245



246

247 Figure 1. Illustration of non-dissolved fraction in 5 wt% cellulose (DP 640)-NaOH-water  
 248 solution (a), softwood kraft fiber (b) and carbon fiber (c) together with their length  
 249 distributions

250

251 Fiber length and its distribution strongly depend on the type of the fiber. Non-dissolved  
 252 fragments in solution of DP 640 are short with length of  $185 \mu\text{m} (\pm 105 \mu\text{m})$  while kraft and  
 253 carbon fibers are long, with mean length of  $1.3 \text{ mm} (\pm 0.02 \text{ mm})$  and  $2.2 \text{ mm} (\pm 0.5 \text{ mm})$ ,  
 254 respectively (Figure 1). Length distribution of natural softwood fibers is much wider



255 compared to the carbon fibers. Additionally, carbon fibers are thinner, only 8  $\mu\text{m}$  wide,  
256 whereas kraft fibers have average width of 26  $\mu\text{m}$  and non-dissolved fibers in solutions of DP  
257 640 are 52  $\mu\text{m}$  wide as the latter are swollen. The percolation concentration, which can be  
258 roughly estimated as the inverse value of fiber aspect ratio, is around 2 and 0.4 vol% for kraft  
259 and carbon fibers, respectively. The weight % based percolation concentration is around 3  
260 and 0.72 wt% for kraft and carbon fibers, respectively, and it is estimated taking solvent  
261 density equal to water and densities of kraft and carbon fibers equal to 1.5  $\text{g}/\text{cm}^3$  (Sixta,  
262 Potthast & Krottschek, 2006) and 1.8  $\text{g}/\text{cm}^3$  (Minus & Kumar, 2005), respectively. It is  
263 important to note that all kraft fiber suspensions are thus below fiber percolation  
264 concentration. This choice was made to ensure  $G' < G''$  at the beginning of the rheological  
265 experiment, to be able to trace gelation of cellulose solutions in time.

266

### 267 **3.3. Rheological properties**

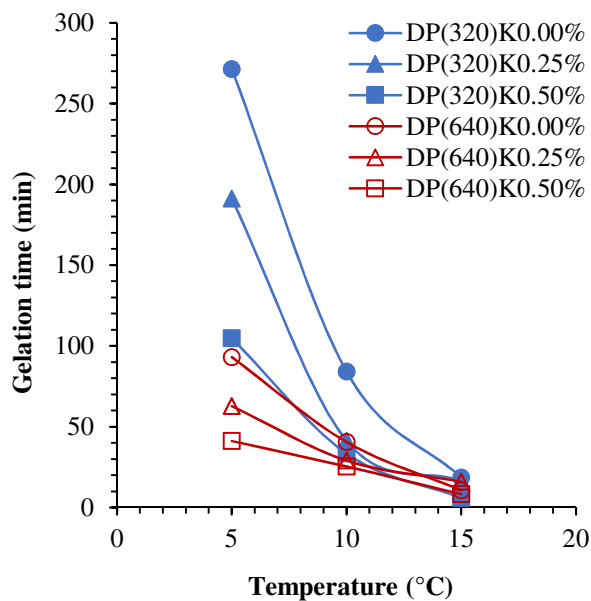
268 The influence of added fibers on the kinetics of cellulose solutions' and suspensions' gelation  
269 was studied following the evolution of storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of  
270 time at different fiber concentrations, for two dissolved cellulose DP, and at various  
271 temperatures. Kraft fibers are of very high DP and in the conditions they were added and  
272 mixed with cellulose solution fibers did not dissolve and even did not swell.

273 Gel point was taken, in the first approximation, as crossover of  $G'$  and  $G''$ . At short times,  $G'$   
274 is lower than  $G''$  indicating that the system is more viscous than elastic and thus has liquid-  
275 like properties. Over time both moduli increase and  $G'$  overcomes  $G''$  showing that the  
276 system is more elastic (or solid-like). According to Winter and Chambon gelation theory  
277 (1986),  $G' \sim \omega^a$  and  $G'' \sim \omega^b$ , where  $\omega$  is frequency, and the gel point is reached when  $a = b =$   
278 0.5. However, there are several complications that do not allow direct application of gelation

279 theory to our system. First, contrary to classical polymer solutions, cellulose is not  
280 molecularly dispersed in NaOH-water solvent (Lu, Liu, Zhang & Potthast 2011). Second,  
281 gelation of cellulose-NaOH-water solutions is accompanied by micro-phase separation  
282 (Gavillon & Budtova 2008). Finally, the systems studied here are suspensions of fibers  
283 dispersed in solution. In the following, for simplicity, we will call “gelation” and “gel point”  
284 the state of the system when  $G' = G''$ . The examples of  $G'$  and  $G''$  evolution in time at a  
285 given temperature are shown in Supporting information (Fig. S2).

286 Figure 2 shows that gelation of all cellulose solutions and suspensions occurs faster with  
287 increasing temperature, which is well in line with results reported previously (Roy et al.,  
288 2003). The reason is that with the increase of temperature solvent thermodynamic quality  
289 decreases which leads to the preferential intra- and intermolecular cellulose-cellulose  
290 interactions inducing gelation in semi-dilute solutions (Budtova & Navard, 2016). Increasing  
291 concentration of kraft fibers accelerates gelation as well. For example, by adding 0.5 wt% of  
292 kraft fibers to cellulose(DP 320)-NaOH solution, gelation time at 5 °C decreases from 271  
293 minutes without fibers to 105 minutes with kraft. Similar decrease in gelation time is  
294 observed for DP 640 solution: the addition of 0.5 wt% fibers leads to a drop of gelation time  
295 from 93 minutes without fibers to 41 minutes.

296



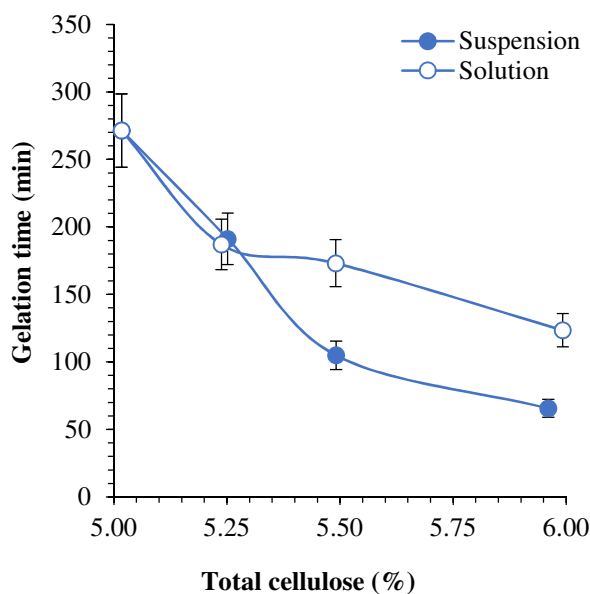
297

298 Figure 2. Effect of temperature and added kraft fiber concentration on gelation time. Lines  
 299 are to guide the eye. The errors in gelation time are less than 10%, but are not shown in order  
 300 not to overload the graph.

301

302 It is known that increasing cellulose concentration accelerates gelation (Roy et al., 2003;  
 303 Gavillon & Budtova, 2008) since higher concentration of macromolecules in the solution  
 304 leads to a higher probability of the formation of a network. Thus the next step was to  
 305 understand if the added kraft fibers have a special role in accelerating gelation. Gelation  
 306 kinetics of several cellulose-NaOH solutions with varying concentration of DP 320 pulp was  
 307 investigated and compared with that of suspensions of the same total cellulose concentration.  
 308 Figure 3 shows that gelation accelerates (decrease of gelation time) with increasing cellulose  
 309 concentration, as expected (Roy et al., 2003; Gavillon & Budtova, 2008), but this  
 310 phenomenon is even stronger in the presence of added kraft fibers. For example, when the  
 311 total cellulose concentration is 6 wt%, suspension with added fibers is gelling in 66 minutes  
 312 whereas gelation of the solution is twice longer.

313



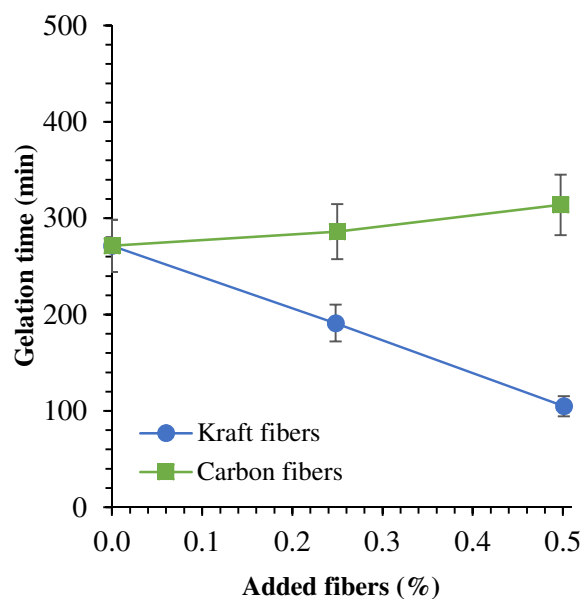
314

315 Figure 3. Gelation time at 5°C as a function of total cellulose concentration for cellulose(DP  
 316 320)-NaOH-water solutions and 5 wt% cellulose(DP 320)-NaOH-water suspensions with  
 317 added kraft fibers. Lines are to guide the eye.

318

319 For the further understanding of the possible interactions during gelation between cellulose  
 320 dissolved in 8 wt% NaOH-water and added fibers, a series of suspensions with “inert” fibers  
 321 (towards cellulose and NaOH-water) were prepared. Carbon fibers were selected for this  
 322 purpose, and gelation kinetics of their suspensions in 5 wt% cellulose(DP 320)-NaOH-water  
 323 was investigated and compared with the corresponding suspensions with added kraft fibers  
 324 (Figure 4). Increasing carbon fiber content has practically no effect on gelation kinetics of  
 325 cellulose-NaOH solutions **despite that carbon fiber percolation concentration is lower than**  
 326 **that of kraft fibers, and thus the addition of carbon fibers might be expected to have stronger**  
 327 **influence on gelation.** We can thus conclude that it is the interactions between dissolved  
 328 cellulose and added cellulose fibers in suspension which accelerate gelation of cellulose-  
 329 NaOH systems.

330



331

332 Figure 4. Gelation time at 5 °C as a function of added fiber's concentration for suspensions  
 333 with carbon or kraft fibers added to 5 wt%cellulose(DP 320)-NaOH-water.

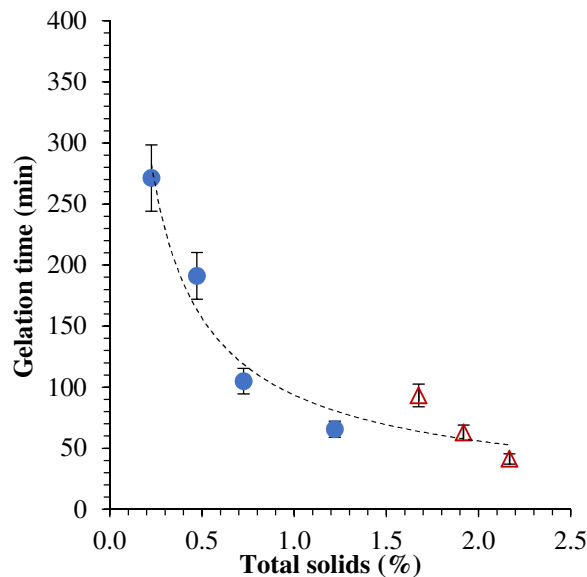
334

#### 335 4. Discussion

336 The results presented above show that the increase in the concentration of added kraft fibers  
 337 and of total cellulose concentration accelerate gelation of cellulose-NaOH-water suspensions.  
 338 Based on these experimental results we will demonstrate the importance of considering non-  
 339 dissolved fragments (or "solid fraction", eq. 1) originating from the incomplete dissolution in  
 340 the case of the pulp of DP 640.

341 Figure 2 demonstrates a strong influence of the DP of dissolved cellulose: at the same  
 342 temperature and kraft fiber concentration, higher DP provokes quicker gelation. This is also  
 343 the case when no kraft fiber is added, which is somehow surprising as solution of DP 640  
 344 contains lower dissolved cellulose (3.3 wt%) compared to the samples with DP 320 (4.8  
 345 wt%). This result indicates that non-dissolved fraction must also be considered as  
 346 contributing to gelation. An example of the influence of total solid content, which includes  
 347 both non-dissolved fraction and added kraft fiber (eq. 3), is presented in Figure 5. The results

348 show that gelation occurs faster for samples with higher total solids content whatever is their  
349 “origin”. The exponential fit shown in Figure 5 is very rough and does not take into account  
350 the DP of dissolved cellulose; what we want to show here is that non-dissolved fraction also  
351 contributes to solution and suspension gelation.



352

353 Figure 5. Effect of total solids concentration on gelation time at 5°C. Dashed line corresponds  
354 to the power law approximation  $y = 93.68x^{-0.741}$

355

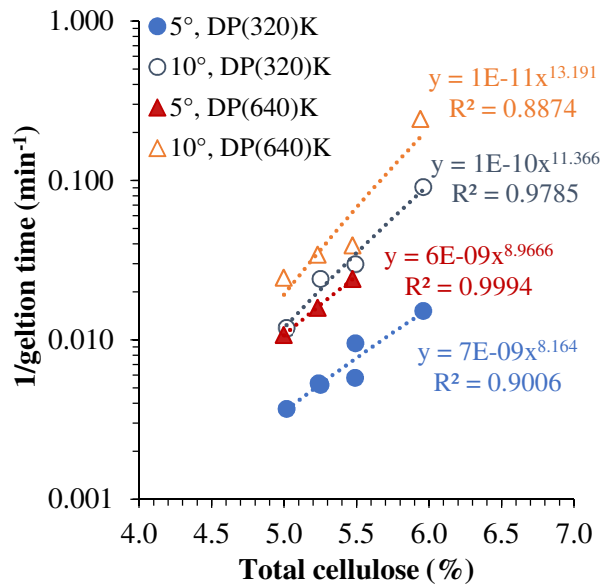
356 It is interesting to compare the obtained trends with those known in literature for similar  
357 systems. While all literature on cellulose dissolved in NaOH-water based solvent, with or  
358 without additives (ZnO, urea, thiourea or both), agrees that gelation time decreases with  
359 temperature increase as shown in Figure 2 (Roy et al. 2003; Cai & Zhang, 2006; Gavillon &  
360 Budtova, 2008; Liu et al., 2011; Pereira et al., 2018), not much is known about the influence  
361 of cellulose concentration on gelation process and nothing is reported about the role of  
362 “solids”.

363 To the best of our knowledge only one publication studied the influence of the presence of  
364 cellulose fibers on the rheological properties of cellulose-NaOH solutions; the fibers were  
365 microfibrillated cellulose (MFC) and ZnO was used to delay gelation (Saarikoski, Rissanen  
366 & Seppälä 2015). Authors focused on the comparison of the flow and visco-elastic properties  
367 of MFC dispersed in water and MFC dispersed in cellulose-NaOH-ZnO-water solution.  
368 Gelation was not considered despite that in the conditions used cellulose chains' aggregation  
369 could have started. Surprisingly, it was reported that at low MFC concentrations the elastic  
370 modulus of MFC-cellulose-NaOH-ZnO-water suspension was lower than viscous modulus  
371 indicating liquid-like behavior, and both being lower than those of MFC-water system. On  
372 the contrary, MFC-water showed gel-like behavior indicating that MFC is above the  
373 percolation concentration. With the increase of MFC concentration above a certain threshold  
374 MFC-cellulose-NaOH-ZnO-water suspension showed gel-like behavior with elastic modulus  
375 becoming much higher than that of MFC-water (Saarikoski et al., 2015). Authors suggested a  
376 synergy between MFC and dissolved cellulose (Saarikoski et al., 2015).

377 Polymer concentration was shown to have an effect on gelation time by Ross-Murphy (1991)  
378 who suggested a power-law dependence of the inverse gelation time as a function of  
379 concentration for the case of gelling carrageenan solution. This trend was confirmed for  
380 cellulose-NaOH-ZnO-water solutions (Liu et al., 2011). The decrease of gelation time with  
381 the increase of polymer concentration is due to higher number of potential junctions that can  
382 be formed since chains are closer to each other. The inverse gelation time as a function of  
383 total cellulose concentration (eq. 2) is plotted in Figure 6 for all suspensions studied and  
384 approximated with power laws for each temperature and cellulose DP showing that higher  
385 temperature and DP results in quicker gelation. The inverse gelation time fits reasonably well  
386 power-law cellulose concentration dependence for each case, with exponents varying from 8

387 to 13. Lower exponents were obtained for cellulose-NaOH-ZnO-water solutions, from 7 to 11  
 388 (Liu et al., 2011). This again confirms that “solids” accelerate the gelation of suspensions.

389



390

391 Figure 6. Inverse gelation time vs. total cellulose concentration for all suspensions studied.

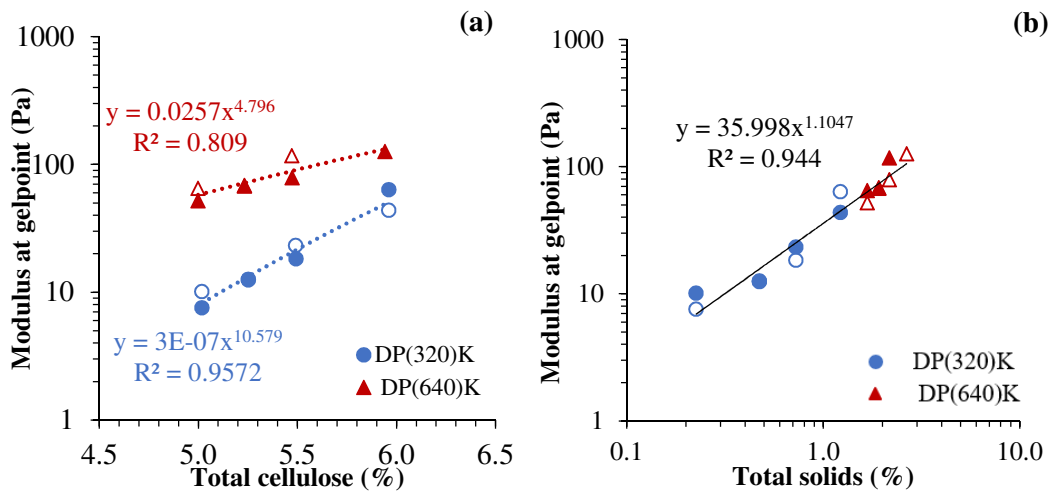
392 Lines are power-law approximations

393

394 The modulus at gel point,  $G_{gel}$ , is plotted in Figure 7 as a function of total cellulose and total  
 395 solids concentration. It was previously shown that  $G_{gel}$  increases with the concentration of  
 396 dissolved cellulose (Cai & Zhang, 2006; Gavillon & Budtova, 2008; Liu et al., 2011) and  
 397 Figure 7a also shows this trend, as expected. The modulus is higher for DP 640: on one hand,  
 398 longer cellulose chains have higher probability in forming junctions, and on the other hand,  
 399 the amount of non-dissolved fraction in solutions of DP 640 is much higher than that in  
 400 solutions of DP 320. Both reasons act towards gel reinforcement. Even though gelation  
 401 kinetics depends on the temperature, the latter does not influence gel modulus within the  
 402 experimental errors, as shown in Figure 7a and previously reported by Roy et al., (2003).



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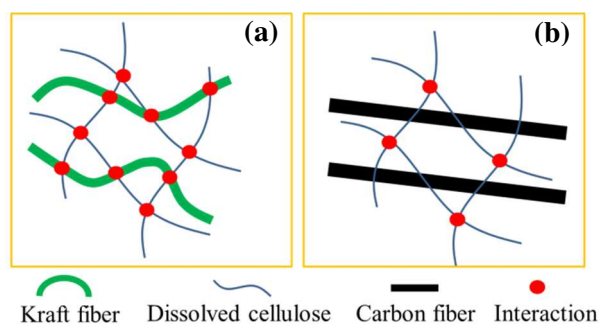
Figure 7. Modulus at gel point as a function of total cellulose (a) and total solids (b) concentrations for all suspensions studied. Filled points correspond to the measurements performed at 5°C and open points at 10°C. The errors are smaller or of the size of points.

Figure 7b shows that when the modulus at gel point is plotted as a function of total solids concentration, all data fall on one master plot emphasizing the role of all cellulose “fibers” present in the suspension, whatever their origin is. However, this plot does not take into account cellulose concentration in the continuous phase, which obviously also contributes to suspension gelation.

It was suggested that elastic modulus is power-law dependent on cellulose concentration in cellulose-NaOH-water solution, and the exponents are around 3-4 (Gavillon & Budtova, 2008; Liu et al., 2011). Figure 7a shows that power-law exponents obtained for suspensions studied are much higher, from around 4.8 to 10.6. Cellulose concentration interval is small which may induce incertainties, but slopes are much steeper as non-dissolved fraction and

419 added kraft fibers strongly reinforce the network despite being below the percolation  
420 concentration.

421 Summarizing, Figure 8 shows a schematic presentation of gelling cellulose suspensions with  
422 “interacting” (cellulose-based) and “non-interacting” (carbon) fibers. The additional bonds  
423 formed between dissolved cellulose and cellulose-based “solids” (non-dissolved fraction and  
424 added fibers) accelerate suspension gelation and increase gel modulus while no bonds are  
425 formed between dissolved cellulose and carbon fibers. **We speculate that the interactions are  
426 between dissolved cellulose chains and hydrated and partly deprotonated cellulose on the  
427 surface of the “solids”.** The nature of the bonds leading to gelation of cellulose-NaOH-water  
428 solutions is still under debates. Traditionally, gelation of aqueous cellulose-NaOH solutions  
429 is said to be due to the formation of hydrogen bonds between overlapping cellulose  
430 macromolecules, leading to a micro-phase separation in time (gels become opaque) and  
431 formation of polymer-rich and polymer-poor phases (Gavillon & Budtova, 2008; Budtova &  
432 Navard, 2016). Another option was suggested by Pereira et al. (2018): gelation of cellulose-  
433 NaOH solutions is due to crystallization and precipitation of cellulose. Finally, it was  
434 demonstrated that cellulose carbonates are formed in cellulose-NaOH solutions as a result of  
435 the interactions of dissolved deprotonated cellulose and CO<sub>2</sub>, the latter always being present  
436 in air (Gunnarsson, Bernin, Östlund & Hasani, 2018). Carbonate bridges were suggested to  
437 be the reason of gelation. All three mechanisms can theoretically explain the interactions  
438 between dissolved and non-dissolved cellulose leading to suspension gelation, however, the  
439 formation of hydrogen and carbonate bonds seem to be more probable.



440

441 Figure 8. **Simplified** schematic illustration of larger number of interactions between cellulose  
 442 chains and cellulose fibers (a) as compared to the case of added inert carbon fibers (b).

443

## 444 5. Conclusions

445 Gelation of cellulose-NaOH-water in the presence of non-dissolved cellulose fibers was  
 446 studied using dynamic rheology. Certain phenomena were general for solutions (**without**  
 447 **fibers**) and suspensions (**with fibers**), such as **acceleration of gelation** with the increase of  
 448 temperature and of total cellulose concentration, as known from literature on cellulose-  
 449 NaOH-water solutions. The presence of non-dissolved fibers (either from non-dissolved  
 450 fraction, or from added fibers, or from both) strongly accelerated suspension gelation and  
 451 increased gel modulus. **This phenomenon is** supposed to be due to the additional **interactions**  
 452 **between cellulose chains in solution and on the surface of non-dissolved fibers.** The  
 453 **mechanism** can be either **due to** hydrogen and/or carbonate bonds, the latter being formed due  
 454 to the interactions between deprotonated cellulose and CO<sub>2</sub> from air. Both **total and solid**  
 455 **cellulose** concentrations were shown to be important for describing and interpreting gelation  
 456 **of** cellulose solutions in the presence of non-dissolved cellulose.

457

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