



# Gelation of cellulose-NaOH solutions in the presence of cellulose fibers

Oona Korhonen, Tatiana Budtova

## ► To cite this version:

Oona Korhonen, Tatiana Budtova. Gelation of cellulose-NaOH solutions in the presence of cellulose fibers. Carbohydrate Polymers, 2019, 224, pp.115152. 10.1016/j.carbpol.2019.115152 . hal-02419087

**HAL Id: hal-02419087**

**<https://hal.science/hal-02419087>**

Submitted on 20 Jul 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 *Submitted to Carbohydrate Polymers June 3d, 2019*

2 *Revised July 26<sup>th</sup>, 2019*

3

4

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

6

7

8 Oona Korhonen<sup>1</sup> and Tatiana Budtova<sup>1,2\*</sup>

9

10

11

12 <sup>1</sup> Aalto University, School of Chemical Engineering, Department of Bioproducts and  
13 Biosystems, P.O. Box 16300, 00076 Aalto, Finland

14 <sup>2</sup> MINES ParisTech, PSL Research University, CEMEF – Center for materials forming,  
15 UMR CNRS 7635, CS 10207, 06904 Sophia Antipolis, France

16

17 Corresponding author: Tatiana Budtova

18 Tatiana.Budtova@mines-paristech.fr

19 Tatiana.Budtova@aalto.fi

20

21

22

## 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

## Abstract

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

## Key words:

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

## 1. Introduction

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

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

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

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

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

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

## 2. Materials and Methods

### 2.1. Materials

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

## 2.2. Methods

### 2.2.1. Pulp characterization and acid hydrolysis

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

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

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

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

Fiber size distribution of softwood kraft fibers was determined in triplicate via FiberLab<sup>TM</sup> (Metso Automatization) device.



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

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

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

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

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

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

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

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

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

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

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

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			
Kraft fibers added	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
						15 204
	DP(640)K1.00%		6.0	2.66	1.00	10 204
<b>Cellulose solutions</b>	DP(320)5.25%		5.25	0.21	0	5 205
<b>of various</b>	DP(320)5.5%	320	5.5	0.22	0	5 206
<b>concentrations</b>	DP(320)6%		6	0.24	0	5 207
<b>Carbon fibers</b>	DP(320)C0.25%		5	0.44	0.25	5 208
<b>added</b>	DP(320)C0.5%	320	5	0.70	0.5	5 208

#### 2.2.6. Rheological measurements

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

### 3. Results

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

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

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

Table 2. Characteristics of neat 5 wt% cellulose-NaOH solutions for DP 320 and 640: solid 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

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

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

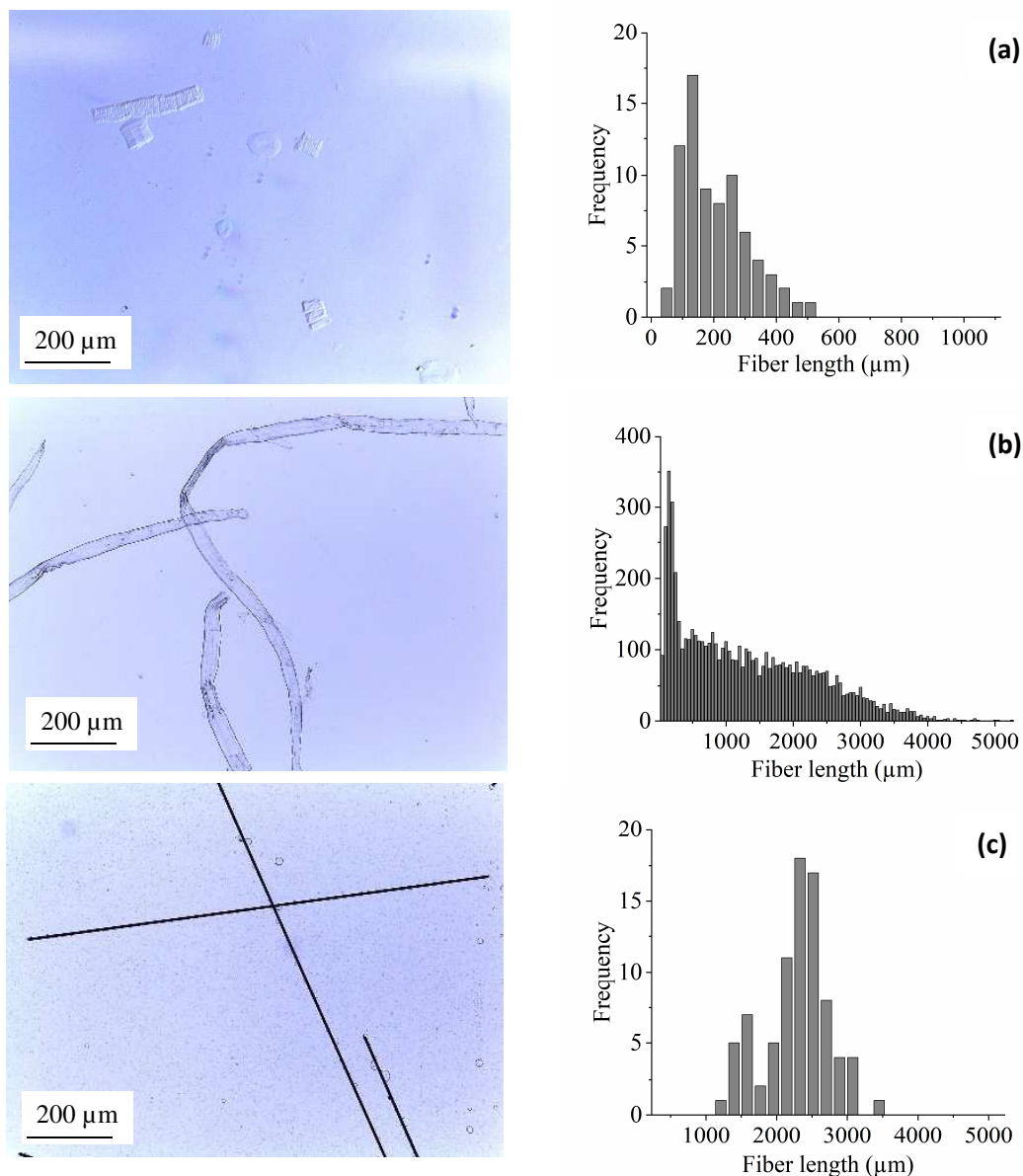


Figure 1. Illustration of non-dissolved fraction in 5 wt% cellulose (DP 640)-NaOH-water solution (a), softwood kraft fiber (b) and carbon fiber (c) together with their length distributions

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



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

### 3.3. Rheological properties

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

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

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

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

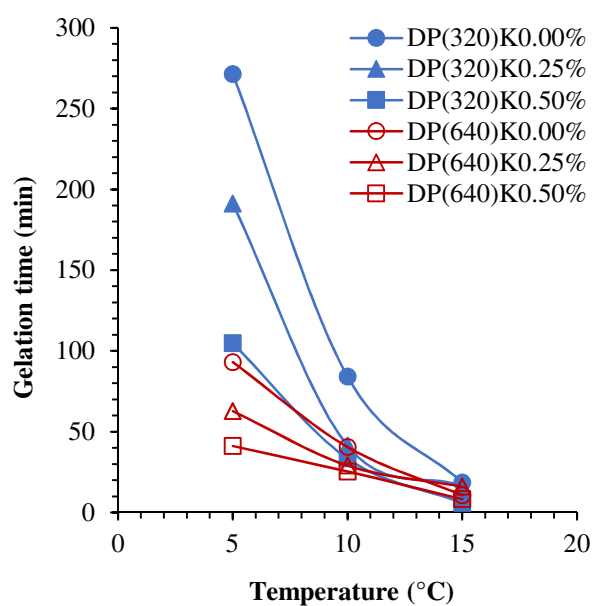


Figure 2. Effect of temperature and added kraft fiber concentration on gelation time. Lines are to guide the eye. The errors in gelation time are less than 10%, but are not shown in order not to overload the graph.

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

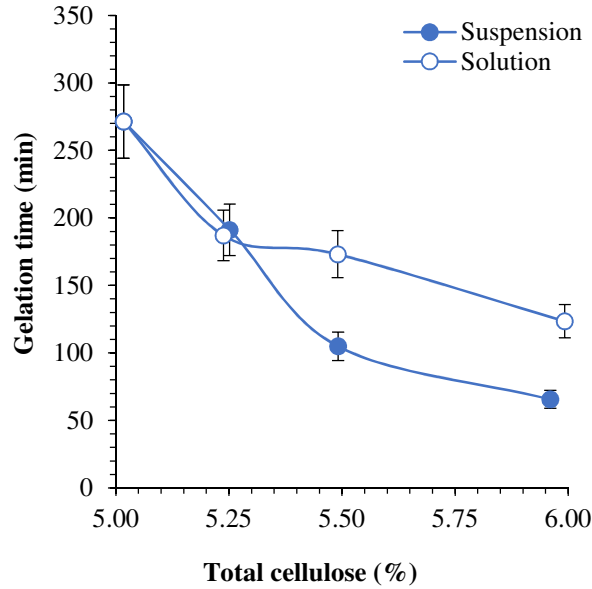


Figure 3. Gelation time at 5°C as a function of total cellulose concentration for cellulose(DP 320)-NaOH-water solutions and 5 wt% cellulose(DP 320)-NaOH-water suspensions with added kraft fibers. Lines are to guide the eye.

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

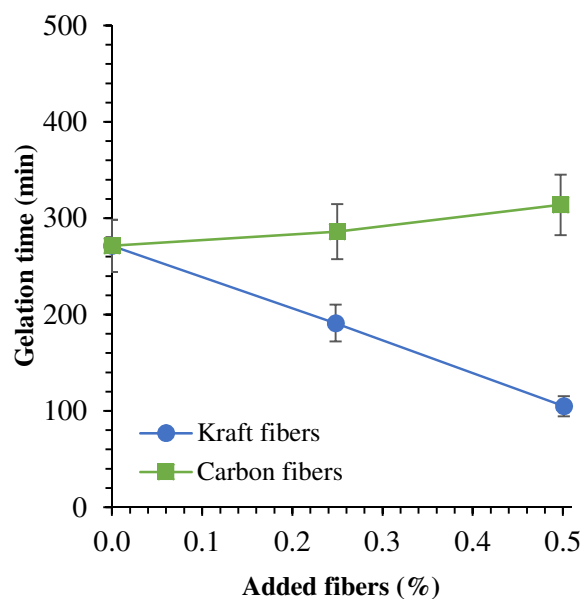


Figure 4. Gelation time at 5 °C as a function of added fiber's concentration for suspensions with carbon or kraft fibers added to 5 wt%cellulose(DP 320)-NaOH-water.

## 4. Discussion

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

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

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

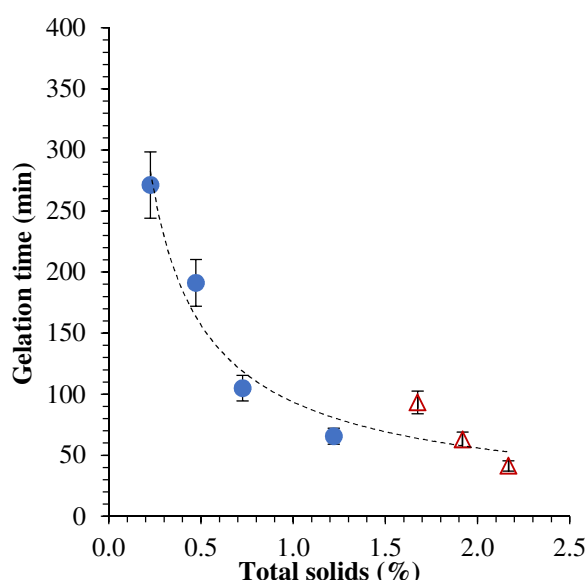


Figure 5. Effect of total solids concentration on gelation time at 5°C. Dashed line corresponds to the power law approximation  $y = 93.68x^{-0.741}$

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

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

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

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

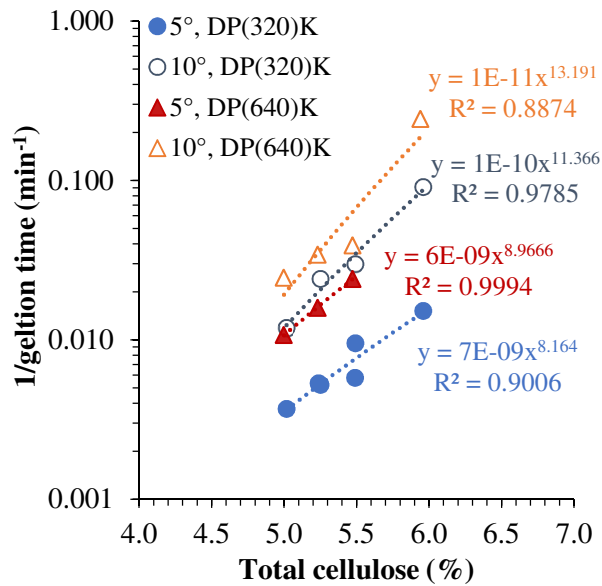


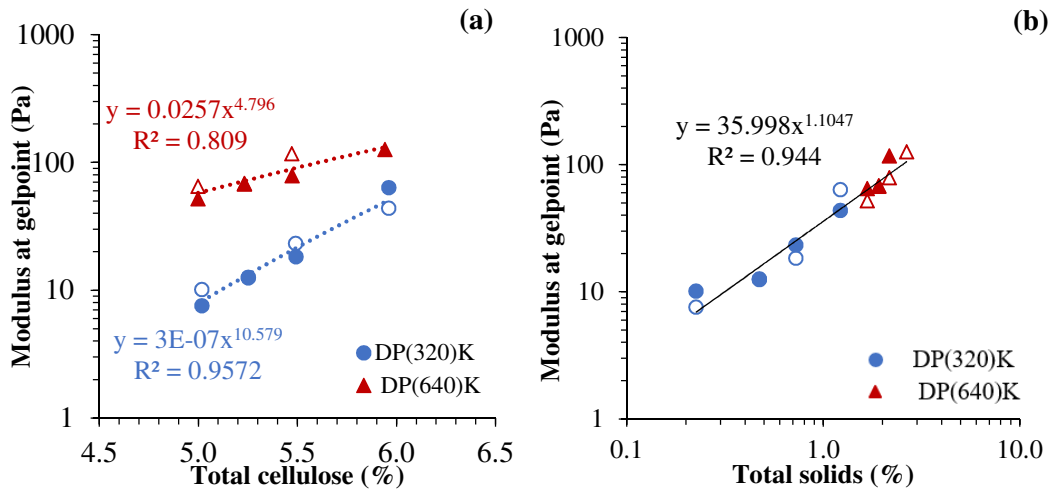
Figure 6. Inverse gelation time vs. total cellulose concentration for all suspensions studied.

Lines are power-law approximations

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



403



404

405

406

407

408

409

410

411

412

413

414

415

416

417

418

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.

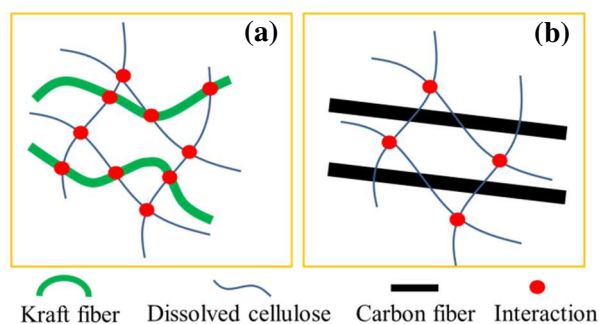


Figure 8. **Simplified** schematic illustration of larger number of interactions between cellulose chains and cellulose fibers (a) as compared to the case of added inert carbon fibers (b).

## 5. Conclusions

Gelation of cellulose-NaOH-water in the presence of non-dissolved cellulose fibers was studied using dynamic rheology. Certain phenomena were general for solutions (**without fibers**) and suspensions (**with fibers**), such as **acceleration of gelation** with the increase of temperature and of total cellulose concentration, as known from literature on cellulose-NaOH-water solutions. The presence of non-dissolved fibers (either from non-dissolved fraction, or from added fibers, or from both) strongly accelerated suspension gelation and increased gel modulus. **This phenomenon is** supposed to be due to the additional **interactions between cellulose chains in solution and on the surface of non-dissolved fibers**. The **mechanism** can be either **due to** hydrogen and/or carbonate bonds, the latter being formed due to the interactions between deprotonated cellulose and  $\text{CO}_2$  from air. Both **total and solid cellulose** concentrations were shown to be important for describing and interpreting gelation **of** cellulose solutions in the presence of non-dissolved cellulose.

## Acknowledgements

459 Authors wish to acknowledge the funding from Business Finland, Stora Enso Oyj and UPM-  
460 Kymmene Oyj. We also want thank Separation Research Oy Ab and Fibertus Oy for  
461 collaboration, Romain Castellani (CEMEF, MINES ParisTech) for the help with rheological  
462 experiments, Rita Hatakka (Aalto University) for the assistance with pulp composition  
463 determination, Kaalro Nieminen (Aalto University) for the assistance with fiber size  
464 distributions and Michael Hummel (Aalto University) for rewarding discussions.  
465 Additionally we wish to sincerely thank Nolene Byrne (Deakin University) for providing the  
466 carbon fibers for this study.

## References

- Abbot, A., & Bismarck, A. (2010). Self-reinforced cellulose nanocomposites. *Cellulose*, 17, 779-791.
- Abdennadher, A., Vincent, M., & Budtova T. (2016) Rheological properties of molten flax- and Tencel ®-polypropylene composites: Influence of fiber morphology and concentration. *Journal of Rheology*, 60, 191-201.
- Budtova, T., & Navard, P. (2016). Cellulose in NaOH-water based solvents: a review. *Cellulose*, 23, 5-55.
- Cai, J., & Zhang, L. (2006). Unique gelation behavior of cellulose in NaOH/urea aqueous solution. *Biomacromolecules*, 7, 183-189.
- Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y., & He, J. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, 147, 13-21.
- Capiati NJ, Porter RS (1975) The concept of one polymer composites modelled with high density polyethylene. *Journal of materials science* 10: 1671-1677.
- Davidson, G. F. (1934). The dissolution of chemically modified cotton cellulose in alkaline solutions. Part I: In solutions of NaOH, particularly at T°C below the normal. *The Journal of the Textile Institute*, 25, T174-T196.
- Duchemin, B. J. C., Newman, R. H., & Staiger, M.P. (2009). Structure-property relationship of all-cellulose composites. *Composites Science and Technology*, 69, 1225-1230.
- Egal, M., Budtova, T., & Navard, P. (2007) Structure of aqueous solutions of microrcrystalline cellulose/sodium hydroxide below 0 °C and the limit of cellulose dissolution. *Biomacromolecules*, 8, 2282-2287.

490 Fink, H-P., Weigel, P., Purz, H. J., & Ganster, J. (2001). Structure formation of regenerated  
 491 cellulose materials from NMMO-solutions. *Progress in Polymer Science*, 26, 1473-1524.

492 Gavillon, R., & Budtova, T. (2008). Aerocellulose: new highly porous cellulose prepared  
 493 from cellulose–NaOH aqueous solutions. *Biomacromolecules*, 9, 269–277.

494 Gindl, W., & Keckes, J. (2005). All-cellulose nanocomposite. *Polymer*, 46, 10221-10225.

495 Gunnarsson, M., Bernin, D., Östlund, Å., & Hasani, M. (2018). The CO<sub>2</sub> capturing ability of  
 496 cellulose dissolved in NaOH (aq) at low temperature. *Green Chemistry*, 20, 3279-3286.

497 Hildebrandt, N., Piltonen, P., Valkama, J., & Illikainen, M. (2017). Self-reinforcing  
 498 composites from commercial pulps via partial dissolution with NaOH/urea. *Industrial Crops*  
 499 *& Products*, 109, 79-84.

500 Huber, T., Müssig, J., Curnow, O., Pang, S., Bickerton, S., & Staiger, M.P. (2012). A critical  
 501 review of all-cellulose composites. *Journal of Materials Science*, 47, 1171-1186.

502 Janson, J. (1970). Calculation of the polysaccharide composition of wood and pulp. *Paperi ja*  
 503 *puu*, 5, 323-329.

504 Kamide, K., Okajima, K., & Kowsaka, K. (1992). Dissolution of natural cellulose into  
 505 aqueous alkali solution: role of supermolecular structure of cellulose. *Polymer Journal*, 24,  
 506 71-96.

507 Korhonen, O., Sawada, D., & Budtova, T. (2019). All-cellulose composites via short fiber  
 508 dispersion approach using NaOH-water solvent. *Cellulose*, 26, 4881-4893.

509 Labidi, K., Korhonen, O., Zrida, M., Hamzaoui, A.H., & Budtova, T. (2019). All-cellulose  
 510 composites from alfa and wood fibers. *Industrial crops & products*, 127, 135-141.

511 Liu, W., Budtova, T., & Navard, P. (2011). Influence of ZnO on the properties of dilute and  
512 semi-dilute cellulose-NaOH-water solutions. *Cellulose*, 18, 911-920.

513 Lu, A., Liu, Y., Zhang, L. & Potthast, A. (2011) Investigation on metastable solution of  
514 cellulose dissolved in NaOH/urea aqueous system at low temperature. *Journal of Physical*  
515 *Chemistry B*. 115, 12801-12808.

516 McCormick, C.L., & Lichatowich, D. K. (1979). Homogeneous solution reactions of  
517 cellulose, chitin, and other polysaccharides to produce controlled-activity pesticide systems.  
518 *Journal of Polymer Science: Polymer Letters Edition*, 17, 479-484.

519 Minus, M., & Kumar, S. (2005). The Processing, Properties and Structure of Carbon Fibers.  
520 *The Journal of the Minerals, Metals & Materials Society*, 57, 52-58.

521 Nadhan, A. V., Rajulu, A. V., Li, R., Jie, C., & Zhang, L. (2012). Properties of regenerated  
522 cellulose short fibers/cellulose green composite films. *Journal of Polymers and the*  
523 *Environment*, 20, 454-458.

524 Nishino, T., Matsuda, I., & Hirao, K. (2004). All-cellulose Composite. *Macromolecules*, 37,  
525 7683-7687.

526 Ouajai, S., & Shanks, R. A. (2009). Preparation, structure and mechanical properties of all-  
527 hemp cellulose biocomposites. *Composites Science and Technology*, 69, 2119-2126.

528 Pereira, A., Duarte, H., Nosrati, P., Gubitosi, M., Gentile, L., Romani, A., Medronho, B., &  
529 Olsson, U. (2018). Cellulose gelation in NaOH solutions is due to cellulose crystallization.  
530 *Cellulose*, 25, 3205-3210.

531 Piltanen, P., Hildebrandt, N., Westerlind, B., Valkama, J., Tervahartiala, T., & Illikainen, M.  
532 (2016). Green and efficient method for preparing all-cellulose composites with NaOH/urea  
533 solvent. *Composites Science and Technology*, 135, 153-158.

534 Ross-Murphy, S. B. (1991). Concentration dependence of gelation time. In E. Dickinson  
 535 (Ed), *Food Polymers. Gels and Colloids* (pp. 357-368). Cambridge: Royal Chemistry.

536 Roy, C., Budtova, T., & Navard, P. (2003). Rheological properties and gelation of aqueous  
 537 cellulose-NaOH solutions. *Biomacromolecules*, 4, 259-264.

538 Ruan, D., Lue, A., & Zhang, L. (2008). Gelation behaviors of cellulose solution dissolved in  
 539 aqueous NaOH/thiourea at low temperature. *Polymer*, 49, 1027-1036.

540 Saarikoski, E., Rissanen, M., & Seppälä, J. (2015). Effect of rheological properties of  
 541 dissolved cellulose/microfibrillated cellulose blend suspensions on film forming.  
 542 *Carbohydrate polymers*, 119, 62-7.

543 Sirviö, J. A., Visanko, M., & Hildebrandt, N. C. (2017). Rapid preparation of all-cellulose  
 544 composites by solvent welding based on the use of aqueous solvent. *European Polymer*  
 545 *Journal*, 97, 292-298.

546 Sixta, H., Potthast, A., & Krottschek, A. W. (2006). Chemical pulping processes. In H. Sixta  
 547 (Ed), *Handbook of pulp* (pp. 109-510). Weinheim: WILEY-VCH Verlag GmbH & Co.  
 548 KGaA.

549 Sojoudiasli, H., Heuzey, M-C., & Carreau, P. J. (2014). Rheological, morphological and  
 550 mechanical properties of flax fiber polypropylene composites: Influence of compatibilizers.  
 551 *Cellulose*, 21, 3797–3812.

552 Ward IM, Hine P. J. (1997). Novel composites by hot compaction of fibers. *Polymer*  
 553 *Engineering and Science*, 37, 1809-1814.

554 Weng, L., Zhang, L., Ruan, D., Shi, L., & Xu, J. (2004). Thermal gelation of cellulose in a  
 555 NaOH/Thiourea aqueous solution. *Langmuir*, 20, 2086-2093.

556 Winter, H. H. & Chambon, F. J. (1986). Analysis of linear viscoelasticity of a crosslinking  
 557 polymer at the gel point. *Journal of Rheology*, 30, 367.



- 558 Yang, Q., Le, A., & Zhang, L. (2010). Reinforcement of ramie fibers on regenerated cellulose  
559 films. *Composites Science and Technology*, 70, 2319-1214.
- 560 Zhou, J., & Zhang, L. (2000). Solubility of cellulose in NaOH/urea aqueous solution.  
561 *Polymer journal*, 32, 866-870.