

# Swelling and dissolution kinetics of natural and man-made cellulose fibers in solvent power tuned ionic liquid

Feng Chen, Daisuke Sawada, Michael Hummel, Herbert Sixta, Tatiana Budtova

## ▶ To cite this version:

Feng Chen, Daisuke Sawada, Michael Hummel, Herbert Sixta, Tatiana Budtova. Swelling and dissolution kinetics of natural and man-made cellulose fibers in solvent power tuned ionic liquid. Cellulose, 2020, 27 (13), pp.7399-7415. 10.1007/s10570-020-03312-5. hal-03100443

## HAL Id: hal-03100443 https://hal.science/hal-03100443

Submitted on 22 Mar 2023

**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.

# Swelling and Dissolution Kinetics of Natural and Man Made Cellulose Fibers in Solvent Power Tuned Ionic Liquid

4

Feng Chen<sup>a</sup>, Daisuke Sawada<sup>a</sup>, Michael Hummel<sup>a</sup>, Herbert Sixta<sup>a</sup>, Tatiana Budtova<sup>a, b, \*</sup>

- <sup>a</sup> Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto
  University, P.O. Box 16300, 00076 Aalto, Helsinki, Finland;
- 9 <sup>b</sup> MINES ParisTech, PSL Research University, Center for Materials Forming-CEMEF,
- 10 UMR CNRS 7635, CS 10207, 06904 Sophia Antipolis, France.
- 11

12 \* Correspondence: <u>tatiana.budtova@mines-paristech.fr</u>, <u>tatiana.budtova@aalto.fi</u>

13

14 Abstract: The kinetics of the dissolution and swelling of different cellulose fibers in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) was studied by varying solvent power and 15 temperature. Natural fiber, flax, and man-made fibers, Cordenka and Lyocell-type (Ioncell) were 16 17 used with one Ioncell fiber containing lignin and hemicelluloses. Through the addition of water, the solvent power was modified from very good (neat ionic liquid), to moderate (with 5 wt.% water) and 18 19 weak (15 wt.% water). The temperature was varied to correlate the fiber dissolution rate with the 20 solvent viscosity. All fibers were characterized by chemical composition, crystallinity, molecular 21 weight distribution and dynamic vapor sorption. It was demonstrated that while the rate of fiber 22 dissolution in neat ionic liquid depends on fiber accessibility and solvent viscosity, the water-induced 23 decreased solvent power dominates the general fiber behavior. Flax appeared to be the most 24 "sensitive" to the solvent power due to its hierarchical structure. The fastest dissolution or swelling 25 was recorded for Ioncell and the slowest for Cordenka.

- 26
- ~ 7

27 *Keywords:* cellulose fiber, ionic liquid, dissolution, swelling, accessibility

## 29 **1 Introduction**

Cellulose is a fascinating biopolymer present on the Earth in almost inexhaustible quantity. It is a linear polymer built of anhydroglucose units linked by  $(1\rightarrow 4)$ - $\beta$  glycosidic bonds, and until recently it was used mainly for making paper, textile fibers and films (Klemm et al. 2005; Ragauskas et al. 2006). Cellulose cannot be melt-processed (Chen et al. 2015) and thus its shaping requires dissolution (Gross et al. 2010). During the past decades, new cellulose-based materials were developed involving complete or partial dissolution, for example, aerogels (Budtova 2019) and all-cellulose composites (Takashi et al. 2004).

Several direct cellulose solvents are known, with LiCl/N,N-dimethylacetamide (DMAc) 37 (McCormick et al. 1985), NaOH-based aqueous solutions (Budtova and Navard 2016), N-38 methylmorpholine N-oxide (NMMO) monohydrate (Fink et al. 2001) and ionic liquids (ILs) 39 (Swatloski et al. 2002) being the most popular ones. Among these solvents, only NMMO 40 monohydrate is used as direct cellulose solvent on an industrial scale for spinning textile 41 fibers (Lyocell process); the use of ionic liquids, resulting in Ioncell fibers (also Lyocell 42 process), is seen as approach alternative to that using NMMO-based technology (Sixta et al. 43 44 2015).

While fibers, films and aerogels require complete cellulose dissolution, all-cellulose 45 46 composites are based on partial dissolution of natural or man-made fibers (Takashi et al. 47 2004; Soykeabkaew et al. 2009; Huber et al. 2012). All-cellulose composites are produced 48 either by the dissolution of the surface of cellulose fibers with the dissolved cellulose "gluing" fibers together upon coagulation (Huber et al. 2012), or by dispersing cellulose 49 fibers in a cellulose solution, the latter acting as a continuous matrix (Korhonen et al. 2019). 50 To control the properties of all-cellulose composite, the understanding and quantification of 51 52 the kinetics of fiber dissolution is a prerequisite. Too short dissolution times will result in an insufficient amount of dissolved cellulose in-between the fibers while too long dissolution 53 will result in the destruction of natural fibers' cell walls and the formation of excessive 54 amount of mechanically weaker cellulose II. 55

Although the dissolution of cellulose fibers in various direct solvents has been studied since the first half of the 20th century, detailed investigations of the dissolution mechanisms emerged only during the past 20 years due to a significant improvement of analytical tools. For example, the development of optical microscopy with various set-ups allowed for precise visualization, temperature control, video capture, and image analysis to follow the fibers' evolution during dissolution. The majority of studies was focusing on wood fibers (Olsson 62 et al. 2014; Cuissinat et al. 2006; Mäkelä et al. 2018; Le Moigne et al. 2010; Parviainen et al. 2014), most probably because of practical reasons, as films and textile fibers are made 63 from wood dissolving pulps. By varying the solvent dissolution power, it was demonstrated 64 that wood fibers dissolve either directly from the surface resulting in their diameter decrease, 65 sometimes by disintegration into particles, or via ballooning followed by their burst 66 (Cuissinat et al. 2006). In moderate and bad solvents fibers only swell either via ballooning 67 or by a homogeneous increase in diameter, respectively (Cuissinat et al. 2006). The same 68 69 mechanisms apply to cotton fibers but, interestingly, not to flax or ramie (Cuissinat et al. 2008). Lyocell fibers either radially dissolve in a good solvent or radially swell in a moderate 70 solvent (Chaudemanche et al. 2011). Various factors have to be taken into account to 71 72 understand fiber swelling and dissolution behavior: their composition, properties of primary and secondary layers in natural fibers or properties of a skin in man-made fibers (Abu-Rous 73 74 et al. 2007), accessibility, porosity, and ,potentially, cellulose crystallinity and molecular 75 weight.

76 The studies of the kinetics of fiber dissolution are very scarce. Microcrystalline cellulose was used as a model substance to study the kinetics of its dissolution in ionic liquids and the 77 influence of a co-solvent, dimethylsulfoxide (DMSO), on the dissolution (Andanson et al. 78 2014). Cellulose dissolution was assessed by the decrease of birefringence which arises from 79 the crystalline regions in polarized light (Andanson et al. 2014). Optical microscopy coupled 80 with semi-automated data processing was used to evaluate the dissolution kinetics of two 81 82 kraft pulps in 0.2 M cupriethylene diamine by tracing the fiber surface area (Mäkelä et al. 2018). A first-order kinetic model was shown to be applicable to describe fibers' dissolution 83 84 (Mäkelä et al. 2018). The kinetics of wood fiber homogeneous swelling in NMMO in the presence of water at 18–22 % was reported by H. Peng et al. (Peng et al. 2017). To the best 85 of our knowledge, there is no report comparing the kinetics of dissolution and/or swelling of 86 different fibers, natural and man-made, under the same conditions. In the view of making 87 88 all-cellulose composites, the evolution of long natural fibers, such as flax, are of particular 89 interest (Chen et al. 2020). The beginning of the dissolution and/or swelling processes is of 90 special importance and has to be well understood and controlled.

The goal of this work was to perform a comprehensive study comparing both the dissolution and swelling kinetics of flax and various man-made fibers with different characteristics. Room temperature ionic liquid, 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), was used, and temperature was varied to tune solvent viscosity. Solvent dissolution power was varied by adding water. The correlations between fiber dissolution and swelling kinetics, fiber characteristics (structure, composition, cellulose molecular
weight and accessibility), solvent power and viscosity were built.

## 98 2 Experimental Part

#### 99 2.1 Materials

Flax fibers were from the outer bast layer of the plant stem. A commercially available 100 high-strength rayon filament yarn Cordenka 700 was kindly donated by Cordenka GmbH & 101 Co. KG., and two other man-made fibers were produced by spinning of an unbleached birch 102 kraft pulp-ionic liquid solutions resulting in Ioncell-FL fibers (coded "H50" in the ref. Ma 103 et al. 2018), and of a prehydrolysed kraft birch pulp-IL solution, resulting in Ioncell-F fibers 104 105 (see, for example, Asadi et al. 2018). The characteristics of the fibers are presented in the Results section. The ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 106 107 purity > 95%, was purchased from IoLiTec, Germany. The moisture content of 108 [EMIM][OAc] was 0.27 wt.% as determined by Karl-Fischer titration. The milli-Q® water 109 was used to dilute the IL to IL-water mixtures to tune solvent power.

#### 110 **2.2 Methods**

#### 111 2.2.1 Chemical composition of fibers

112 The composition (carbohydrates, total lignin) of all fibers was determined according to 113 NREL/TP-510-42618 norm. The amount of carbohydrates was detected by high 114 performance anion exchange chromatography with pulse amperometric detection (HPAEC-115 PAD) using a Dionex ICS-300 system. Cellulose and hemicellulose contents were calculated 116 according to the amount of monosaccharides following the Janson formula (Janson 1970). 117 The acid-soluble lignin was determined by using a Shimadzu UV 2550 spectrophotometer 118 at a wavelength of 205 nm using absorption coefficient of 110 Lg<sup>-1</sup>cm<sup>-1</sup>.

#### 119 2.2.2 Molecular weight distribution of cellulose in fibers

The molecular weight distribution of cellulose in all fibers was characterized by gel permeation chromatography (GPC) according to the procedure described elsewhere (Ma et al. 2018), and number-average and weight-average molecular weights,  $M_n$  and  $M_w$ , were calculated. Prior to the analysis, fibers were cut into small pieces. The GPC system consisted of a pre-column (PLgel Mixed-A,  $7.5 \times 50$  mm), four analytical columns (4 × PLgel Mixed125 A,  $7.5 \times 300$  mm) and a RI-detector (Shodex RI-101). The fibers were pre-activated by 126 water/acetone/DMAc solvent exchange sequence. The samples were then dissolved in a 90 127 g/L lithium chloride (LiCl)/DMAc mixture at room temperature. The solution was diluted to 128 9 g/L LiCl/DMAc, filtered through a 0.2 mm syringe filter and analyzed by using a Dionex 129 Ultimate 3000 system with refractive index (RI) detection (Shodex RI-101).

130 2.2.3 Determination of the crystallinity index by X-ray diffractometer (XRD)

131 XRD patterns were collected on an X-ray diffractometer (a X'Pert Pro MRD, 132 PAN'alytical, Lelyweg, The Netherlands) with Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Fiber 133 samples were grinded to powder and then mounted on multi-position sample holder. Data 134 were collected in a 2 $\theta$  range between 5° and 60° in reflection mode.

The background profile was estimated using a smoothing method (Brückner 2000; Frost et al. 2009) applying Savitzky-Golay (Savitzky et al. 1964) filter in the 2 $\theta$  range from 6 to 55° for each diffraction profile. Window size and polynomial order for the Savitzky-Golay filter were set to 51 data points (corresponding to 4° by 2 $\theta$ ) and 1, respectively. Iteration for the background estimation was repeated 50 times. The crystallinity index (*CRI*<sub>total</sub>) of fibers was estimated using the ratio of the area of total intensity (*I*<sub>total</sub>) and of background intensity (*I*<sub>bka</sub>) from 10 to 30° 2 $\theta$ :

142

$$CRI_{total} = 100 \times \frac{\int I_{total} \, d2\theta - \int I_{bkg} \, d2\theta}{\int I_{total} \, d2\theta} \tag{1}$$

143 In this method the crystallinity index is calculated over the total material.

#### 144 2.2.4 Dynamic vapor sorption (DVS)

A dynamic vapor sorption apparatus with a measuring accuracy of 0.1 mg was used to 145 record kinetics of water vapor sorption by the fibers. Around 15 mg of grinded fibers were 146 147 placed in the sample pan and their weight evolution was recorded upon decrease of the relative humidity (RH) to 0 % at 25 °C under nitrogen (flow rate 100 cm<sup>3</sup>/s). Equilibrium 148 149 was considered to be reached when sample mass change was below 0.001 % per minute over 10 min. Then RH was increased to 60 % and sample weight evolution and time to reach 150 151 equilibrium  $(t_s)$  were recorded. Moisture desorption  $M_{des}$  (from  $M_{amb}$  at ambient conditions to  $M_0$  at 0% RH) and sorption  $M_s$  (from  $M_0$  to  $M_{60}$  at 60% RH) were calculated as follows: 152

153 
$$M_{des} = \frac{M_{amb} - M_0}{M_0} \times 100\%$$
(2)

154 
$$M_s = \frac{M_{60} - M_0}{M_0} \times 100\%$$
(3)

#### 155 2.2.5 Rheological characterization

The rheological properties of the IL and IL-water mixtures were characterized using an Anton Paar MCR 302 rheometer equipped with a plate-plate geometry (25 mm plate diameter, 1 mm gap) and a Peltier temperature control system. Viscosity-shear rate dependences were recorded from 1 to 100 s<sup>-1</sup> at fixed temperature which was varied from 20 °C to 60 °C.

#### 161 2.2.6 Kamlet-Taft Parameters

The Kamlet-Taft parameters of the neat [EMIM][OAc] and [EMIM][OAc]-water 162 mixtures were determined from the absorption peaks of three different dyes: Reichardt's dye 163 (RD, range 518-585 nm), N,N-diethyl-4-nitroaniline (DENA, 402-414 nm), and 4-164 165 nitroaniline (NA, 406-398 nm). The dyes were weighed and mixed with the IL or IL-water mixture. A Varian UV-vis spectrometer equipped with a thermostat (precision  $\pm 0.1$  °C) 166 was used. The milli-O<sup>®</sup> water was measured for background subtraction. Spectra were 167 collected at a resolution of 1 nm and 10-30 nm of absorbance and data around the peak were 168 fitted with a Gaussian function in order to precisely locate the maximum ( $v_{max}$ ). More details 169 on the measurement of Kamlet-Taft parameters can be found in Hauru et al. 2012. 170

171

#### 172 2.2.7 Optical microscopy observations of fiber swelling and dissolution

One fiber was placed between two glass plates with the in-between distance around 140 173 µm controlled by spacers. The distance between two glass slides is much larger than the 174 fiber's thickness. As the proportion between fiber and solvent was approximately  $7 \times 10^{-4}$  g/g, 175 176 we assume that the fiber was in an infinite solvent, i.e. the overall polymer concentration during and after complete dissolution can be neglected. The ends of the fiber were fixed by 177 tape and solvent added. Fiber diameter was recorded by a DM4500P (Leica) optical 178 179 microscope in transmission mode equipped with a CCD camera (Metallux 3, Leitz) and Linkam TMS 91 hot stage to control temperature. The evolution of the fiber diameter in time 180 181 t was calculated as  $D_t/D_0$ , where  $D_0$  and  $D_t$  are initial diameter of the fiber at t = 0 and 182 diameter of fiber at time *t*, respectively.

## 184 **3 Results**

This section is structured as follows. Because different types of fibers were studied, their composition, cellulose molecular weight, crystallinity index and accessibility are reported first. Then solvent properties, such as Kamlet-Taft parameters and viscosity as a function of temperature and water content, are presented. Based on these results, solvents to study fiber swelling and dissolution were selected. Finally, the fiber behavior upon the addition of the solvents at different temperatures, monitored with optical microscopy, are presented and discussed.

#### 192 **3.1** Physiochemical properties of cellulose fibers

193 Flax is a natural fiber with a complex morphology; its elementary fiber consists of several cell wall layers and a lumen. The outer layer (or a primary cell wall) is the first layer 194 195 formed during the cell wall growth; it is relatively thin and contains mainly less ordered 196 cellulose, hemicelluloses and pectins. The secondary cell wall is much thicker than the primary wall and consists of highly crystalline cellulose fibrils spirally wound in a matrix of 197 198 hemicellulose and pectins. Cellulose fibrils in this layer are oriented in the axis of the fiber and hence display a unidirectional structure (Rong et al. 2001; Charlet et al. 2010; Baley 199 200 2002). Two types of man-made fibers were selected, Cordenka, a modified viscose fiber, and Lyocell-type Ioncell fibers. Cordenka consists of a dense skin and spongy core (Rous et 201 202 al. 2006). Fibers made via Lyocell process have more homogeneous morphology, with a 203 semipermeable skin, porous middle zone and dense fiber center (Rous et al. 2006; Rous et 204 al. 2007).

The composition of the fibers used in this work is shown in Table 1. Flax contains 83.3% cellulose, 11.3% hemicellulose and 2.3% lignin; the results are in line with those reported in literature (Yan et al. 2014; Bolton 1994). Cordenka filament is spun from a high-grade dissolving pulp and thus contains only small amounts of hemicellulose. Ioncell-F, prepared from a standard dissolving-grade pulp, has a higher hemicellulose content. Ioncell-FL is spun from an unbleached kraft pulp and thus contains notable amounts of both hemicellulose and lignin.

- 212
- 213
- 214
- 215

Samulas	Cellulose	Hemicellulose	Lignin	$M_n$	$M_{\rm w}$	CRI <sub>total</sub>	M <sub>des</sub>	$M_s$	ts
Samples	%	%	%	kDa	kDa	%	%	%	min
Flax	83.3	11.3	2.3	652	714	45.1	1.3	7.15	115.7
Cordenka	92.3	2.4	-	68	133	28.1	7.2	11.91	305.2
Ioncell-F	88.9	8.2	-	45	134	40.3	7.5	9.82	177.5
Ioncell-FL	51.1	21.3	22.9	45	176	27.3	10	9.87	177.5

Table 1. Characteristics of fibers used in this study

The number-average  $(M_n)$  and weight-average  $(M_w)$  molecular weights of cellulose in each fiber are presented in Table 1, and the corresponding molecular weight distributions are shown in Figure 1a. The results are similar for all man-made fibers and are much higher for flax. A distinct low molecular weight peak for Ioncell-FL and a subtle shoulder for flax and Ioncell-F correspond to the hemicellulose fraction, as shown in Table 1.





224

Fig. 1 Cellulose molecular mass distribution (a) and X-ray diffraction profiles (b) of flax,
Cordenka, Ioncell-F and Ioncell-FL

227

Figure 1b presents the XRD profiles of all fibers. Flax contains cellulose I with crystallinity index of around 45%, which is typical for plant cellulose (Placet et al. 2012; Moryganov et al. 2018). The man-made fibers contain the cellulose II allomorph, as expected. The crystallinity index ( $CRI_{total}$ ) is around 28 %, 40 % and 27 % for Cordenka, Ioncell-F and Ioncell-FL, respectively (Table 1). Cordenka, a viscose type cellulose fiber, has low crystallinity, in-line with data in literature (Kreze et al. 2003; Okubayashi et al. 2005). As the crystallinity is calculated over the total material, and non-cellulose fraction in Ioncell-FL is around 50%, cellulose crystallinity in Ioncell-FL is higher than  $CRI_{total}$ ; for this fiber it was reported to be around 40% (Ma et al. 2018).

237 To compare the accessibility of the fibers, the dynamic water vapor desorption and sorption were measured. The desorption (to 0% RH) and sorption (to 60% RH) curves are 238 239 shown in Figure S1. Moisture desorption ( $M_{des}$ ), time to reach equilibrium  $t_s$  from 0 to 60 % RH and moisture sorption  $(M_s)$  for each fiber are shown in Table 1 (see also Methods 240 sections and eqs. 2 and 3).  $M_{des}$  reflects the amount of water which is desorbed from ambient 241 242 conditions to 0 % RH and it is the lowest for flax. Cordenka, as viscose fiber, absorbs the highest amount of moisture  $(M_s)$  due to its lowest crystallinity and larger pore volume 243 244 (Okubayashi et al. 2005). Time to reach equilibrium,  $t_s = 305.2$  s, is the longest for Cordenka 245 (Table 1) probably because of hornification phenomena (Siroka et al. 2008) as viscose fibers can be overdried, and also because absorption of a larger amount of vapor takes more time. 246 247 The lignin-free fiber Ioncell-F and lignin-containing fiber Ioncell-FL show the same 248 moisture sorption characteristics, similar to those of commercial Lyocell fibers with a moisture sorption around 9% - 10% at 60% RH and room temperature (Okubayashi et al. 249 2004). The presence of hydrophobic lignin does not influence the water vapor sorption 250 behavior, in line with previously reported results (Ma et al. 2015). Flax absorbs the least 251 252 amount of vapor probably because of the "resistant" primary wall (Okubayashi et al. 2004; 253 Xie et al. 2011; Le Moigne et al. 2008) and higher cellulose crystallinity (Table 1).

254

#### 255 3.2 [EMIM][OAc] and [EMIM][OAc]-water properties

It was demonstrated that the dissolution power of cellulose solvents is correlated with the Kamlet–Taft parameters  $\beta$  (H-bond basicity) and  $\alpha$  (H-bond acidity) (Spange et al. 1998; Fukaya et al. 2006).  $\beta$  describes the ability to accept hydrogen bonds and has been correlated to the breakage of inter- and intra-chain hydrogen bonds within the cellulose chains. High  $\beta$ values were found to positively correlate with cellulose dissolution. In solvent systems with more than one component, as aqueous solutions of ionic liquids, each species might act predominantly as hydrogen bond acceptor or donor. The anions in cellulose-dissolving ILs

usually accept H-bonds, and thus are mostly responsible for the total  $\beta$  value. However, in 263 264 mixtures of ionic liquid and water, water competes with the hydroxyl groups of cellulose for the hydrogen bond acceptance of the anion. It was demonstrated that the ability of such 265 266 solvents to dissolve cellulose is described by  $\beta - \alpha$  (net basicity) which takes the adverse effect of any intrinsic H-donor into account (Hauru et al. 2012). It was further shown that 267 cellulose solvents should be located in a region roughly defined by  $0.80 < \beta < 1.20$  and 0.35268  $<\beta-\alpha < 0.9$  with higher dissolution power corresponding to higher values within these 269 intervals (Hauru et al. 2012). The Kamlet-Taft parameters of [EMIM][OAc] with different 270 271 water contents were measured in the range of 20 - 60 °C. Figure 2 shows the values of  $\beta$  and  $\beta$ - $\alpha$  as a function of water content at 25 °C and 60 °C; the effect of temperature on Kamlet-272 273 Taft values was very small. Within the range of the studied water content, both  $\beta$  and  $\beta$ - $\alpha$ 274 values show a linear decrease with the increase of water content indicating a decreased 275 dissolution ability with 15 wt.% water being at the limit of the solubility window. It was 276 reported that above 15 wt.% water in [EMIM][OAc] microcrystalline cellulose is not 277 dissolved but forms swollen aggregates (Le et al. 2012). Therefore, in the following study 278 [EMIM][OAc] containing 0, 5 and 15 wt.% of water was used as solvents with different power to monitor fiber swelling and dissolution behavior. 279



280

**Fig. 2**  $\beta$  (red symbols) and  $\beta-\alpha$  (blue symbols) plotted against water content in IL [EMIM][OAc] at 25 °C (solid symbol) and 60 °C (open symbol)

283

Solvent viscosity is another important parameter to consider for polymer dissolution. In general, for the same solvent quality and at the same temperature, lower viscosity should accelerate the dissolution rate because of a quicker solvent diffusion. On the one hand, the 287 addition of water to [EMIM][OAc] is known to decrease ionic liquid viscosity (Hall et al. 288 2012), but on the other hand, water is cellulose anti-solvent. In order to take both solvent characteristics into account, we measured the viscosity of [EMIM][OAc] with various water 289 290 content of 0 - 15 wt.% as a function of shear rate at different temperatures (Figure S2). All studied mixtures are Newtonian liquids. Their viscosity is plotted as a function of water 291 292 content at 25, 30 and 40 °C; the arrows show that [EMIM][OAc] at 40 °C and [EMIM][OAc]-5 wt.% water at 30 °C have the same viscosity (Figure 3). These two solvents 293 294 will be used in the following as an example of a solvent with the same viscosity but different 295 dissolution power (Figure 2).





297

Fig. 3 Viscosity of [EMIM][OAc] and [EMIM][OAc]-water mixtures as a function of water
content at various temperatures. The arrows show the same viscosity of [EMIM][OAc] at 40
°C and of [EMIM][OAc]-5 wt.% water at 30 °C

301

#### 302 3.3 Kinetics of fiber dissolution and swelling

As mentioned in the Experimental section, in our set-up both fiber ends were fixed as the goal is to quantitatively analyze the kinetics of fiber behavior and thus fiber displacements should be prevented. It has been reported that depending on the solvent power, uniaxial elongational stress applied on a fiber may influence its dissolution (Le Moigne et al. 2010). We tested if fixed fiber ends modified its behavior in the solvents used. Two cases should be distinguished: good cellulose solvents and moderate/bad ones (Cuissinat et al. 2006). [EMIM][OAc] is known to be very good cellulose solvent; in this case fixing the fiber
ends only slightly slowed down the dissolution kinetics but did not change the dissolution
mechanism (see Supporting Information, Figure S3). In the presence of water, the dissolution
capacity of [EMIM][OAc] is known to be decreased (Hauru et al. 2012; Le et al. 2012;
Minnick et al. 2016; Olsson et al. 2014); however, fixing fiber ends did not modify its
behavior for the given composition of ionic liquid-water (Figure S4). All fibers studied in
this work were always analyzed under the same conditions.

316

## 317 3.3.1 Dissolution in [EMIM][OAc]

The examples of fibers' evolution in [EMIM][OAc] at 30 °C are shown in Figure 4 and at other temperatures in Figure S5. All fibers dissolved without swelling, and temperature strongly accelerated the dissolution. While flax, Cordenka and Ioncell-F dissolved radially in a homogeneous way, the dissolution of Ioncell-FL occurred via small fragments exfoliating from fiber surface. This was especially pronounced at higher temperatures (Figure S5d). The reason is that Ioncell-FL contains high amount of hemicellulose and lignin making fiber heterogeneous and allowing solvent penetration in the amorphous domains.







Fig. 4 Optical microscopy images of fibers in [EMIM][OAc] at 30 °C

The normalized diameter  $D_t/D_0$  of each fiber placed in [EMIM][OAc] is plotted in Figure 328 329 5 as a function of time at different temperatures. The evolution of the Ioncell-F diameter at 60 °C is not shown as fiber dissolution was too fast. Figure 5 shows the dissolution within 330 the first hour; all fibers were dissolved within 12 hours even at 25 °C. To quantify and 331 compare the dissolution kinetics of different fibers, the dissolution rate  $R_d$  was calculated, in 332 the first approximation, as a slope to each set of experimental data approximated by a linear 333 dependence. At all temperatures the dissolution rate follows the order Ioncell-F > Ioncell-334 FL > flax > Cordenka (Figure 5e) which can be explained by the physico-chemical 335 characteristics of fibers, see Section 3.1 and Table 1. Cordenka has the lowest dissolution 336 rate as it has the lowest accessibility as determined by DVS. The second lowest dissolution 337 338 rate shows flax, mainly due to its hierarchical morphology together with high molecular weight cellulose. Ioncell-F has a higher dissolution rate as compared to that of Ioncell-FL. 339 340 We speculate that slower dissolution of Ioncell-FL is due to the presence of lignin (Table 1) which is known to slow down cellulose dissolution (Isogai and Atalla 1998; Shi et al. 2014). 341



**Fig. 5** Evolution of flax (a), Cordenka (b), Ioncell-F (c) and Ioncell-FL (d) normalized diameter as a function of time at 25 °C (1), 30 °C (2), 40 °C (3), 50 °C (4) and 60 °C (5) in [EMIM][OAc] and the dissolution rate of all fibers as a function of temperature (e)

346

Figure 5 shows that increasing the temperature increases the dissolution rate, which is expected due to quicker solvent diffusion in a medium of lower viscosity. The dependence of [EMIM][OAc] viscosity  $\eta$  on temperature can be approximated by Arrhenius-type law (Figure S6a) (Gericke et al. 2009):

351  $\eta \sim \exp(\frac{E_v}{RT})$  (4)

where *T* is temperature in K, *R* is universal gas constant and  $E_v$  the activation energy of viscous flow. The rate of fiber dissolution  $R_d$  can also be roughly approximated by the same law, analogous to other processes' rates (Powell et al. 1941). In this case, the viscosity in eq.4 is substituted by  $R_d$  and the activation energy of viscous flow by the activation energy of dissolution  $E_d$ . Figure S6b shows a linear dependence of  $\ln R_d$  on 1/T. As far as both solvent viscosity and dissolution rate follow Arrhenius-type dependence as a function of inverse temperature, it was logical to probe their direct correlation in natural logarithm form:

$$lnR_d \sim \frac{E_d}{E_v} ln\eta \tag{5}$$

Figure 6 shows a linear decrease of  $\ln R_d$  with the increase of  $\ln \eta$ , with the slope being the ratio between the activation energies  $E_d$  and  $E_v$ . All dependences can be roughly approximated by linear trends confirming the applicability of this analysis for [EMIM][OAc] as solvent of cellulose fibers.





Fig. 6 Dissolution rate as a function of [EMIM][OAc] viscosity

### 367 3.3.2 Dissolution and swelling of fibers in [EMIM][OAc]-5 wt.% water

The presence of a low amount of water, 5 wt.%, should decrease the dissolution power 368 but still allow the dissolution (Figure 2). Examples of fiber behavior in [EMIM][OAc]-5 wt.% 369 water at 30 °C is presented in Figure 7. All man-made fibers were dissolving in this solvent 370 371 in a similar manner as in [EMIM][OAc]. In contrast, flax was only swelling showing a coreshell structure and was not dissolved in [EMIM][OAc]-5 wt.% after 18 hours. This is the 372 direct indication of the decreased solvent power of [EMIM][OAc]-5 wt.% water apparent 373 for a natural fiber. No ballooning was observed irrespective of whether the fiber ends were 374 375 fixed or free (see Figure S4). This is in accordance with previous observations for flax 376 swelling in NMMO containing more than 19-20% of water (Cuissinat et al. 2008).



378

Fig. 7 Optical microscopy images of the fiber evolution in time in [EMIM][OAc]-5% water
at 30 °C. Red marks show core-shell structure

The addition of water to the ionic liquid strongly decreases its viscosity as shown in 382 Figure 3, which could, theoretically, increase the dissolution rate according to Figure 6. It 383 was interesting to check which input, solvent quality or viscosity, is more important in 384 controlling the dissolution rate. To answer this question, the fibers' behavior in two solvent 385 386 systems with the same viscosity was compared: [EMIM][OAc]-5 wt.% water at 30 °C and neat [EMIM][OAc] at 40 °C, see Figure 3. Figure 8 shows the evolution of the normalized 387 388 diameter in these two solvents for each fiber. Except for flax which is not dissolving in [EMIM][OAc]-5 wt.% water, the dissolution rate of man-made fibers decreased in the 389 presence of water as compared to the neat ionic liquid. This indicates that the dissolution 390 kinetics of fibers is governed by the solvent power rather than viscosity of the solvent system. 391 392 The comparison of  $D_t/D_0$  of Cordenka, Ioncell-F and Ioncell-FL as a function of time at 30 °C in [EMIM][OAc]-5 wt.% water is presented in Figure 9; it shows the same dissolution 393 394 rate order as for neat [EMIM][OAc]: Ioncell-F > Ioncell-FL > Cordenka, see the values in Supporting information Table S1. 395



Fig. 8 Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
Ioncell-FL (d) as a function of time in the solvents of the same viscosity: [EMIM][OAc] at
40 °C (solid symbol) and [EMIM][OAc]-5 wt.% water at 30 °C (open symbol). Shaded area
shows swelling



404 Fig. 9 Comparison of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL
405 as a function of time at 30 °C in [EMIM][OAc]-5 wt.% water mixture solvent

#### 407 3.3.3 Swelling of fibers in [EMIM][OAc]-15 wt.% water

The addition of 15 wt.% of water to [EMIM][OAc] pushes this solvent system to the limit of the solubility region, see Figure 2. Figure 10 provides the representative optical microscope images of all four fibers in [EMIM][OAc]-15 wt.% water at 30 °C. No fiber dissolved; all were swelling via core-shell structure similar to flax in [EMIM][OAc]-5 wt.% water. Cordenka showed poor swelling in these conditions. To check that it can swell in this solvent a test at 50 °C was performed, and it showed that temperature increase induced higher swelling (Figure S7).

415



416

417 Fig. 10 Optical microscopy images of fibers in [EMIM][OAc]-15% water at 30 °C. Red
418 marks show core-shell structure

419

The evolution of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL in [EMIM][OAc]-15 wt.% water as function of time at 30 °C is compared in Figure 11. As well as for fibers' dissolution rate (Figure 5), the swelling rate follows the same order: Ioncell-

423 F > Ioncell-FL > flax > Cordenka.



Fig. 11 Comparison of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL
as a function of time at 30 °C in [EMIM][OAc]-15 wt.% water solvent

425

## 429 **4 Discussion**

The comparison of the behavior of all fibers in three solvent systems is summarized in 430 431 Figure 12. At high solvent power (ionic liquid) and fixed temperature, all fibers dissolve and the dissolution rate is controlled mainly by the fiber accessibility. Within the same family of 432 433 man-made fibers, Ioncell, the presence of lignin slows down the dissolution rate, and Ioncell-FL dissolves via partial fragmentation. With the decrease of solvent power, the nature of 434 435 fibers, man-made versus natural, becomes the main factor controlling their behavior. Flax, which has a hierarchical structure with strong secondary layer, turned out to be the most 436 437 "sensitive" to the presence of water. Despite that [EMIM][OAc]-5 wt.% water was expected 438 to dissolve cellulose, flax was only swelling. All fibers had a similar water content at ambient 439 conditions, with flax has the least, thus ruling out that the "intrinsic" water could be the 440 reason of its insolubility in [EMIM][OAc]-5 wt.% water. It should be reminded here that the dissolution experiments were performed in static conditions, without mixing. Finally, in the 441 presence of 15 wt.% water in ionic liquid, all fibers showed only swelling. 442

The results also reveal that under the same experimental conditions (solvent power and temperature), not only the kinetics of dissolution but also the kinetics of swelling correlate to the accessibility of fibers: man-made Ioncell-type fibers showed the highest dissolution

and swelling rates, followed by flax and finally Cordenka with the lowest rates. Temperature

447 increase amplifies the phenomena but does not change the general trend.

448



Fig. 12 Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
Ioncell-FL (d) as a function of time in neat [EMIM][OAc] (1), [EMIM][OAc]-5% water
mixture (2) and [EMIM][OAc]-15% water mixture (3) at 30 °C

453

449

## 454 **5 Conclusions**

The kinetics of fiber evolution in ionic liquid, [EMIM][OAc], was studied for four cellulose fibers, natural (flax) and man-made: viscose type (Cordenka) and Lyocell-type (Ioncell: one similar to Cordenka in composition (Ioncell-F) and the other one with high amounts of lignin and hemicelluloses (Ioncell-FL)). This set of fibers allowed studying the role of the fiber morphology, accessibility, composition and cellulose molecular weight and crystallinity. Temperature was varied to modify solvent viscosity, and water was added to tune solvent power. In the case of high solvent power all fibers are radially dissolving. The main factors influencing the dissolution rate are solvent viscosity (for the same type of fiber) and fiber accessibility (for the same solvent temperature), the latter revealed by water vapor sorption. An Arrhenius-type law was applied to both solvent viscosity and dissolution rate resulting in log-log direct correlation between them.

The decrease of solvent quality due to the addition of water showed that despite the decrease in viscosity, the solvent quality controls the kinetics of the fiber behavior. Flax turned out to be the most "sensitive" to the presence of water, since even a moderate amount of water (5 wt.%) in the [EMIM][OAc] leads to fiber homogeneous swelling with a coreshell structure while all man-made fibers were still dissolving under this condition. Further increase of water content induced radial swelling of all fibers but prevented dissolution.

It is remarkable that both the kinetics of dissolution (the cases of all fibers in neat 473 474 [EMIM][OAc] and all man-made fibers in [EMIM][OAc]-5 wt.% water) and of swelling (the cases of all fibers in [EMIM][OAc]-15 wt.% water) show the same order: Ioncell-F > 475 476 Ioncell-FL > flax > Cordenka. Rising temperature was found to amplify both the dissolution 477 and swelling phenomena but did not change the observed behavior. The results obtained in 478 this study are important to consider when preparing all-cellulose composites in which complete dissolution is not required and the substrates are typically impregnated under static 479 conditions without mixing. 480

481

482 Acknowledgements: The financial support from Business Finland, Stora Enso Oyj and UPM-Kymmene Oyj
483 is gratefully acknowledged. Authors wish to thank Separation Research Oy Ab and Fibertus Oy for
484 collaboration. We thank Gabriel Monge (CEMEF, MINES ParisTech) and Leena Pitänen (Aalto University)
485 for XRD and GPC measurement, respectively.

#### 487 **References**

- Abu-Rous M, Varga K, Bechtold T, Schuster KC (2007) A new method to visualize and characterize the pore
   structure of TENCEL®(Lyocell) and other man-made cellulosic fibres using a fluorescent dye
   molecular probe. J Appl Polym Sci 106:2083-91.
- Andanson JM, Bordes E, Devémy J, Leroux F, Pádua AA, Gomes MF (2014) Understanding the role of cosolvents in the dissolution of cellulose in ionic liquids. Green Chem 16:2528-38.
- 493 Asaadi S, Hummel M, Ahvenainen P, Gubitosi M, Olsson U, Sixta H (2018) Structural analysis of Ioncell-F
  494 fibres from birch wood. Carbohydr Polym 181:893-901.
- Baley C (2000) Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase.
  Compos Part A-Appl S 33:939-48.
- 497 Bolton AJ (1994) Natural fibers for plastic reinforcement. Mater Technol 9:12-20.
- Brückner S (2000) Estimation of the background in powder diffraction patterns through a robust smoothing
   procedure. J Appl Crystallogr 33: 977-979.
- 500 Budtova T, Navard P (2016) Cellulose in NaOH–water based solvents: a review. Cellulose 23:5-5.
- 501 Budtova T (2019) Cellulose II aerogels: A review. Cellulose 26:81-121.
- 502 Charlet K, Jernot JP, Eve S, Gomina M, Bréard J (2010) Multi-scale morphological characterisation of flax:
  503 From the stem to the fibrils. Carbohydr Polym 82:54-61.
- 504 Chaudemanche C, Navard P (2011) Swelling and dissolution mechanisms of regenerated Lyocell cellulose
   505 fibers. Cellulose 18:1-5.
- 506 Chen F, Kan Z, Hua S, Liu Z, Yang M (2015) A new understanding concerning the influence of structural
  507 changes on the thermal behavior of cellulose. J Polym Res 22:225.
- 508 Chen F, Sawada D, Hummel M, Sixta H, Budtova T (2020) Unidirectional all-cellulose composites from flax
   509 via controlled impregnation with ionic liquid. Polymers 12:1010.
- 510 Cuissinat C, Navard P (2006) Swelling and Dissolution of Cellulose Part 1: Free floating cotton and wood
  511 fibres in N-methylmorpholine-N-oxide–water mixtures. Macromol Symp 244:1-18.
- 512 Cuissinat C, Navard P (2008) Swelling and dissolution of cellulose, Part III: plant fibres in aqueous systems.
  513 Cellulose 15:67-74.
- Fink HP, Weigel P, Purz HJ, Ganster J (2001) Structure formation of regenerated cellulose materials from
   NMMO-solutions. Prog Polym Sci 26:1473-524.
- Frost K, Kaminski D, Kirwan G, et al (2009) Crystallinity and structure of starch using wide angle X-ray
  scattering. Carbohydr Polym 78: 543-548.
- Fukaya Y, Sugimoto, A, Ohno, H (2006) Superior Solubility of Polysaccharides in Low Viscosity, Polar, and
   Halogen-Free 1,3-Dialkylimidazolium Formates. Biomacromolecules 12:3295–3297.
- Gericke M, Schlufter K, Liebert T, Heinze T, Budtova T (2009) Rheological properties of cellulose/ionic liquid
   solutions: from dilute to concentrated states. Biomacromolecules 10:1188-94.
- Gross AS, Chu JW (2010) On the molecular origins of biomass recalcitrance: the interaction network and
   solvation structures of cellulose microfibrils. J Phys Chem B 114:13333-41.
- Hall CA, Le KA, Rudaz C, Radhi A, Lovell CS, Damion RA, Budtova T, Ries ME (2012) Macroscopic and
  microscopic study of 1-ethyl-3-methyl-imidazolium acetate–water mixtures. J Phys Chem B
  116:12810-8.

- Hauru LK, Hummel M, King AW, Kilpelainen I, Sixta H (2012) Role of solvent parameters in the regeneration
  of cellulose from ionic liquid solutions. Biomacromolecules 13:2896-905.
- Huber T, Müssig J, Curnow O, Pang S, Bickerton S, Staiger MP (2012) A critical review of all-cellulose
  composites. J Mater Sci 47(3):1171-86.
- 531 Isogai A, Atalla RH (1998) Dissolution of cellulose in aqueous NaOH solutions. Cellulose 5:309-19.
- Janson J (1970) Calculation of the polysaccharide composition of wood and pulp. Pap Puu-Pap Tim 52:323-9.
- 533 Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw
  534 material. Angew Chem Int Ed Engl 44:3358-93.
- Korhonen O, Sawada D, Budtova T (2019) All-cellulose composites via short-fiber dispersion approach using
   NaOH–water solvent. Cellulose. 26:4881-93.
- 537 Kreze T, Malej S (2003) Structural characteristics of new and conventional regenerated cellulosic fibers. Text
   538 Res J 73:675-84.
- Le KA, Sescousse R, Budtova T (2012) Influence of water on cellulose-EMIMAc solution properties: a
   viscometric study. Cellulose 19:45-54.
- Le Moigne N, Montes E, Pannetier C, Höfte H, Navard P (2008) Gradient in dissolution capacity of
   successively deposited cell wall layers in cotton fibres Macromol Symp 262:65-71.
- Le Moigne N, Jardeby K, Navard P (2010) Structural changes and alkaline solubility of wood cellulose fibers
  after enzymatic peeling treatment. Carbohydr Polym 79:325-32.
- Le Moigne N, Spinu M, Heinze T, Navard P (2010) Restricted dissolution and derivatization capacities of
  cellulose fibres under uniaxial elongational stress. Polymer 51:447-53.
- Ma Y, Asaadi S, Johansson LS, Ahvenainen P, Reza M, Alekhina M, Rautkari L, Michud A, Hauru L, Hummel
   M, Sixta H (2015) High-strength composite fibers from cellulose–lignin blends regenerated from ionic
   liquid solution. ChemSusChem 8:4030-9.
- Ma Y, Stubb J, Kontro I, Nieminen K, Hummel M, Sixta H (2018) Filament spinning of unbleached birch kraft
  pulps: Effect of pulping intensity on the processability and the fiber properties. Carbohydr Polym
  179:145-51.
- Mäkelä V, Wahlström R, Holopainen-Mantila U, Kilpeläinen I, King AW (2018) Clustered single cellulosic
  fiber dissolution kinetics and mechanisms through optical microscopy under limited dissolving
  conditions. Biomacromolecules 2018 19:1635-45.
- McCormick CL, Callais PA, Hutchinson Jr BH (1985) Solution studies of cellulose in lithium chloride and N,
   N-dimethylacetamide. Macromolecules 18: 2394-2401.
- 558 Minnick DL, Flores RA, DeStefano MR, Scurto AM (2016) Cellulose solubility in ionic liquid mixtures:
   559 temperature, cosolvent, and antisolvent effects. J Phys Chem B 120:7906-19.
- Moryganov AP, Zavadskii AE, Stokozenko VG. (2018) Special features of X-ray analysis of cellulose
   crystallinity and content in flax fibres. Fibre Chem 49:382-7.
- 562 Okubayashi S, Griesser UJ, Bechtold T (2004) A kinetic study of moisture sorption and desorption on lyocell
   563 fibers. Carbohydr Polym 58(3):293-9.
- Okubayashi S, Griesser UJ, Bechtold T (2005) Water accessibilities of man-made cellulosic fibers–effects of
   fiber characteristics. Cellulose 12:403-10.

- Olsson C, Idström A, Nordstierna L, Westman G (2014) Influence of water on swelling and dissolution of
   cellulose in 1-ethyl-3-methylimidazolium acetate. Carbohydr Polym 99:438-46.
- Parviainen H, Parviainen A, Virtanen T, Kilpeläinen I, Ahvenainen P, Serimaa R, Grönqvist S, Maloney T,
  Maunu SL (2014) Dissolution enthalpies of cellulose in ionic liquids. Carbohydr Polym 113:67-76.
- 570 Peng H, Dai G, Wang S, Xu H (2017) The evolution behavior and dissolution mechanism of cellulose in
  571 aqueous solvent. J Mol Liq 241:959-66.
- 572 Placet V, Trivaudey F, Cisse O, Gucheret-Retel V, Boubakar ML (2012) Diameter dependence of the apparent
  573 tensile modulus of hemp fibres: A morphological, structural or ultrastructural effect? Compos Part A574 Appl S 43:275-87.
- 575 Powell RE, Roseveare WE, Eyring H (1941) Diffusion, thermal conductivity, and viscous flow of liquids. Ind
  576 Eng Chem 33:430-5.
- 577 Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick WJ, Hallett JP, Leak
  578 DJ, Liotta CL, Mielenz JR (2006) The path forward for biofuels and biomaterials. Science 311:484579 9.
- Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM (2001) The effect of fiber treatment on the mechanical
   properties of unidirectional sisal-reinforced epoxy composites. Compos Sci Technol 61:1437-47.
- 582 Rous MA, Ingolic E, Schuster KC (2006) Visualisation of the fibrillar and pore morphology of cellulosic fibres
  583 applying transmission electron microscopy. Cellulose 13:411-9.
- Rous MA, Varga K, Bechtold T, Schuster KC (2007) A new method to visualize and characterize the pore
  structure of TENCEL®(Lyocell) and other man-made cellulosic fibres using a fluorescent dye
  molecular probe. J Appl Polym Sci 106:2083-91.
- 587 Savitzky A, Golay MJ (1964) Smoothing and differentiation of data by simplified least squares procedures.
  588 Anal Chem 36:1627-1639.
- Shi Z, Yang Q, Cai J, Kuga S, Matsumoto Y (2014) Effects of lignin and hemicellulose contents on dissolution
  of wood pulp in aqueous NaOH/urea solution. Cellulose 21:1205-15.
- Siroka B, Noisternig M, Griesser UJ, Bechtold T (2008) Characterization of cellulosic fibers and fabrics by
   sorption/desorption. Carbohydr Res 343:2194-9.
- Sixta H, Michud A, Hauru L, et al (2015) Ioncell-F: a high-strength regenerated cellulose fibre. Nord Pulp
   Paper Res J, 30:43-57.
- Soykeabkaew N, Nishino T, Peijs T (2009) All-cellulose composites of regenerated cellulose fibres by surface
   selective dissolution. Compos Part A-Appl S 40:321-8.
- Spange S, Reuter A, Vilsmeier E, Heinze T, Keutel D, Linert WJ (1998) Determination of empirical polarity
  parameters of the cellulose solvent N, N-dimethylacetamide/LiCl by means of the solvatochromic
  technique. Polym Sci Part A: Polym Chem 36: 1945–1955.
- 600 Swatloski R P, Spear S K, Holbrey J D, et al (2002) Dissolution of cellulose with ionic liquids. J Am Chem
  601 Soc 124: 4974-4975.
- Takashi N, Ikuyo M, Koichi H (2004) All-cellulose composite. Macromolecules 37:7683-7.
- Kie Y, Hill CA, Jalaludin Z, Curling SF, Anandjiwala RD, Norton AJ, Newman G (2011) The dynamic water
   vapour sorption behaviour of natural fibres and kinetic analysis using the parallel exponential kinetics
   model. J Mater Sci 46(2):479-89.

606 607 608 609	Yan L, Chouw N, Jayaraman K (2014) Flax fibre and its composites–A review. Compos Part B-Eng 56:296- 317.
610	Figure legends
611	
612	Fig. 1 Cellulose molecular mass distribution (a) and X-ray diffraction profiles (b) of flax,
613	Cordenka, Ioncell-F and Ioncell-FL
614	Fig. 2 $\beta$ (red symbols) and $\beta$ - $\alpha$ (blue symbols) plotted against water content in IL
615	[EMIM][OAc] at 25 °C (solid symbol) and 60 °C (open symbol)
616	Fig. 3 Viscosity of [EMIM][OAc] and [EMIM][OAc]-water mixtures as a function of water
617	content at various temperatures. The arrows show the same viscosity of [EMIM][OAc] at 40
618	°C and of [EMIM][OAc]-5 wt.% water at 30 °C
619	Fig. 4 Optical microscopy images of fibers in [EMIM][OAc] at 30 °C
620	Fig. 5 Evolution of flax (a), Cordenka (b), Ioncell-F (c) and Ioncell-FL (d) normalized
621	diameter as a function of time at 25 °C (1), 30 °C (2), 40 °C (3), 50 °C (4) and 60 °C (5) in
622	[EMIM][OAc] and the dissolution rate of all fibers as a function of temperature (e)
623	Fig. 6 Dissolution rate as a function of [EMIM][OAc] viscosity
624	Fig. 7 Optical microscopy images of the fiber evolution in time in [EMIM][OAc]-5% water
625	at 30 °C. Red marks show core-shell structure
626	Fig. 8 Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
627	Ioncell-FL (d) as a function of time in the solvents of the same viscosity: [EMIM][OAc] at
628	40 °C (solid symbol) and [EMIM][OAc]-5 wt.% water at 30 °C (open symbol). Shaded area
629	shows swelling
630	Fig. 9 Comparison of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL
631	as a function of time at 30 °C in [EMIM][OAc]-5 wt.% water mixture solvent
632	Fig. 10 Optical microscopy images of fibers in [EMIM][OAc]-15% water at 30 °C. Red

633 marks show core-shell structure

- **Fig. 11** Comparison of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL
- as a function of time at 30 °C in [EMIM][OAc]-15 wt.% water solvent
- **Fig. 12** Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
- 637 Ioncell-FL (d) as a function of time in neat [EMIM][OAc] (1), [EMIM][OAc]-5% water
- 638 mixture (2) and [EMIM][OAc]-15% water mixture (3) at 30 °C





644	Supporting Information
645	
646	Swelling and Dissolution kinetics of Natural and Man-
647	Made Cellulose Fibers in Solvent Power Tuned Ionic
648	Liquid
649	
650	Feng Chen <sup>a</sup> , Daisuke Sawada <sup>a</sup> , Michael Hummel <sup>a</sup> , Herbert Sixta <sup>a</sup> , Tatiana Budtova <sup>a, b, *</sup>
651	
652	
653	<sup>a</sup> Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto
654	University, P.O. Box 16300, 00076 Aalto, Helsinki, Finland;
655	<sup>b</sup> MINES ParisTech, PSL Research University, Center for Materials Forming-CEMEF,
656	UMR CNRS 7635, CS 10207, 06904 Sophia Antipolis, France.
657	
658	* Correspondence: tatiana.budtova@mines-paristech.fr, tatiana.budtova@aalto.fi
659	



















714 Optical microscopy images of Ioncell-F in [EMIM][OAc] at different temperature. 









	<b>Dissolution rate</b> (s <sup>-1</sup> )	Cordenka	Flax	Ioncell-FL	Ioncell-F
	in [EMIM][OAc]	8.51*10 <sup>-5</sup>	1.49*10 <sup>-4</sup>	4.4*10 <sup>-4</sup>	6.48*10 <sup>-4</sup>
	in [EMIM][OAc]-5 wt. % water	3.58*10 <sup>-5</sup>	Swelling	2.1*10 <sup>-4</sup>	5.1*10 <sup>-4</sup>
730					





735 Optical microscopy images of Cordenka swelling in [EMIM][OAc]+15% water at 50°C.