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

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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 temperature. Natural fiber, flax, and man-made fibers, Cordenka and Lyocell-type (Ioncell) were 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 weak (15 wt.% water). The temperature was varied to correlate the fiber dissolution rate with the solvent viscosity. All fibers were characterized by chemical composition, crystallinity, molecular weight distribution and dynamic vapor sorption. It was demonstrated that while the rate of fiber dissolution in neat ionic liquid depends on fiber accessibility and solvent viscosity, the water-induced decreased solvent power dominates the general fiber behavior. Flax appeared to be the most “sensitive” to the solvent power due to its hierarchical structure. The fastest dissolution or swelling was recorded for Ioncell and the slowest for Cordenka.

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

29 **1 Introduction**

30 Cellulose is a fascinating biopolymer present on the Earth in almost inexhaustible
31 quantity. It is a linear polymer built of anhydroglucose units linked by (1→4)-β glycosidic
32 bonds, and until recently it was used mainly for making paper, textile fibers and films
33 (Klemm et al. 2005; Ragauskas et al. 2006). Cellulose cannot be melt-processed (Chen et al.
34 2015) and thus its shaping requires dissolution (Gross et al. 2010). During the past decades,
35 new cellulose-based materials were developed involving complete or partial dissolution, for
36 example, aerogels (Budtova 2019) and all-cellulose composites (Takashi et al. 2004).

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

45 While fibers, films and aerogels require complete cellulose dissolution, all-cellulose
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
49 “gluing” fibers together upon coagulation (Huber et al. 2012), or by dispersing cellulose
50 fibers in a cellulose solution, the latter acting as a continuous matrix (Korhonen et al. 2019).
51 To control the properties of all-cellulose composite, the understanding and quantification of
52 the kinetics of fiber dissolution is a prerequisite. Too short dissolution times will result in an
53 insufficient amount of dissolved cellulose in-between the fibers while too long dissolution
54 will result in the destruction of natural fibers’ cell walls and the formation of excessive
55 amount of mechanically weaker cellulose II.

56 Although the dissolution of cellulose fibers in various direct solvents has been studied
57 since the first half of the 20th century, detailed investigations of the dissolution mechanisms
58 emerged only during the past 20 years due to a significant improvement of analytical tools.
59 For example, the development of optical microscopy with various set-ups allowed for precise
60 visualization, temperature control, video capture, and image analysis to follow the fibers’
61 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
63 al. 2014), most probably because of practical reasons, as films and textile fibers are made
64 from wood dissolving pulps. By varying the solvent dissolution power, it was demonstrated
65 that wood fibers dissolve either directly from the surface resulting in their diameter decrease,
66 sometimes by disintegration into particles, or via ballooning followed by their burst
67 (Cuissinat et al. 2006). In moderate and bad solvents fibers only swell either via ballooning
68 or by a homogeneous increase in diameter, respectively (Cuissinat et al. 2006). The same
69 mechanisms apply to cotton fibers but, interestingly, not to flax or ramie (Cuissinat et al.
70 2008). Lyocell fibers either radially dissolve in a good solvent or radially swell in a moderate
71 solvent (Chaudemanche et al. 2011). Various factors have to be taken into account to
72 understand fiber swelling and dissolution behavior: their composition, properties of primary
73 and secondary layers in natural fibers or properties of a skin in man-made fibers (Abu-Rous
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
77 was used as a model substance to study the kinetics of its dissolution in ionic liquids and the
78 influence of a co-solvent, dimethylsulfoxide (DMSO), on the dissolution (Andanson et al.
79 2014). Cellulose dissolution was assessed by the decrease of birefringence which arises from
80 the crystalline regions in polarized light (Andanson et al. 2014). Optical microscopy coupled
81 with semi-automated data processing was used to evaluate the dissolution kinetics of two
82 kraft pulps in 0.2 M cupriethylene diamine by tracing the fiber surface area (Mäkelä et al.
83 2018). A first-order kinetic model was shown to be applicable to describe fibers' dissolution
84 (Mäkelä et al. 2018). The kinetics of wood fiber homogeneous swelling in NMMO in the
85 presence of water at 18–22 % was reported by H. Peng et al. (Peng et al. 2017). To the best
86 of our knowledge, there is no report comparing the kinetics of dissolution and/or swelling of
87 different fibers, natural and man-made, under the same conditions. In the view of making
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.

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

96 and swelling kinetics, fiber characteristics (structure, composition, cellulose molecular
97 weight and accessibility), solvent power and viscosity were built.

98 **2 Experimental Part**

99 **2.1 Materials**

100 Flax fibers were from the outer bast layer of the plant stem. A commercially available
101 high-strength rayon filament yarn Cordenka 700 was kindly donated by Cordenka GmbH &
102 Co. KG., and two other man-made fibers were produced by spinning of an unbleached birch
103 kraft pulp-ionic liquid solutions resulting in Ioncell-FL fibers (coded “H50” in the ref. Ma
104 et al. 2018), and of a prehydrolysed kraft birch pulp-IL solution, resulting in Ioncell-F fibers
105 (see, for example, Asadi et al. 2018). The characteristics of the fibers are presented in the
106 Results section. The ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]),
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 $110 \text{ Lg}^{-1}\text{cm}^{-1}$.

119 *2.2.2 Molecular weight distribution of cellulose in fibers*

120 The molecular weight distribution of cellulose in all fibers was characterized by gel
121 permeation chromatography (GPC) according to the procedure described elsewhere (Ma et
122 al. 2018), and number-average and weight-average molecular weights, M_n and M_w , were
123 calculated. Prior to the analysis, fibers were cut into small pieces. The GPC system consisted
124 of a pre-column (PLgel Mixed-A, $7.5 \times 50 \text{ mm}$), four analytical columns ($4 \times \text{PLgel Mixed-}$

125 A, 7.5 × 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 α radiation ($\lambda = 1.5418 \text{ \AA}$). Fiber
 133 samples were grinded to powder and then mounted on multi-position sample holder. Data
 134 were collected in a 2θ range between 5° and 60° in reflection mode.

135 The background profile was estimated using a smoothing method (Brückner 2000; Frost
 136 et al. 2009) applying Savitzky-Golay (Savitzky et al. 1964) filter in the 2θ range from 6 to
 137 55° for each diffraction profile. Window size and polynomial order for the Savitzky-Golay
 138 filter were set to 51 data points (corresponding to 4° by 2θ) and 1, respectively. Iteration for
 139 the background estimation was repeated 50 times. The crystallinity index (CRI_{total}) of fibers
 140 was estimated using the ratio of the area of total intensity (I_{total}) and of background intensity
 141 (I_{bkg}) from 10 to $30^\circ 2\theta$:

$$142 \quad CRI_{total} = 100 \times \frac{\int I_{total} d2\theta - \int I_{bkg} d2\theta}{\int I_{total} d2\theta} \quad (1)$$

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

144 2.2.4 Dynamic vapor sorption (DVS)

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

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

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

155 2.2.5 Rheological characterization

156 The rheological properties of the IL and IL-water mixtures were characterized using an
157 Anton Paar MCR 302 rheometer equipped with a plate-plate geometry (25 mm plate
158 diameter, 1 mm gap) and a Peltier temperature control system. Viscosity-shear rate
159 dependences were recorded from 1 to 100 s⁻¹ at fixed temperature which was varied from
160 20 °C to 60 °C.

161 2.2.6 Kamlet–Taft Parameters

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

171

172 2.2.7 Optical microscopy observations of fiber swelling and dissolution

173 One fiber was placed between two glass plates with the in-between distance around 140
174 μm controlled by spacers. The distance between two glass slides is much larger than the
175 fiber’s thickness. As the proportion between fiber and solvent was approximately 7×10^{-4} g/g,
176 we assume that the fiber was in an infinite solvent, i.e. the overall polymer concentration
177 during and after complete dissolution can be neglected. The ends of the fiber were fixed by
178 tape and solvent added. Fiber diameter was recorded by a DM4500P (Leica) optical
179 microscope in transmission mode equipped with a CCD camera (Metallux 3, Leitz) and
180 Linkam TMS 91 hot stage to control temperature. The evolution of the fiber diameter in time
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.

183

184 **3 Results**

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

192 **3.1 Physiochemical properties of cellulose fibers**

193 Flax is a natural fiber with a complex morphology; its elementary fiber consists of
194 several cell wall layers and a lumen. The outer layer (or a primary cell wall) is the first layer
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
197 primary wall and consists of highly crystalline cellulose fibrils spirally wound in a matrix of
198 hemicellulose and pectins. Cellulose fibrils in this layer are oriented in the axis of the fiber
199 and hence display a unidirectional structure (Rong et al. 2001; Charlet et al. 2010; Baley
200 2002). Two types of man-made fibers were selected, Cordenka, a modified viscose fiber,
201 and Lyocell-type Ioncell fibers. Cordenka consists of a dense skin and spongy core (Rous et
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).

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

212

213

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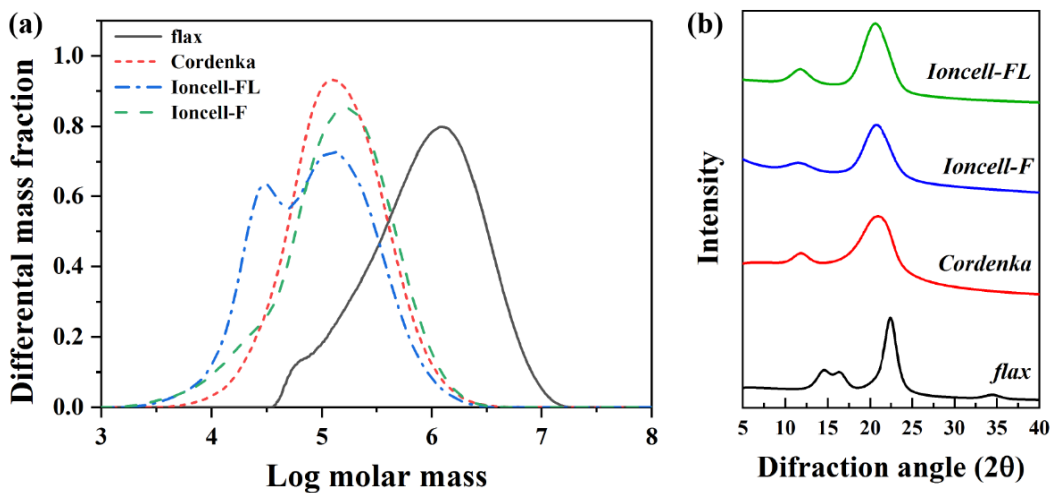
216 Table 1. Characteristics of fibers used in this study

Samples	Cellulose %	Hemicellulose %	Lignin %	M_n kDa	M_w kDa	CRI_{total} %	M_{des} %	M_s %	t_s 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

217

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

223



224

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

227

228 Figure 1b presents the XRD profiles of all fibers. Flax contains cellulose I with
 229 crystallinity index of around 45%, which is typical for plant cellulose (Placet et al. 2012;

230 Moryganov et al. 2018). The man-made fibers contain the cellulose II allomorph, as expected.
231 The crystallinity index (CRI_{total}) is around 28 %, 40 % and 27 % for Cordenka, Ioncell-F and
232 Ioncell-FL, respectively (Table 1). Cordenka, a viscose type cellulose fiber, has low
233 crystallinity, in-line with data in literature (Kreze et al. 2003; Okubayashi et al. 2005). As
234 the crystallinity is calculated over the total material, and non-cellulose fraction in Ioncell-
235 FL is around 50%, cellulose crystallinity in Ioncell-FL is higher than CRI_{total} ; for this fiber
236 it was reported to be around 40% (Ma et al. 2018).

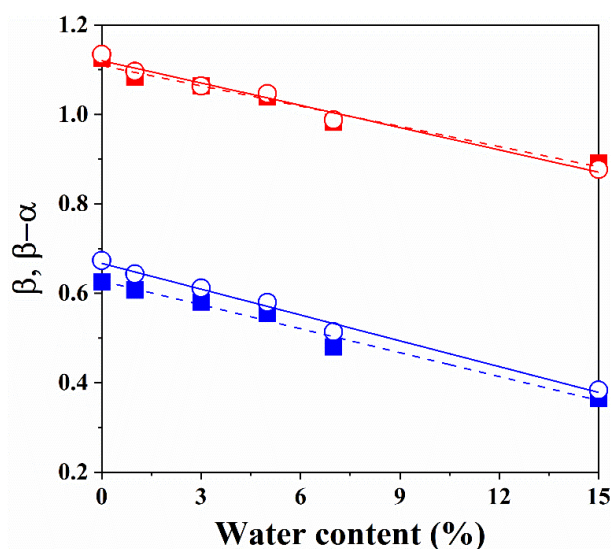
237 To compare the accessibility of the fibers, the dynamic water vapor desorption and
238 sorption were measured. The desorption (to 0% RH) and sorption (to 60% RH) curves are
239 shown in Figure S1. Moisture desorption (M_{des}), time to reach equilibrium t_s from 0 to
240 60 %RH and moisture sorption (M_s) for each fiber are shown in Table 1 (see also Methods
241 sections and eqs. 2 and 3). M_{des} reflects the amount of water which is desorbed from ambient
242 conditions to 0 % RH and it is the lowest for flax. Cordenka, as viscose fiber, absorbs the
243 highest amount of moisture (M_s) due to its lowest crystallinity and larger pore volume
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
246 can be overdried, and also because absorption of a larger amount of vapor takes more time.
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
249 moisture sorption around 9% - 10% at 60% RH and room temperature (Okubayashi et al.
250 2004). The presence of hydrophobic lignin does not influence the water vapor sorption
251 behavior, in line with previously reported results (Ma et al. 2015). Flax absorbs the least
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**

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

263 usually accept H-bonds, and thus are mostly responsible for the total β value. However, in
 264 mixtures of ionic liquid and water, water competes with the hydroxyl groups of cellulose for
 265 the hydrogen bond acceptance of the anion. It was demonstrated that the ability of such
 266 solvents to dissolve cellulose is described by $\beta-\alpha$ (net basicity) which takes the adverse
 267 effect of any intrinsic H-donor into account (Hauru et al. 2012). It was further shown that
 268 cellulose solvents should be located in a region roughly defined by $0.80 < \beta < 1.20$ and 0.35
 269 $< \beta-\alpha < 0.9$ with higher dissolution power corresponding to higher values within these
 270 intervals (Hauru et al. 2012). The Kamlet-Taft parameters of [EMIM][OAc] with different
 271 water contents were measured in the range of 20 - 60 °C. Figure 2 shows the values of β and
 272 $\beta-\alpha$ as a function of water content at 25 °C and 60 °C; the effect of temperature on Kamlet-
 273 Taft values was very small. Within the range of the studied water content, both β 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
 279 power to monitor fiber swelling and dissolution behavior.



280

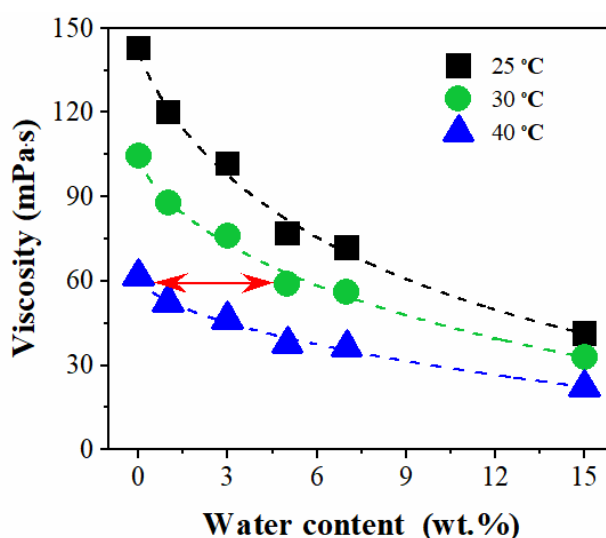
281 **Fig. 2** β (red symbols) and $\beta-\alpha$ (blue symbols) plotted against water content in IL
 282 [EMIM][OAc] at 25 °C (solid symbol) and 60 °C (open symbol)

283

284 Solvent viscosity is another important parameter to consider for polymer dissolution. In
 285 general, for the same solvent quality and at the same temperature, lower viscosity should
 286 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
289 characteristics into account, we measured the viscosity of [EMIM][OAc] with various water
290 content of 0 – 15 wt.% as a function of shear rate at different temperatures (Figure S2). All
291 studied mixtures are Newtonian liquids. Their viscosity is plotted as a function of water
292 content at 25, 30 and 40 °C; the arrows show that [EMIM][OAc] at 40 °C and
293 [EMIM][OAc]-5 wt.% water at 30 °C have the same viscosity (Figure 3). These two solvents
294 will be used in the following as an example of a solvent with the same viscosity but different
295 dissolution power (Figure 2).

296



297

298 **Fig. 3** Viscosity of [EMIM][OAc] and [EMIM][OAc]-water mixtures as a function of water
299 content at various temperatures. The arrows show the same viscosity of [EMIM][OAc] at 40
300 °C and of [EMIM][OAc]-5 wt.% water at 30 °C

301

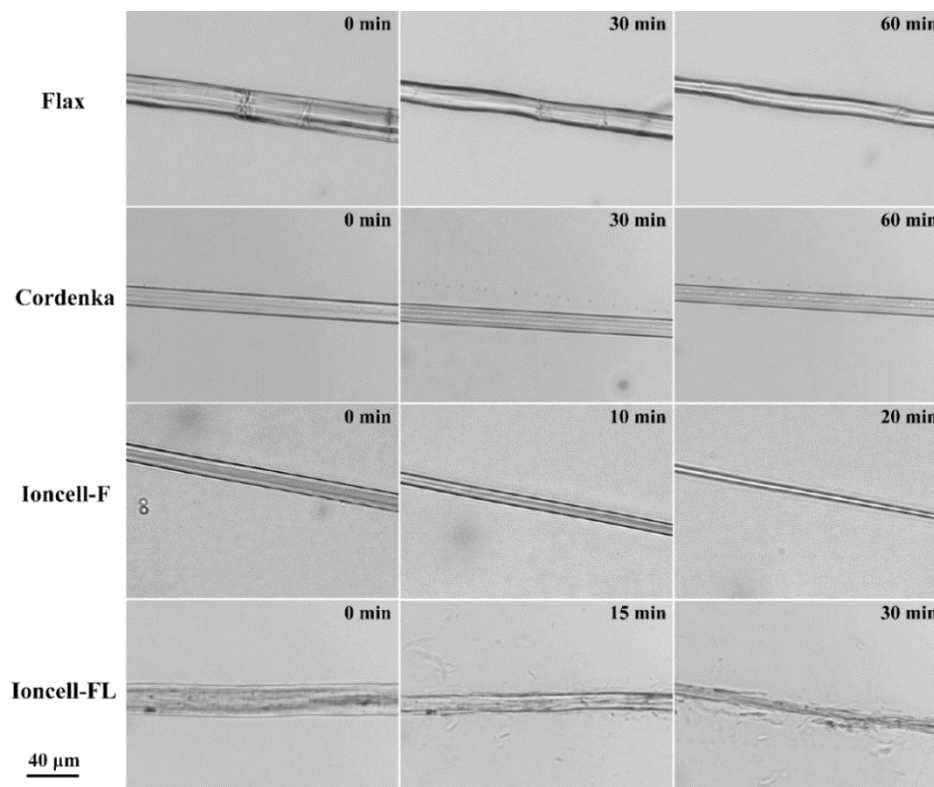
302 3.3 Kinetics of fiber dissolution and swelling

303 As mentioned in the Experimental section, in our set-up both fiber ends were fixed as
304 the goal is to quantitatively analyze the kinetics of fiber behavior and thus fiber
305 displacements should be prevented. It has been reported that depending on the solvent power,
306 uniaxial elongational stress applied on a fiber may influence its dissolution (Le Moigne et
307 al. 2010). We tested if fixed fiber ends modified its behavior in the solvents used. Two cases
308 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.

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.

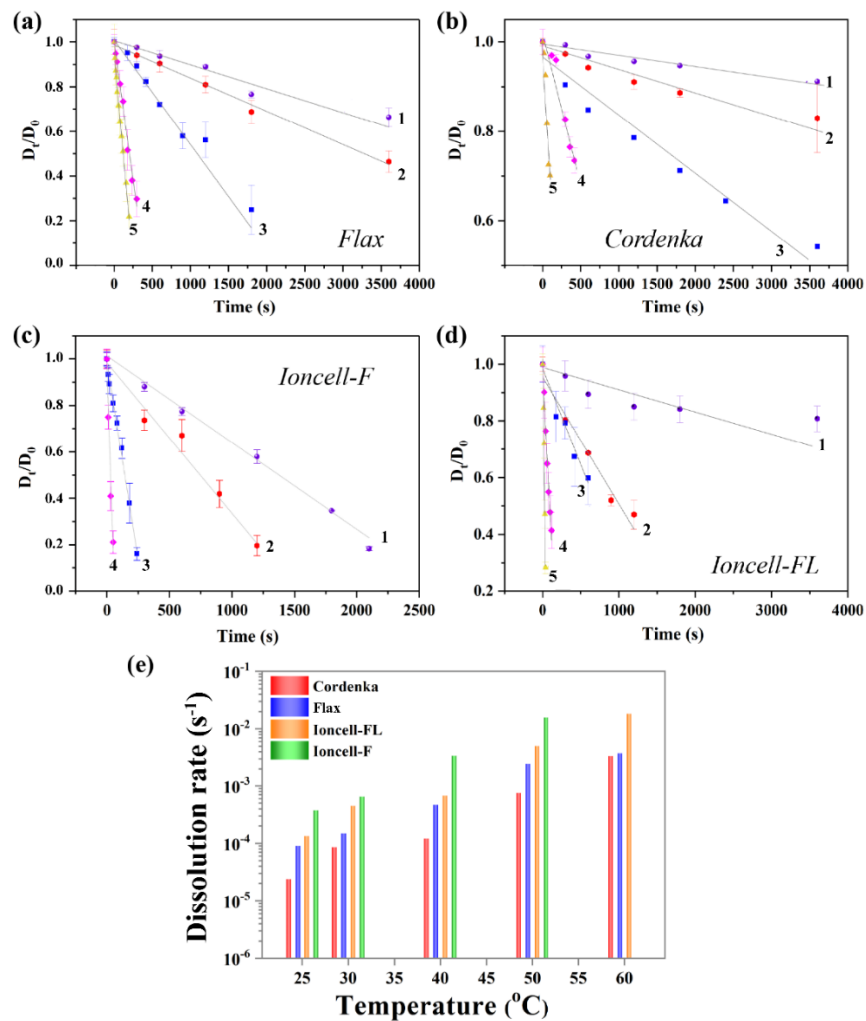


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327

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

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



342

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

346

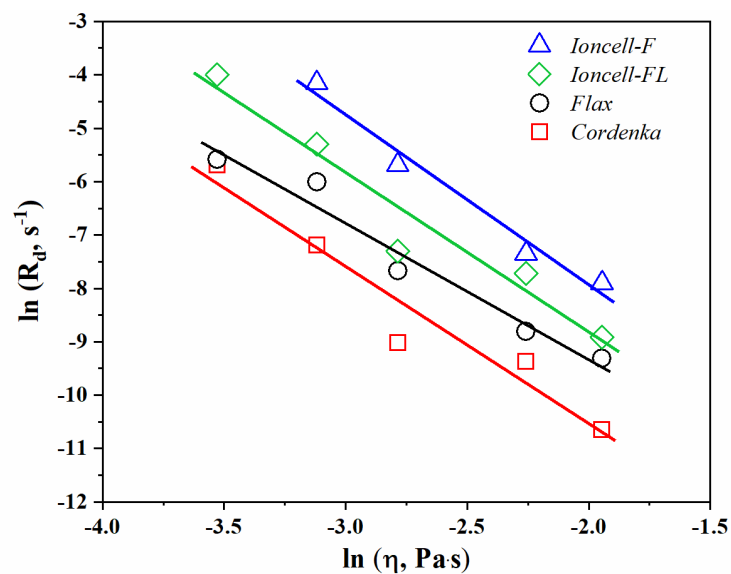
347 Figure 5 shows that increasing the temperature increases the dissolution rate, which is
348 expected due to quicker solvent diffusion in a medium of lower viscosity. The dependence
349 of [EMIM][OAc] viscosity η on temperature can be approximated by Arrhenius-type law
350 (Figure S6a) (Gericke et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

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

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

359
$$\ln R_d \sim \frac{E_d}{E_v} \ln \eta \quad (5)$$

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



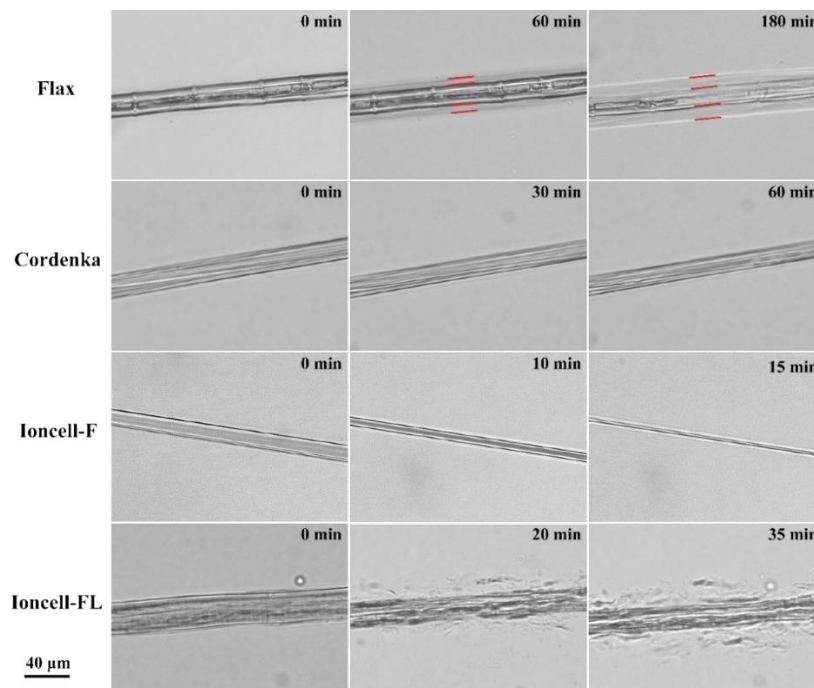
364
365 **Fig. 6** Dissolution rate as a function of [EMIM][OAc] viscosity

366

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

368 The presence of a low amount of water, 5 wt.%, should decrease the dissolution power
369 but still allow the dissolution (Figure 2). Examples of fiber behavior in [EMIM][OAc]-5 wt.%
370 water at 30 °C is presented in Figure 7. All man-made fibers were dissolving in this solvent
371 in a similar manner as in [EMIM][OAc]. In contrast, flax was only swelling showing a core-
372 shell structure and was not dissolved in [EMIM][OAc]-5 wt.% after 18 hours. This is the
373 direct indication of the decreased solvent power of [EMIM][OAc]-5 wt.% water apparent
374 for a natural fiber. No ballooning was observed irrespective of whether the fiber ends were
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).

377



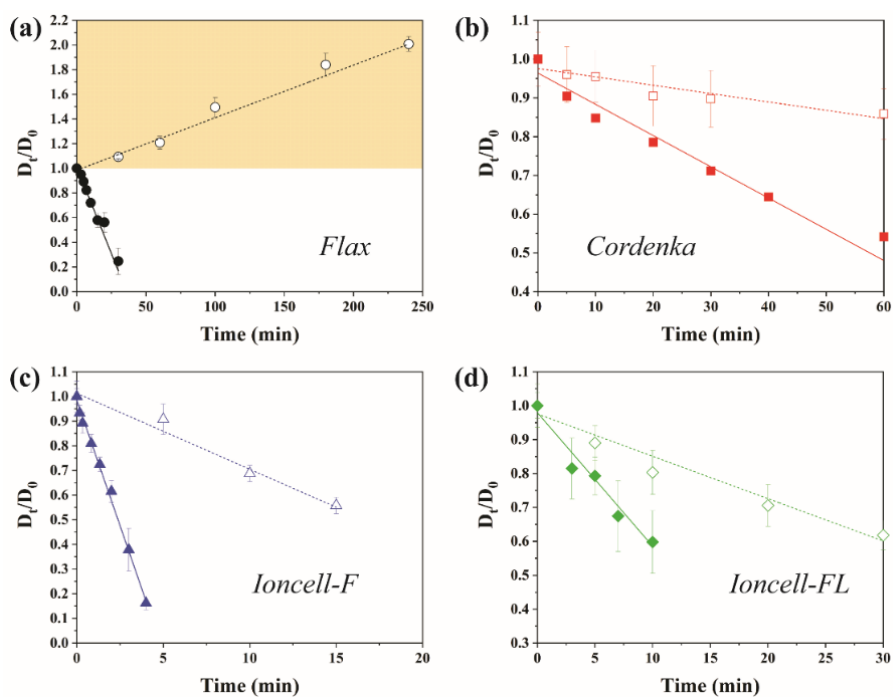
378

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

381

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

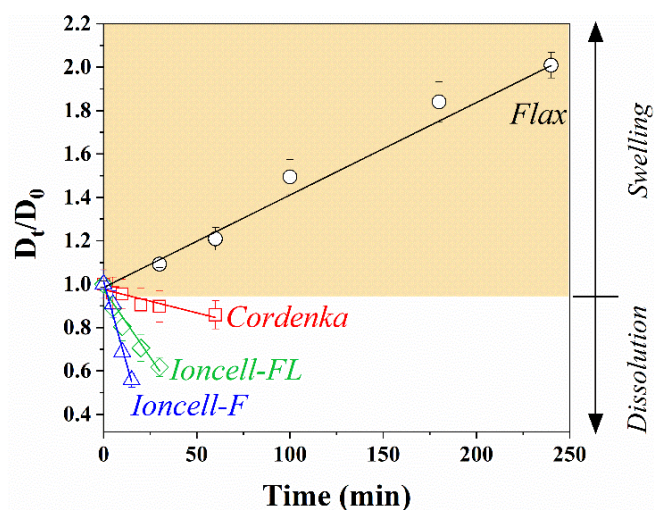
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397

398 **Fig. 8** Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
 399 Ioncell-FL (d) as a function of time in the solvents of the same viscosity: [EMIM][OAc] at
 400 40 °C (solid symbol) and [EMIM][OAc]-5 wt.% water at 30 °C (open symbol). Shaded area
 401 shows swelling

402



403

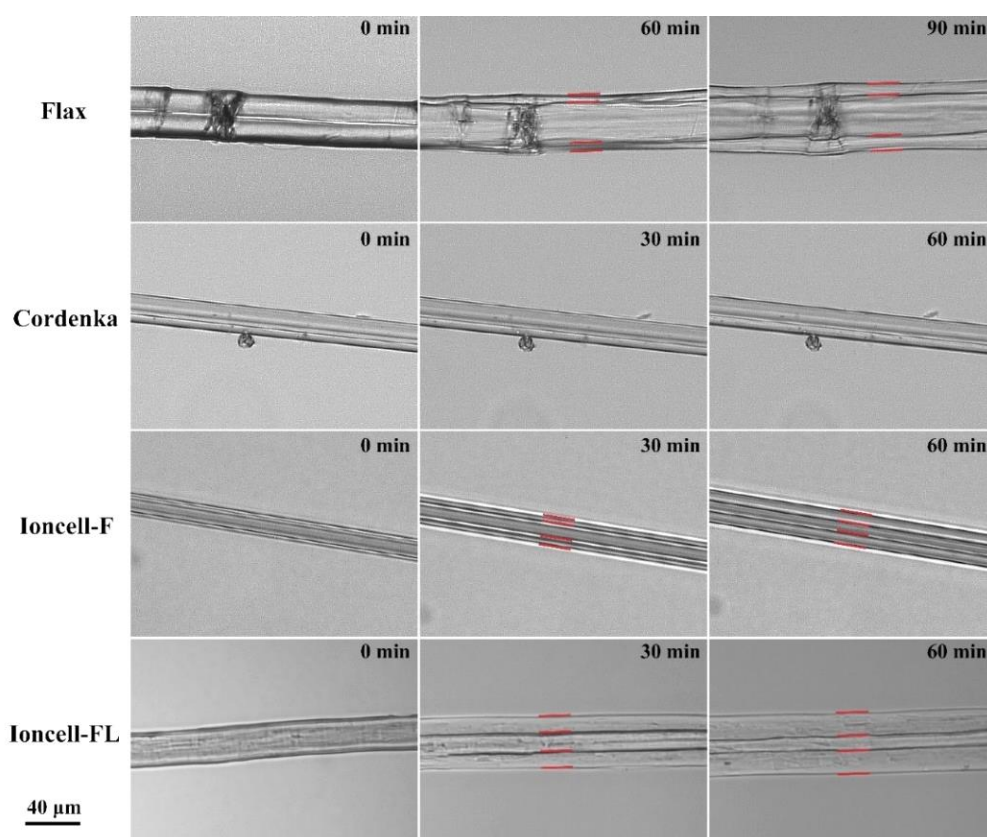
404 **Fig. 9** Comparison of the normalized diameter of flax, Cordenka, Ioncell-F and Ioncell-FL
 405 as a function of time at 30 °C in [EMIM][OAc]-5 wt.% water mixture solvent

406

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

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

415



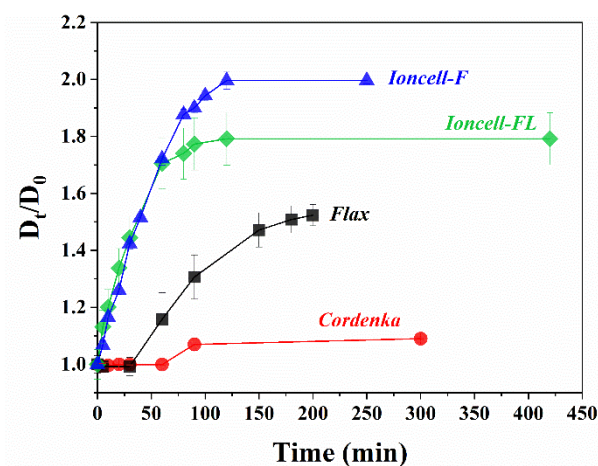
416

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

419

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

424



425

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

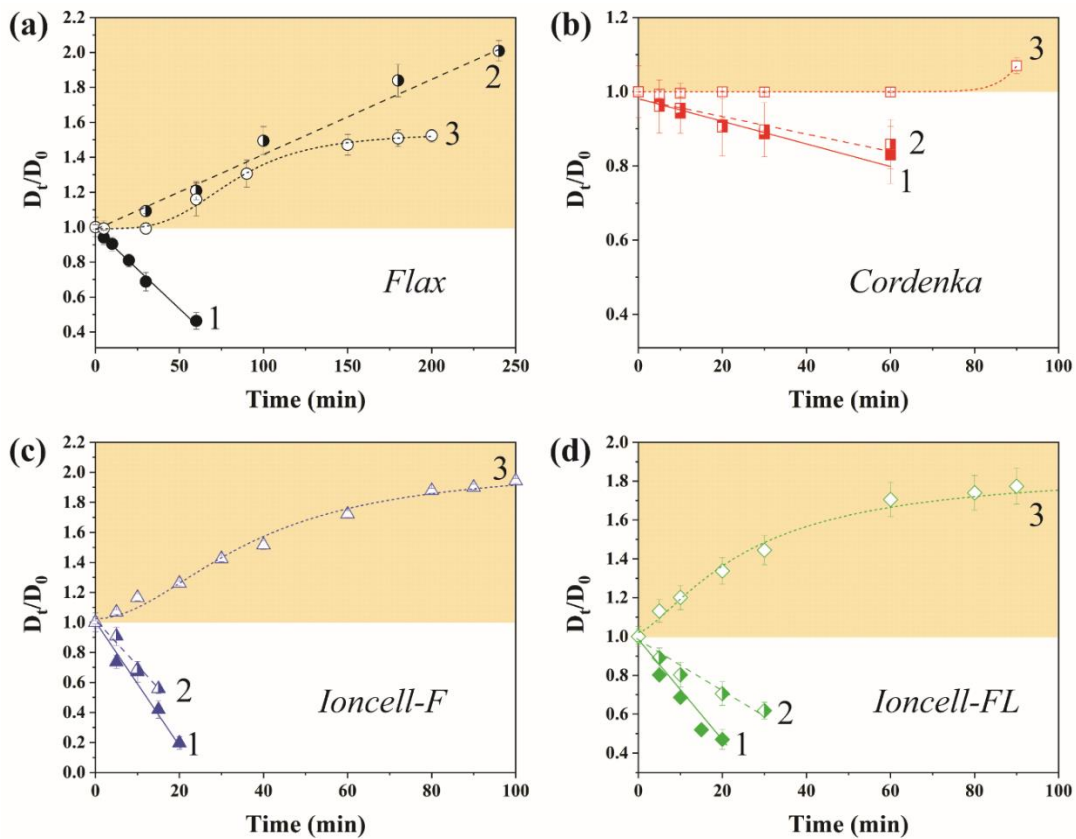
428

429 4 Discussion

430 The comparison of the behavior of all fibers in three solvent systems is summarized in
431 Figure 12. At high solvent power (ionic liquid) and fixed temperature, all fibers dissolve and
432 the dissolution rate is controlled mainly by the fiber accessibility. Within the same family of
433 man-made fibers, Ioncell, the presence of lignin slows down the dissolution rate, and Ioncell-
434 FL dissolves via partial fragmentation. With the decrease of solvent power, the nature of
435 fibers, man-made versus natural, becomes the main factor controlling their behavior. Flax,
436 which has a hierarchical structure with strong secondary layer, turned out to be the most
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
441 dissolution experiments were performed in static conditions, without mixing. Finally, in the
442 presence of 15 wt.% water in ionic liquid, all fibers showed only swelling.

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

446 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



449
 450 **Fig. 12** Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
 451 Ioncell-FL (d) as a function of time in neat [EMIM][OAc] (1), [EMIM][OAc]-5% water
 452 mixture (2) and [EMIM][OAc]-15% water mixture (3) at 30 °C

453

454 5 Conclusions

455 The kinetics of fiber evolution in ionic liquid, [EMIM][OAc], was studied for four
 456 cellulose fibers, natural (flax) and man-made: viscose type (Cordenka) and Lyocell-type
 457 (Ioncell: one similar to Cordenka in composition (Ioncell-F) and the other one with high
 458 amounts of lignin and hemicelluloses (Ioncell-FL)). This set of fibers allowed studying the
 459 role of the fiber morphology, accessibility, composition and cellulose molecular weight and
 460 crystallinity. Temperature was varied to modify solvent viscosity, and water was added to
 461 tune solvent power.

462 In the case of high solvent power all fibers are radially dissolving. The main factors
463 influencing the dissolution rate are solvent viscosity (for the same type of fiber) and fiber
464 accessibility (for the same solvent temperature), the latter revealed by water vapor sorption.
465 An Arrhenius-type law was applied to both solvent viscosity and dissolution rate resulting
466 in log-log direct correlation between them.

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

473 It is remarkable that both the kinetics of dissolution (the cases of all fibers in neat
474 [EMIM][OAc] and all man-made fibers in [EMIM][OAc]-5 wt.% water) and of swelling
475 (the cases of all fibers in [EMIM][OAc]-15 wt.% water) show the same order: Ioncell-F >
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
479 complete dissolution is not required and the substrates are typically impregnated under static
480 conditions without mixing.

481

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486

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609

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** β (red symbols) and β - α (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

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

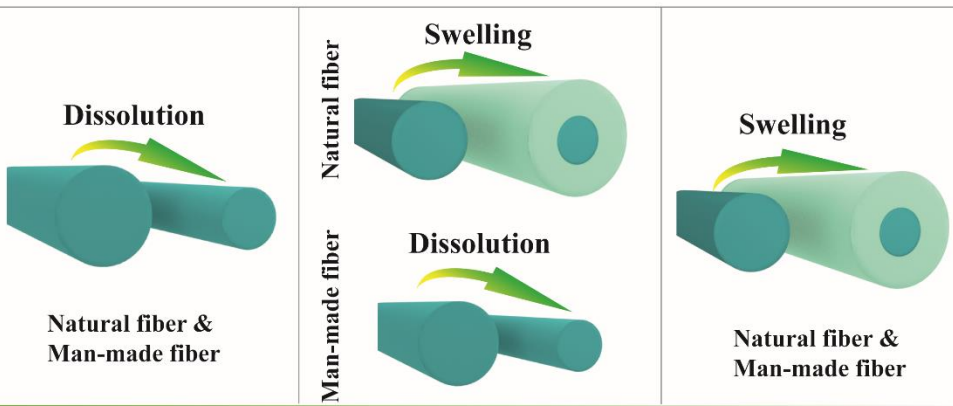
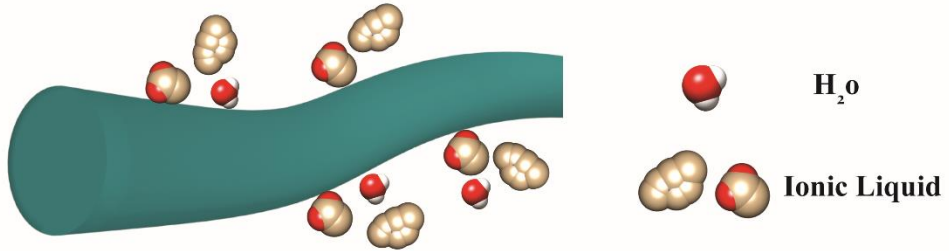
636 **Fig. 12** Comparison of the normalized diameter of flax (a), Cordenka (b), Ioncell-F (c) and
637 Ioncell-FL (d) as a function of time in neat [EMIM][OAc] (1), [EMIM][OAc]-5% water
638 mixture (2) and [EMIM][OAc]-15% water mixture (3) at 30 °C

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TOC image



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Fibers in Neat IL

Fibers in IL-5%water

Fibers in IL-15%water

643

Supporting Information

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645

Swelling and Dissolution kinetics of Natural and Man-Made Cellulose Fibers in Solvent Power Tuned Ionic Liquid

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650 Feng Chen ^a, Daisuke Sawada ^a, Michael Hummel ^a, Herbert Sixta ^a, Tatiana Budtova ^{a, b, *}

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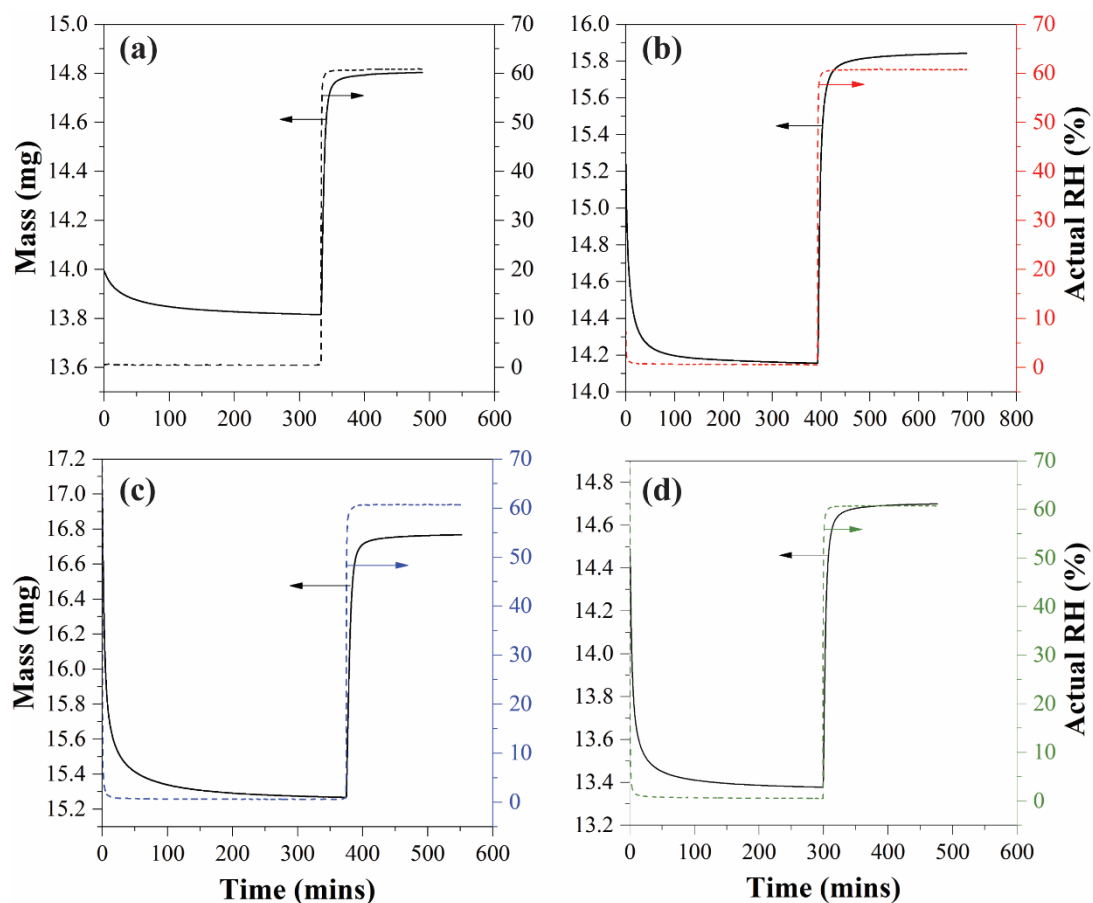
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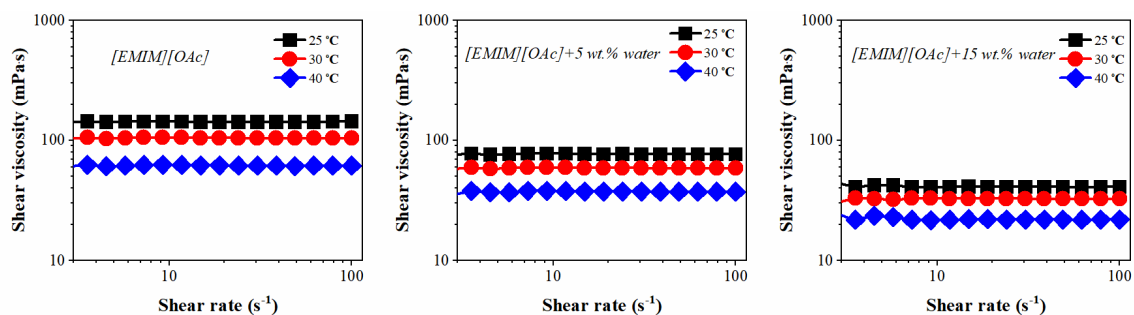
658 * Correspondence: tatiana.budtova@mines-paristech.fr, tatiana.budtova@aalto.fi

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Figure S1.
Equilibrium moisture sorption isotherms of four fibers at 60% RH: (a) flax, (b) Cordenka, (c) Ioncell-FL and (d) Ioncell-F.

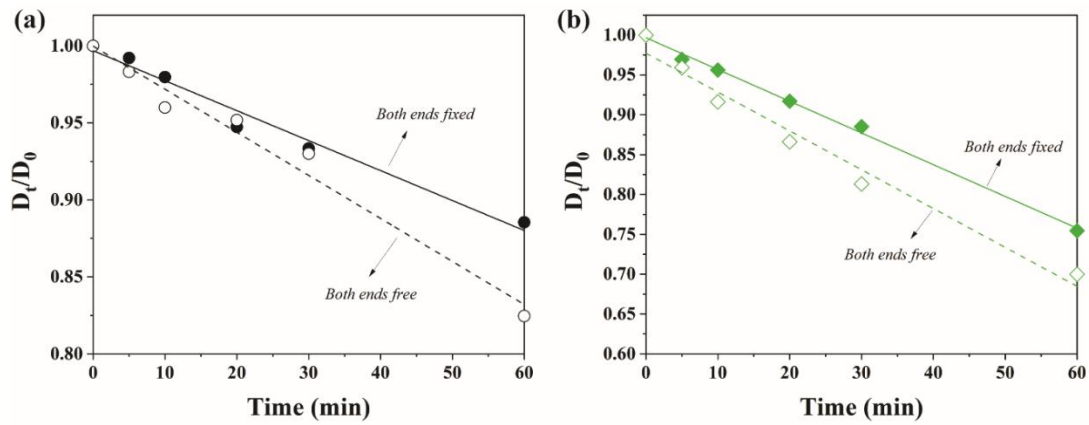


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Figure S2.
Shear viscosity of [EMIM][OAc]-water mixture of different water content at 25°C, 30°C and 40°C.

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Figure S3.

682 Comparison of the normalized diameter of natural fiber flax (a) and Ioncell-FL (b) as an
683 example for man-made fiber in IL [EMIM][OAc] with both ends fixed (filled symbol) and
684 free (open symbol).

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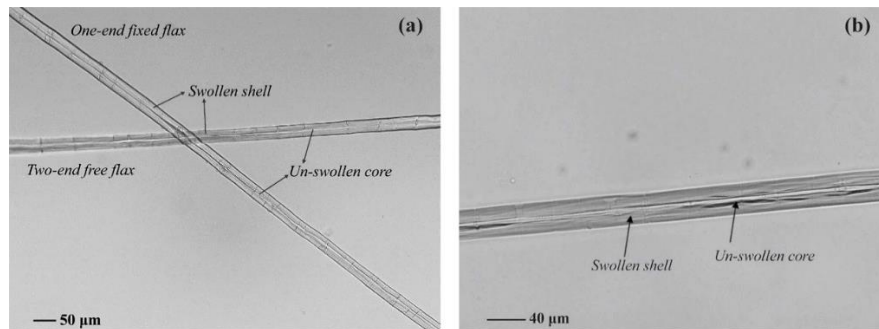
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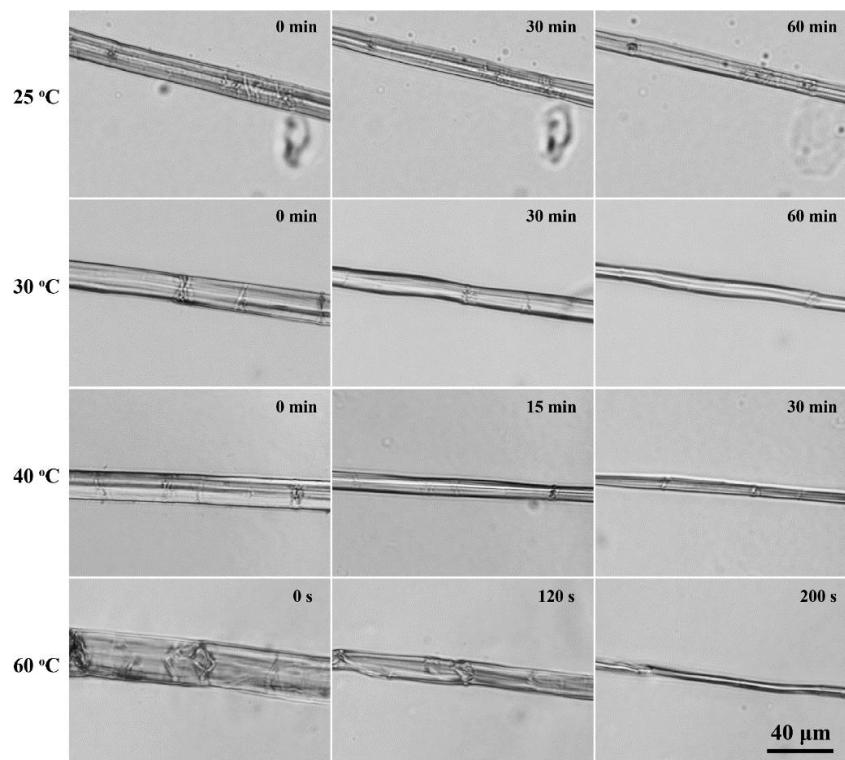
Figure S4.

696 Optical microscopy images of flax fibers in [EMIM][OAc]-5 wt.% water at 50 °C: (a) with
697 one end fixed and with both ends free and (b) both ends fixed.

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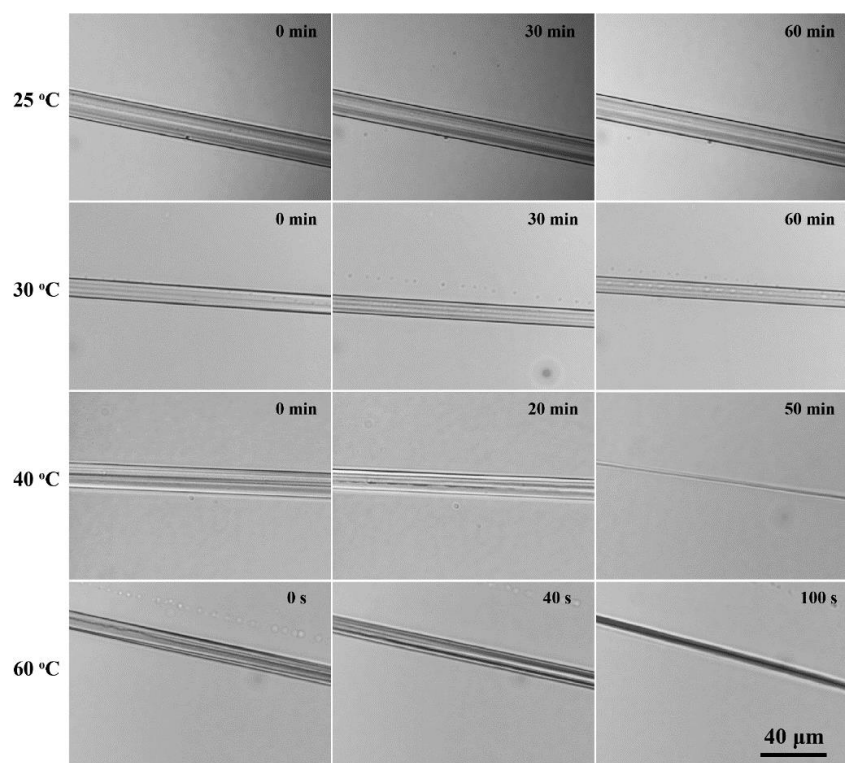
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Figure S5a.

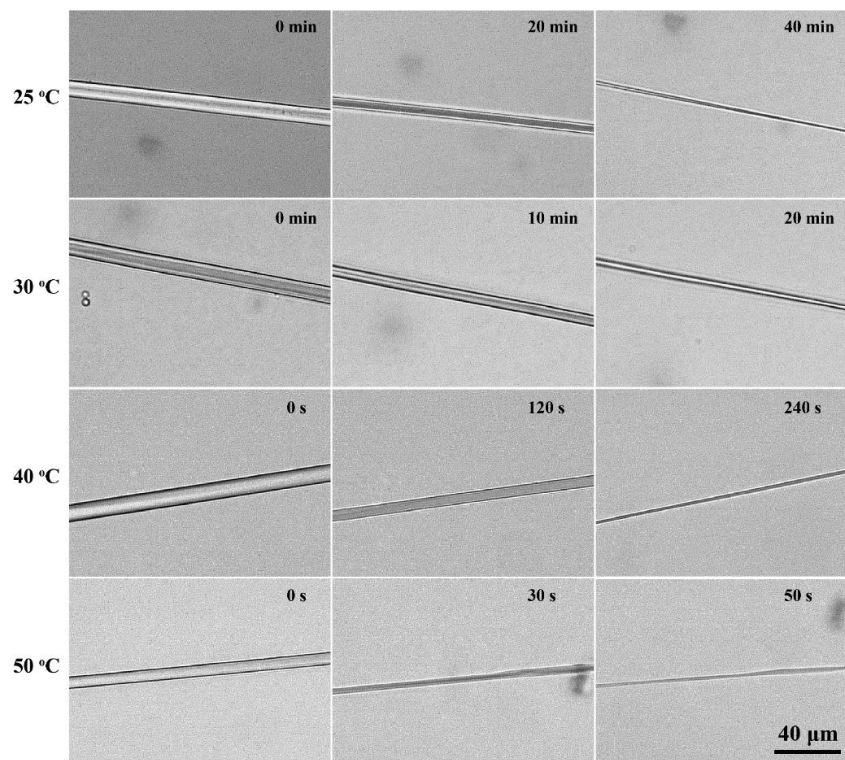
Optical microscopy images of flax in [EMIM][OAc] at different temperatures.



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Figure S5b.

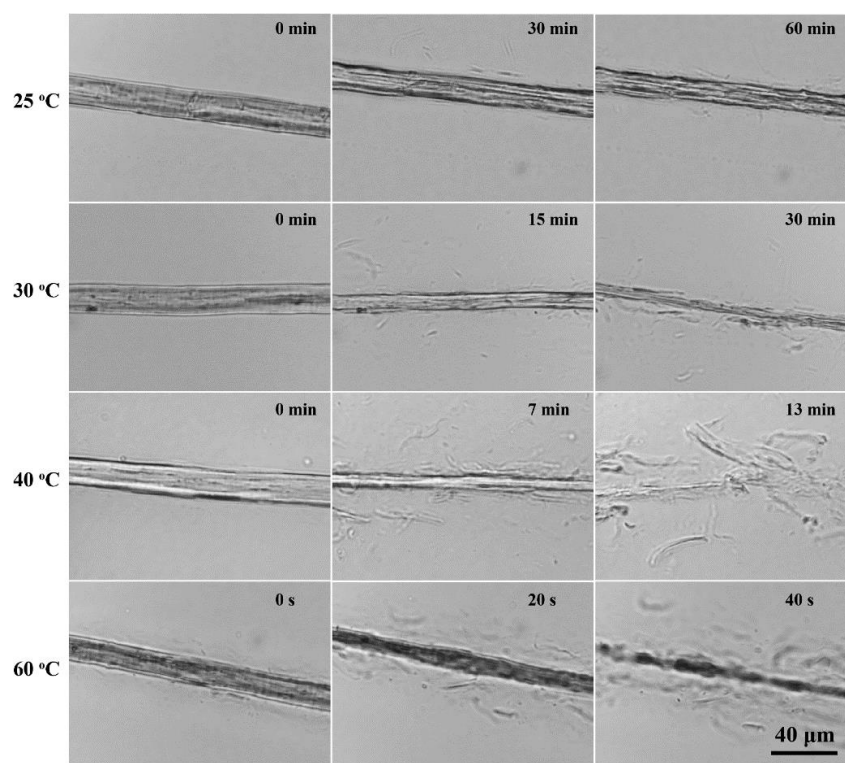
Optical microscopy images of Cordenka in [EMIM][OAc] at different temperatures.



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Figure S5c.

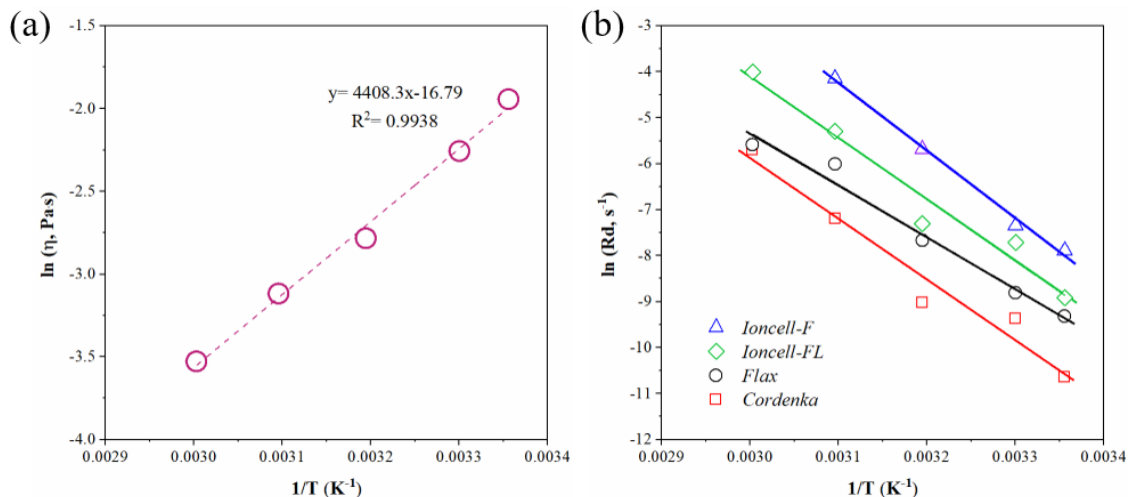
Optical microscopy images of Ioncell-F in [EMIM][OAc] at different temperature.



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Figure S5d.

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



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Figure S6.

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Arrhenius-type plot for [EMIM][OAc] viscosity (a) and fibers' dissolution rate (b) as a function of inverse temperature.

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Table S1. Comparison of dissolution rate of four fibers in [EMIM][OAc] and in [EMIM][OAc]-5 wt.% water at 30°C.

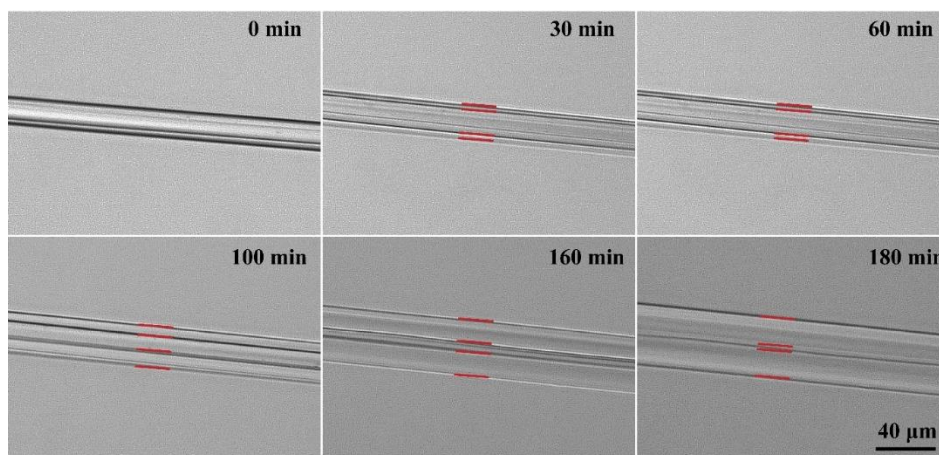
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Dissolution rate (s ⁻¹)	Cordenka	Flax	Ioncell-FL	Ioncell-F
in [EMIM][OAc]	8.51*10 ⁻⁵	1.49*10 ⁻⁴	4.4*10 ⁻⁴	6.48*10 ⁻⁴
in [EMIM][OAc]-5 wt. % water	3.58*10 ⁻⁵	Swelling	2.1*10 ⁻⁴	5.1*10 ⁻⁴

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Figure S7.

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

