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## 2 **Exploring Digital Image Correlation Technique for** 3 **the Analysis of the Tensile Properties of All-** 4 **Cellulose Composites**

5

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16

17 **Abstract:** All-cellulose composites (ACCs) were prepared from filter paper via partial  
18 dissolution in the ionic liquid 1-ethyl-3-methylimidazolium acetate, and material tensile  
19 properties were investigated using various approaches. One is based on data directly taken  
20 from a tensile testing machine, and the other uses two-camera stereovision with digital  
21 image correlation (DIC) technique. In the latter case, virtual extensometer with different  
22 locations on the sample and averaging over sample surface were tested. Nominal and true  
23 stress-strain dependences were built and Young's modulus, tensile strength, elongation at  
24 maximal stress and toughness were evaluated as a function of ACC density. A minor  
25 difference was observed for the stress-strain dependences derived from different  
26 approaches which use the DIC technique, most probably because of low ACC deformation.  
27 However, the results reveal that the nominal stress-strain curve from DIC is significantly  
28 different from that which is directly derived from the data provided by machine sensors  
29 thus strongly impacting Young's modulus and elongation at break values. This study  
30 provides an insight into the evaluation of the mechanical properties of ACCs.

31 **Keywords:** *filter paper, ionic liquid, tensile properties, digital image correlation*

32

## 33 **1 Introduction**

34 The growing concerns on environmental issues motivate the development of  
35 biobased and biodegradable materials such as biocomposites. One of the sub-  
36 classes of biocomposites is all-cellulose composites (ACCs) (Nishino et al. 2004).  
37 The principle of ACC fabrication is based on the concept of all-polymer composites  
38 in which the matrix and the reinforcing fibers are made from the same matter  
39 (Capiati and Porter 1975). The advantage of this concept is that the adhesion  
40 between the matrix and the fibers is perfect, and there is no need of compatibilisers.  
41 The difference between all-polymer and all-cellulose composites is that cellulose is  
42 not melting, and thus ACC preparation requires a dissolution step followed by  
43 washing out the solvent and drying.

44 There are two main routes for making all-cellulose composites: i) one-step  
45 method via partial dissolution of fibers in cellulose solvent with the dissolved  
46 cellulose forming the composite matrix (Soykeabkaew et al. 2008; Huber et al.  
47 2012; Piltonen et al. 2016; Khakalo et al. 2019; Chen et al. 2020a) and ii) two-step  
48 method which involves the preparation of a cellulose solution used for the  
49 impregnation of the reinforcing fibers (Nishino et al. 2004; Spörl et al. 2017; Labidi  
50 et al. 2019; Korhonen et al. 2019). In both cases the reinforcing phase can be natural  
51 or man-made fibers, aligned or isotropic (dispersed short fibers, a fabric, or a filter  
52 paper). Nanocellulose based composites will not be considered here as it is out of  
53 the scope of this work.

54 Various cellulose solvents have been used to make ACCs:  
55 LiCl/dimethylacetamide (DMAc) (Nishino et al. 2004; Soykeabkaew et al. 2008),  
56 NaOH-water based solutions (Piltonen et al. 2016; Korhonen et al. 2019) and,  
57 recently, ionic liquids (Spörl et al. 2017; Khakalo et al. 2019; Chen et al. 2020a).  
58 For application reasons, the tensile properties of ACCs were always in the focus of  
59 most of the publications. For example, when aligned native ramie fibers were  
60 immersed in LiCl/DMAc for 2 h, exceptional longitudinal tensile properties of 460  
61 MPa tensile strength and 28 GPa Young's modulus were obtained (Soykeabkaew  
62 et al. 2008). One of the strongest man-made fibers, Bocell, was also used for making  
63 ACCs with volume fractions of up to 90% of fibers, resulting in an average tensile  
64 strength of 910 MPa and a Young's modulus of 23 GPa with 8% elongation at break  
65 (Soykeabkaew et al. 2009). The above-mentioned mechanical properties far exceed

66 the values reported for the traditional unidirectional natural fiber reinforced  
67 polymer composites. Nevertheless, the majority of the tensile properties of ACCs  
68 lies in the interval of 1 – 20 GPa for Young’s modulus and 50 – 200 MPa for tensile  
69 strength (Baghaei and Skrifvars 2020). The results depend on numerous parameters  
70 such as the origin of the reinforcing fibers, their concentration and alignment, and  
71 processing conditions (type of solvent, dissolution or impregnation time and  
72 temperature, drying mode, etc.) (Baghaei and Skrifvars 2020). It should be noted  
73 that the values obtained with tensile testing also depend on sample geometry and  
74 the method used to obtain the specimen elongation (directly from the tensile  
75 machine, from extensometer in which gauges are “clipped” on the material, using  
76 video extensometers or digital image correlation (DIC)). We will not consider here  
77 “contact” extensometer as it may induce damage or additional stress on the sample.  
78 Mechanical analysis will be performed using DIC technique; for example, it is  
79 commonly used for the analysis of the deformation mechanisms of polymers (Hild  
80 and Roux 2006). This method is accurate and provides crucial information on the  
81 strain field at macroscale level. It also allows measuring non-uniform deformation  
82 and 3D effects. However, DIC is rarely used for natural fiber reinforced polymer  
83 composites (Xu et al. 2019; Ramakrishnan et al. 2020) and, to the best of our  
84 knowledge, was never considered for the evaluation of the tensile properties of all-  
85 cellulose composites.

86 There are different ways to assess the tensile properties of a material. Below we  
87 recall the background equations determining nominal stress ( $\sigma_n$ ) and strain ( $\varepsilon_n$ ):

$$88 \quad \sigma_n = \frac{F}{A_0} \quad (1)$$

$$89 \quad \varepsilon_n = \frac{d}{L_0} = \frac{L - L_0}{L_0} \quad (2)$$

90 where F is force,  $A_0$  is cross-section area of the sample, d is displacement, and  $L_0$   
91 and L are the initial length of the sample and the length at a given applied force,  
92 respectively. The displacement d can be monitored in different ways. One is using  
93 data obtained from the machine displacement sensor; in this work such method will  
94 be named “machine approach”. The other uses local measurement of sample  
95 displacement, i.e. either with video extensometer or DIC techniques; it will be  
96 named “local approach”.

97 Irrespective of the approach used, stress-strain dependences are built to  
98 characterize the material with Young’s modulus in the linear region, maximal stress

99 (often called “tensile strength” or “ultimate stress”), elongation at break and  
100 elongation at maximal stress. The as-obtained results will include different levels  
101 of errors depending on the approach used. For instance, the measurement of  
102 displacement made with the machine approach includes not only the elongation of  
103 the sample in the gauge length region, but also the displacement induced by the  
104 stiffness of the tensile machine, the last one inducing erroneous mechanical  
105 properties (G’Sell et al. 1992). To exclude this problem which is common for all  
106 tensile testing machines, non-contact measurements of the displacement were  
107 developed. For example, video extensometer was introduced in the pioneering work  
108 of G’Sell et al. (G’Sell et al. 1992) to study highly deforming materials showing  
109 “necking”, the latter resulting in the alteration of the cross-section during  
110 experiment. However, the displacement of the specimen may not be homogeneous  
111 along the specimen length. The displacement measured using video extensometer  
112 may depend on the location of the marks on the sample and also on the length  $L$   
113 which can be either sample length (eq.2) or the distance between selected two  
114 points. Finally, the most precise (but the most time-consuming) way of having a  
115 complete information on the deforming material is digital image correlation that  
116 allows obtaining a map of local strains on the specimen surface due to video  
117 cameras in stereovision which monitor the displacements of the markers (or  
118 speckles) randomly placed on the sample surface (Sutton et al. 2009; Candau et al.  
119 2016).

120 As far as all-cellulose composites are concerned, the majority of tensile  
121 properties were obtained using a machine method (see, for example, ref.  
122 Soykeabkaew et al. 2008; Soykeabkaew et al. 2009; Piltonen et al. 2016; Sirviö et  
123 al. 2017; Korhonen et al. 2019; Wei et al. 2020; Chen et al. 2020a). Few works  
124 report the results obtained with a video extensometer (Kröling et al. 2018; Mat  
125 Salleh et al. 2017; Duchemin et al. 2009). In all examples mentioned above nominal  
126 stress-strain dependences were used to calculate Young’s modulus, tensile strength  
127 and elongation at break. The influence of the method on the stress-strain curves and  
128 on the values of Young’s modulus, tensile strength and elongation at break of all-  
129 cellulose composites has never been studied before.

130 The goal of this work was to analyse the tensile properties of all-cellulose  
131 composites applying local and machine approaches and understand the influence of

132 each method on the values of the main mechanical characteristics of the material.  
133 Filter paper-based ACCs were produced using the ionic liquid 1-ethyl-3-  
134 methylimidazolium acetate ([EMIM][OAc]) as cellulose solvent, and the influence  
135 of the dissolution time on composite morphology, density, crystallinity and optical  
136 properties was investigated. Then, the tensile properties of ACCs were evaluated  
137 using data obtained directly from the machine and with a local technique, the latter  
138 using a two-cameras system and digital image correlation. Stress-strain data  
139 corresponding to various approaches were obtained and discussed together with the  
140 main tensile characteristics of the composite materials.

## 141 **2 Experimental Part**

### 142 **2.1 Materials**

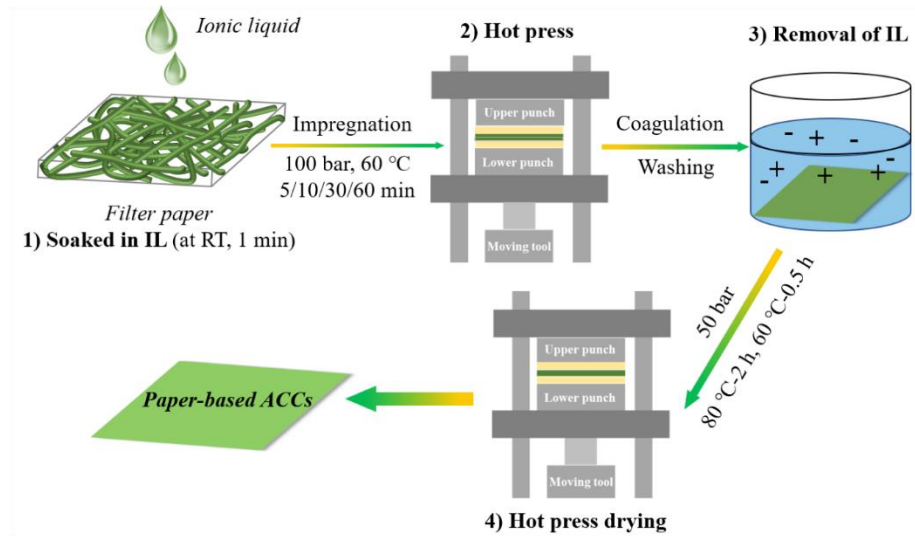
143 Qualitative VWR® Grade 415 filter paper made of pure cellulose was  
144 purchased from VWR International, France. Ionic Liquid 1-ethyl-3-  
145 methylimidazolium acetate ([EMIM][OAc], purity > 95%) was purchased from  
146 IoLiTec. The initial moisture content is 0.27 wt.%, determined by Karl-Fischer  
147 titration. The IL was used as received. Water used in this study was deionized.

### 148 **2.2 Methods**

#### 149 *2.2.1 Manufacturing paper-based ACCs*

150 The paper-based ACCs manufacturing method is illustrated in Figure 1. Two  
151 pieces of filter papers were dipped in [EMIM][OAc] for 1 min, stacked together  
152 and hot pressed at 60 °C. The pressing times were 5 min, 10 min, 30 min and 60  
153 min with the pressure kept constant (around 100 bar). Then the sample was  
154 immersed in a large amount of deionized water for about 72 h (exchanging to fresh  
155 water every day) to remove the ionic liquid from the system. Finally, the specimen  
156 was dried by hot pressing (around 50 bar, 80 °C for 2.5 h and then at 60 °C for 0.5  
157 h). A temperature gradient during drying was shown to prevent the warping and/or  
158 heterogeneous contraction of the sample (Chen et al. 2020a). ACCs produced with  
159 5 min, 10 min, 30 min and 60 min impregnation are named P5, P10, P30 and P60,  
160 respectively.

161



162

163

**Fig. 1** Illustration of the fabrication of the paper-based ACCs

164

### 165 2.2.2 Scanning electron microscopy (SEM)

166 The surface and cross-section morphologies of the filter paper and produced  
 167 ACCs were observed using a scanning electron microscope (Zeiss Sigma VP FE-  
 168 SEM) at an accelerating voltage of 4 kV. Prior to examination, the surface and cross  
 169 section of the samples were coated with a thin layer of gold.

### 170 2.2.3 Sample thickness and density

171 The density of the filter paper and of the produced ACCs was determined by  
 172 measuring sample weight and volume. The volume was calculated from the  
 173 dimensions of the sample measured by using L&W Micrometer (Lorentzen &  
 174 Wettre Products, ABB, Switzerland) with an error of  $\pm 1 \mu\text{m}$  or 0.1 % of reading  
 175 whichever is greater. Porosity was estimated from the density of filter paper and  
 176 ACCs by using a value of  $1.47 \text{ g cm}^{-3}$  as the density of cellulose (Sun 2008), using  
 177 the following equation:

$$178 \quad \text{Porosity (\%)} = \left[ 1 - \frac{\rho_{\text{ACCs}}}{\rho_{\text{cellulose}}} \right] \times 100\% \quad (3)$$

#### 179 2.2.4 Ultraviolet–Visible Light (UV–vis) Spectroscopy

180 The transmittance and haze of the nanopapers in the visible light region were  
181 obtained using a Shimadzu UV-2600 with an ISR-2600 Plus Integrating Sphere  
182 Attachment (Shimadzu, Japan). Optical haze was used to quantify the percentage  
183 of the forward light scattering as follows:

$$184 \quad \text{Haze} = \left[ \frac{T_4}{T_2} - \frac{T_3}{T_1} \right] \times 100\% \quad (4)$$

185 where  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  are defined as background checking, total transmitted  
186 illumination, beam checking and pure diffusive transmittance, respectively.

#### 187 2.2.5 X-ray diffraction (XRD)

188 XRD data were collected in the reflection mode of an X-ray instrument,  
189 SmartLab (RIGAKU), operated at 45 kV and 200 mA. The sample was placed on  
190 a sample holder horizontally to incident X-ray and the scans were performed in the  
191  $2\theta$  range from  $5^\circ$  to  $60^\circ$  by  $\theta/2\theta$  mode. Background intensity profile without sample  
192 was collected in the same conditions, and it was subtracted from the obtained data.  
193 The subtracted data were corrected for the Lorentz-polarization factor for each data  
194 point. The background intensity ( $S_{\text{bkg}}$ ) from the amorphous phase of cellulose was  
195 estimated by robust smoothing procedure as described elsewhere. The total  
196 crystallinity index (CRI) of the initial filter paper and of ACCs was estimated using  
197 the ratio of the area of total intensity ( $S_{\text{total}}$ ) to that of background intensity  $S_{\text{bkg}}$  in  
198 the  $2\theta$  range from  $10^\circ$  to  $32^\circ$ :

$$199 \quad \text{CRI, \%} = 100\% \times \left( 1 - \frac{S_{\text{bkg}}}{S_{\text{total}}} \right) \quad (5)$$

200 The background-corrected profile was fitted with 4 pseudo-Voigt function for  
201 cellulose I ((1-10), (110), (102)/(012) and (200) lattice planes) and 3 pseudo-Voigt  
202 functions for cellulose II ((1-10),(110) and (020) lattice planes). For each  
203 polymorph, the ratio of amplitude for the lattice planes were fixed to be the ratio of  
204 the square of structure factor (Nishiyama et al. 2002, Langan et al. 2001). The  
205 deviation of diffraction positions was limited to be close to those calculated from  
206 the unit cell parameters of the crystal structure of cellulose I and II. The software  
207 LMFIT (Newville et al. 2016) was used for the fitting. As the mass absorption  
208 coefficients are identical for crystalline polymorphs, quantitative phase analysis  
209 was performed using the single peaks of cellulose polymorphs (Alexander and Klug



210 1984). The intensities for the 1–10 lattice plane of cellulose I ( $I_{1-10(1)}$ ) and cellulose  
 211 II ( $I_{1-10(2)}$ ) can be expressed as a function of the structure factor  $F_{1-10(\alpha)}$ , the volume  
 212 of unit cell  $V_{(\alpha)}$  and the volume fraction  $v_{\alpha}$  of each crystalline phase ( $\alpha$  being either  
 213 cellulose I or II crystal) in the total cellulose crystal, as follows:

$$I_{1-10(\alpha)} = \frac{K}{V_{(\alpha)}^2} |F_{1-10(\alpha)}|^2 v_{\alpha} \quad (6)$$

214 where K is a constant for the instrument and sample.

215 Thus, the ratio of the volume fraction of cellulose II to cellulose I,  $v_2/v_1$ , is as  
 216 follows:

$$\frac{v_2}{v_1} = \frac{2.27 I_{1-10(2)}}{I_{1-10(1)}} \quad (7)$$

217 where the coefficient 2.27 was calculated from the unit cell volume and the structure  
 218 factor for the 1–10 lattice of cellulose I (Nishiyama et al. 2002) and cellulose II  
 219 (Langan et al. 2001). This equation was used to calculate the volume fraction of  
 220 cellulose II over the total crystalline cellulose as follows:

$$Cell_{II} \text{ vol } \% = \frac{v_2}{v_1 + v_2} \quad (8)$$

## 221 2.2.6 Tensile Testing

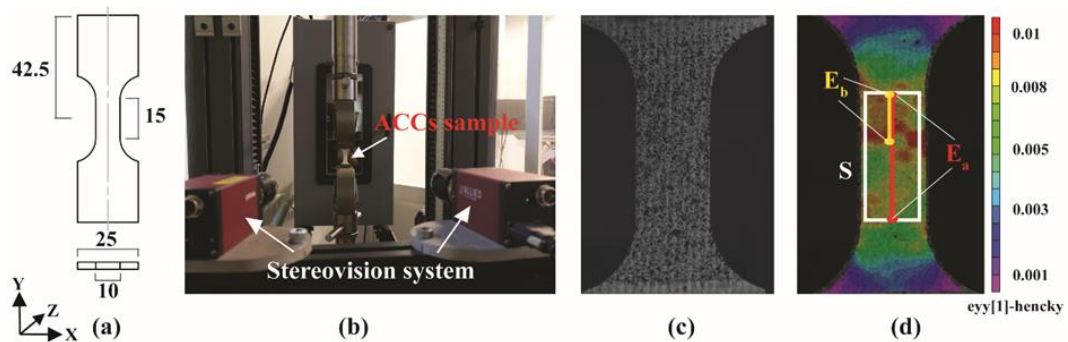
222 The mechanical properties of the filter paper and ACCs were studied using the  
 223 electro-mechanical tensile test machine Zwick-2.5kN at 23 °C and 50% relative  
 224 humidity. Figure 2a presents the geometry of the tensile sample with a gauge length  
 225 ( $L_0$ ) and a width (W) of 15 mm and 10 mm, respectively. Sample thickness was  
 226 measured at different locations within the gauge length area for each sample with  
 227 high-precision caliper and the maximal standard deviation was  $\pm 0.005$  mm/50 mm.  
 228 The tensile measurements were carried out at a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$ .

229 The first set of force-displacement data was collected directly from the tensile  
 230 machine (machine approach). In parallel, two-cameras stereovision system was  
 231 used to monitor the local displacements of ACC (Figure 2b). Stereovision provides  
 232 a 3D image of sample surface using a superposition of two 2D plane images, and  
 233 DIC allows building a 2D displacement field on sample surface. In this work, a 3D  
 234 DIC method was used. The advantages of 3D DIC method compared to the 2D DIC  
 235 can be found elsewhere (Sutton et al. 2008). The calibration of 3D DIC was done  
 236 until a projection error of 0.05 was reached (Sutton et al. 2009).

237 To monitor the local displacements, the front surface of the sample was coated  
 238 with a thin layer of white paint on which black ink was sprayed to generate a random  
 239 speckle pattern (Figure 2c). The displacement field was obtained by tracking the  
 240 positions of speckle patterns on a specimen surface before and after the deformation  
 241 of the body. Practically, two sets of images – corresponding to two different  
 242 mechanical states (i.e. reference and deformed) – are recorded by two fixed cameras  
 243 set with in-between fixed angle. As grey level cannot be a unique characteristic of  
 244 a “point” on sample surface, neighboring pixels must be used to build a  
 245 displacement field using the initial and deformed pictures. Such a collection of pixel  
 246 values is called a subset. Large speckles (e.g. more than 20 pixels) were avoided as  
 247 they need large subset sizes which reduces the spatial resolution of the analysed  
 248 zone.

249 The displacement fields were built from images recorded by a pair of cameras  
 250 AVT PIKE 5 Megapixels with a 2/3' CCD sensors and 50 mm Schneider  
 251 Kreuzwach objectives. The images were taken every second and post-processed  
 252 using VIC-3D software (S. Vic-3D 2007) (Figure 2d). The first step of the analysis  
 253 consists of creating a regular mesh in the region of interest. The meshing allows  
 254 tracking the speckle pattern during the tensile test. In this study, the subset was 23  
 255 pixels with a step of 5 and filter size of 13. More details on the selection of  
 256 parameters and analysis of data are given in the Supporting Information.

257



258

259 **Fig. 2** The tensile testing setup used in this study: (a) geometry of a tensile sample,  
 260 values are in mm; (b) experimental setup with stereovision system; (c) speckled  
 261 sample for the DIC analysis and (d) example of true strain field obtained by DIC  
 262 analysis using VIC-3D software,  $E_a$  and  $E_b$  are locations of a virtual extensometer

263 and S is the surface of the rectangle over which the true strain in the longitudinal  
264 direction is averaged

265 As mentioned in the Introduction, there are different ways of using digital image  
266 correlation approach. One option is to use it as a video extensometer: we select two  
267 different locations of “virtual extensometers”, one monitoring strain evolution  
268 along  $E_a$  and the other along  $E_b$  (Figure 2d). Different locations of the virtual  
269 extensometers are selected to better understand the influence of their location on  
270 strain distribution over the sample and the corresponding stress-strain dependences.  
271 Another option is to average the displacement over a given surface; here we will  
272 use surface S shown by a rectangle in Figure 2d. While virtual extensometer  
273 provides nominal strain evolution over time and further nominal stress-strain  
274 response (eq. 1 and 2), the evolution of true strain over time is obtained from VIC-  
275 3D software by averaging true strain distribution over the surface S. We recall  
276 below the relationship between true strain  $\varepsilon_{true}$  and nominal strain  $\varepsilon_n$ :

$$277 \quad \varepsilon_{true} = \ln\left(1 + \frac{L - L_0}{L_0}\right) = \ln(1 + \varepsilon_n) \quad (9)$$

278 true stress  $\sigma_{true}$  is then determined as follows:

$$279 \quad \sigma_{true} = \frac{F}{A(t)} = \frac{F}{A_0 \exp(-\varepsilon_{true})} \quad (10)$$

280 where  $A(t)$  is sample cross-section area at a given moment.

281

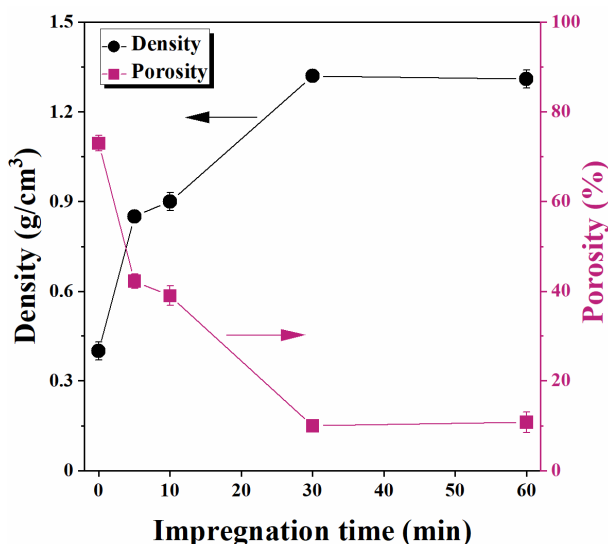
### 282 **3 Results and Discussions**

283 To better understand the mechanical performance of ACCs and the influence of  
284 the analysis method (machine vs local), material properties such as density,  
285 morphology and crystallinity must be first examined. Therefore, we start with the  
286 analysis of the evolution of ACC characteristics as a function of processing  
287 conditions. Then, the local approach using different DIC analyses vs machine  
288 approach applied to ACC will be addressed, using one sample as an example. This  
289 study will be used to setup the methodology of tensile tests analysis. Finally, the  
290 tensile values (tensile (maximal) strength, strain at maximal strength, Young’s  
291 modulus and work of fracture) obtained via machine data and local approach using  
292 stereovision system are compared and discussed.

293

### 294 3.1 Density and crystallinity of ACCs

295 The evolution of ACC density and porosity as a function of impregnation time  
296 is shown in Figure 3. Density increases with the impregnation time under pressure  
297 indicating a strong decrease in material porosity, from 73% for filter paper and 42%  
298 for P5 to 11% for P60 (Figure 3). No noticeable evolution is recorded after 30 min  
299 of dissolution.

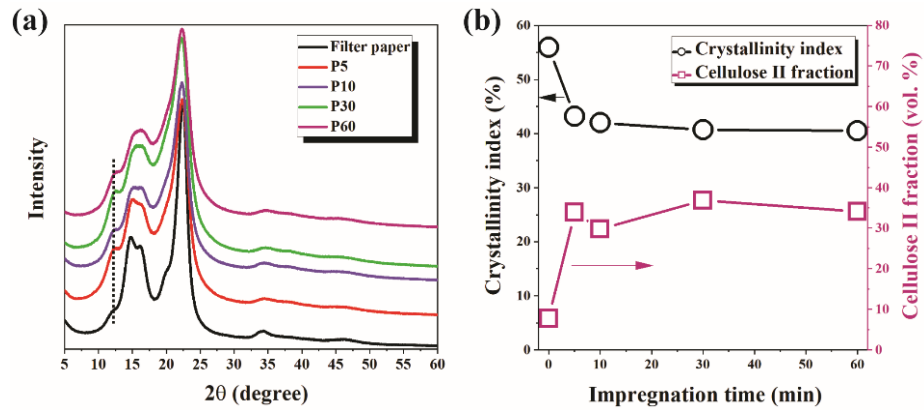


300

301 **Fig. 3** Density and porosity of ACC as a function of impregnation time. The  
302 properties of filter paper are shown at  $t = 0$ . The lines are given to guide the eye

303 The ACCs XRD profiles, crystallinity and cellulose allomorphs as a function of  
304 impregnation time are shown in Figure 4. The filter paper was theoretically  
305 composed of native cellulose which is the cellulose I allomorph. However, a small  
306 diffraction peak at  $2\theta \approx 12^\circ$ , which indicates cellulose II allomorph, was also  
307 observed (Figure 4a). It has been reported that a paper sheet, despite supposed to  
308 be native cellulose, may contain a small amount of cellulose II crystalline structure  
309 (Sirviö et al. 2017; Piltonen et al. 2016). The amount of cellulose II strongly  
310 increases after 5 min impregnation, from around 7 to 34 vol%, but then does not  
311 vary significantly (Figure 4b). Crystallinity drops from around 56% to 43% for 5  
312 min impregnation and then slowly decreased to around 40% for longer  
313 impregnation times. Based on these results we suppose that dissolution was almost  
314 stopped after the first 5 minutes. The reason is that the total cellulose concentration  
315 was too high ( $> 40$  wt.%), above the dissolution limit in the ionic liquid. It was  
316 suggested that at least 3 ionic liquid molecules per anhydroglucose unit are needed

317 to dissolve cellulose in [EMIM][OAc] which corresponds to a maximum cellulose  
318 solubility of around 25-27 wt.% (Le et al. 2014). It should also be taken into account  
319 that the viscosity of the dissolved phase is high and dissolution (impregnation) was  
320 performed in static conditions, without mixing, also preventing cellulose  
321 dissolution.  
322



323

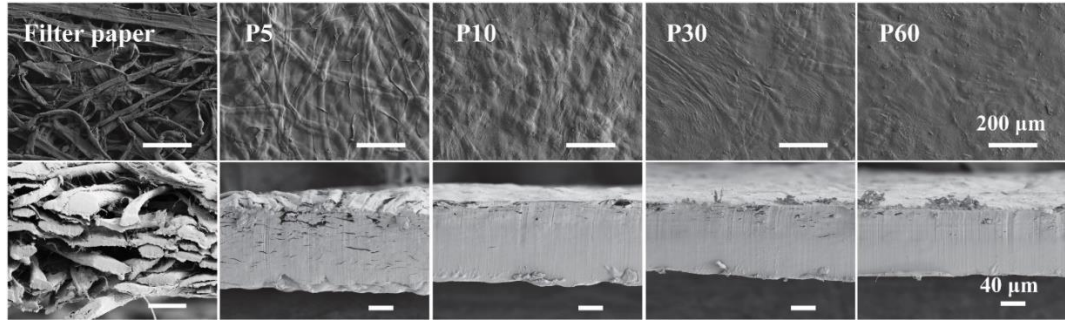
324 **Fig. 4** (a) X-ray diffractograms of filter paper and the produced ACCs, the black  
325 dotted line indicates the characteristic peak of cellulose II. (b) The total crystallinity  
326 index and cellulose II volume fraction of ACC as a function of impregnation time,  
327 the lines are given to guide the eye. The properties of filter paper are shown at  $t =$   
328 0

### 329 3.2. Morphology and optical properties of the ACCs

330 To provide a direct evidence of the gradient dissolution of the fibers in the filter  
331 paper induced by the impregnation time and compression, the surface and cross-  
332 section morphologies of the initial paper and of obtained ACCs were examined by  
333 SEM (Figure 5). The starting material shows individual fibers typical for a filter  
334 paper with large number of voids, as confirmed by the low density. After 5 min of  
335 impregnation, fibers can still be distinguished (Figure 5, images of the surface on  
336 the top row) but they are well embedded into the dissolved cellulose matrix  
337 demonstrating excellent adhesion. The cross-section shows some remaining pores  
338 (Figure 5, lower row). After 10 min and longer impregnation times the fibrous  
339 structure of the paper had almost disappeared and no pores can be seen. Figure 5  
340 also shows the decrease of ACCs cross-section. SEM observations are in-line with  
341 density and XRD results: cellulose that could be dissolved was dissolved during the

342 first 5 minutes (strong increase of cellulose II fraction and drop of crystallinity) and  
343 further morphology evolution is due to the distribution of dissolved phase within  
344 the pores under pressure (no evolution of cellulose II fraction and crystallinity but  
345 continuous increase in density).

346

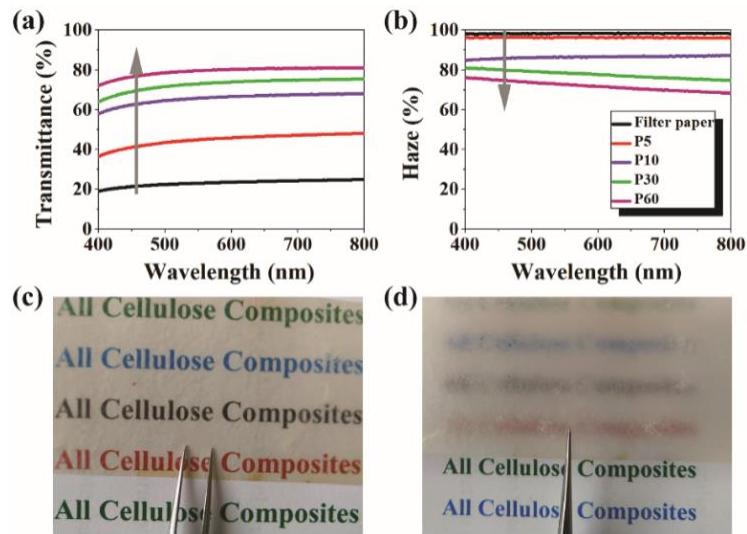


347

348 **Fig. 5** (a) Upper set of images: the surface of filter paper and ACCs P5, P10, P30  
349 and P60; (b) lower set of images: cross-section of filter paper and of the  
350 corresponding ACCs. The scale bar for all images on the upper set is 200  $\mu\text{m}$  and  
351 on the lower set 40  $\mu\text{m}$

352 The optical properties of ACCs are correlated with their morphology. Figure 6  
353 displays the optical transmittance and haze of the filter paper and the as-prepared  
354 ACCs. As the filter paper consists of randomly packed irregular cellulose fibers and  
355 micron-size voids, it is opaque in the visible light due to massive backward light  
356 scattering and possess almost 100% transmission haze because of strong forward  
357 light scattering. In ACCs, the dissolved cellulose fills the voids with the matter of  
358 the same refractive index as fibers, surface roughness is decreased and the material  
359 becomes transparent in the visible light (Figure 6a). Morphology homogenization  
360 also decreases the forward light scattering resulting in the reduction of haze (Figure  
361 6b). Both transmittance and haze show a sharp transition of properties at  
362 impregnation times longer than 5 min, in-line with the ACC morphology (Figure 5)  
363 and density (Figure 4). It is worth noting that ACCs P60 is transparent (optical  
364 transmittance  $\sim 80\%$  at 550 nm) but still with high haze ( $> 70\%$  at 550 nm), which  
365 makes it promising as photonic material for optoelectronic applications such as  
366 solar cells, as haze increases light scattering and absorption (Hou et al. 2020; Chen  
367 et al. 2020b). The digital photographs of ACC P60 confirm high transmittance and  
368 high haze (Figure 6c, d).

369



370

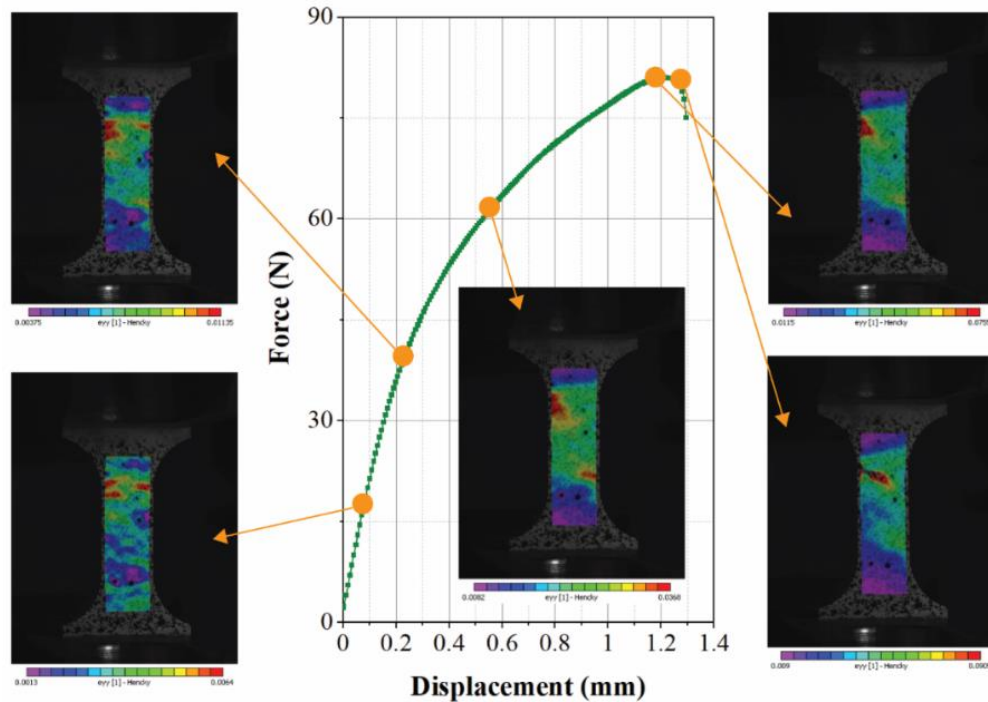
371 **Fig. 6** Optical transmittance (a) and haze (b) of filter paper and the ACCs, ACC  
372 P60 in close contact with the colored letters underneath to show its high light  
373 transmittance (c) and 1 cm away from the same substrate (d) to indicate its high  
374 haze

375

### 376 3.3 Mechanical properties

#### 377 3.3.1 Local vs machine approach

378 Sample P5 was used to test different approaches for the analysis of ACC tensile  
379 properties. An example of strain distributions over the sample surface obtained with  
380 a local (DIC) approach for tensile loading is shown in Figure 7. This type of analysis  
381 was performed for all other samples. Figure 7 shows that the strain field is  
382 heterogeneous with strain concentration on the upper side; failure is initiated in this  
383 area.



384

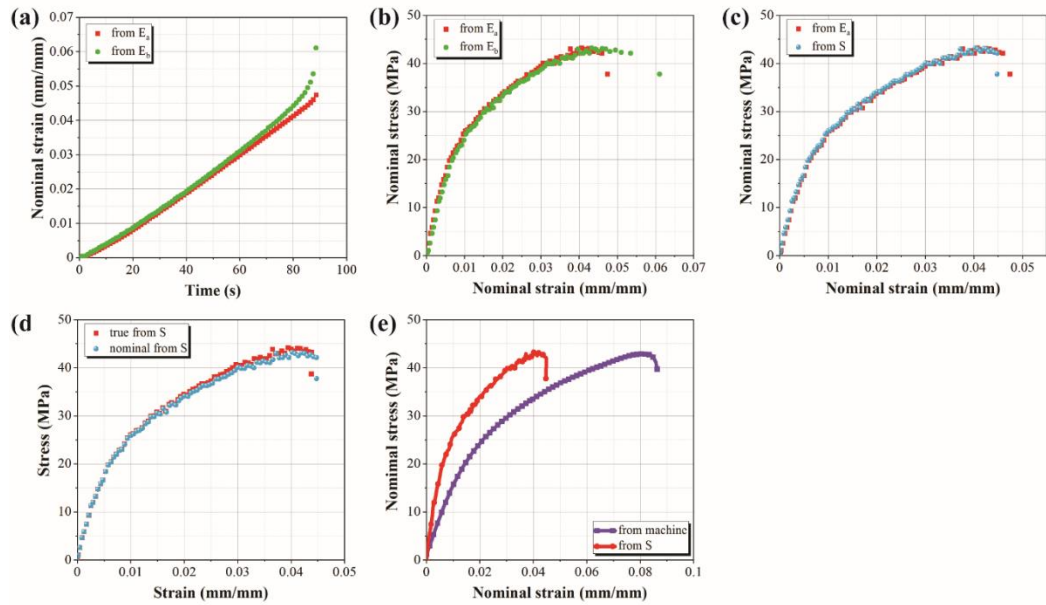
385 **Fig. 7** The true strain field in the longitudinal direction obtained by DIC as function  
 386 of displacement for the sample P5

387

388 To check if this heterogeneity induces differences in stress-strain curves, the  
 389 nominal strain was plotted as a function of time (Figure 8a) and then converted into  
 390 nominal stress-strain curves (Figure 8b) for two locations of the virtual  
 391 extensometer,  $E_a$  and  $E_b$  (see details Methods section). Figure 8a shows similar  
 392 curves for the two positions until a strain of 0.03. Some differences are then  
 393 observed due to the strong localisation of the deformation and the specimen failure.  
 394 It is translated into a quite minor difference in the strain at failure, 0.06 (for  $E_b$ ) vs  
 395 0.05 (for  $E_a$ ). The strain localisation is well captured by  $E_b$  while  $E_a$ , characterized  
 396 by a higher gauge length  $L_0$ , is less sensitive to this strain localisation and as it  
 397 represents the average of the nominal strain distribution over the corresponding  
 398 gauge length. As stress-strain curves are practically identical, Young's modulus and  
 399 tensile strength are the same for both locations of the virtual extensometer. However,  
 400 this may not always be the case especially for the determination of the strain to  
 401 failure.

402





403

404 **Fig. 8** Comparisons of tensile data for P5 obtained with different approaches: (a)  
 405 nominal strain as a function of extension time collected from the virtual  
 406 extensometers E<sub>a</sub> and E<sub>b</sub>, (b) nominal stress-strain curves from the virtual  
 407 extensometers E<sub>a</sub> and E<sub>b</sub>; (c) nominal stress-strain curves from the virtual  
 408 extensometer E<sub>0</sub> and over the surface S; (d) nominal and true stress-strain curves  
 409 obtained with stereovision system over the surface S and (e) nominal stress-strain  
 410 curves obtained from the machine and with stereovision system over the surface S

411

412 Next, we compare nominal stress-strain curve obtained from the virtual  
 413 extensometer E<sub>a</sub> with that averaged over the surface S (Figure 8c). A minor  
 414 difference is observed for the strain at failure. Then nominal and true stress-strain  
 415 curves are compared for the case when the strain averaged over the surface S  
 416 (Figure 8d). The true stress is slightly higher than the nominal one with slightly  
 417 lower strain at failure. Such coincidence can be explained by the overall low  
 418 deformation of the sample. For materials exhibiting large deformations more  
 419 differences between nominal and true strain-stress curves are usually recorded.

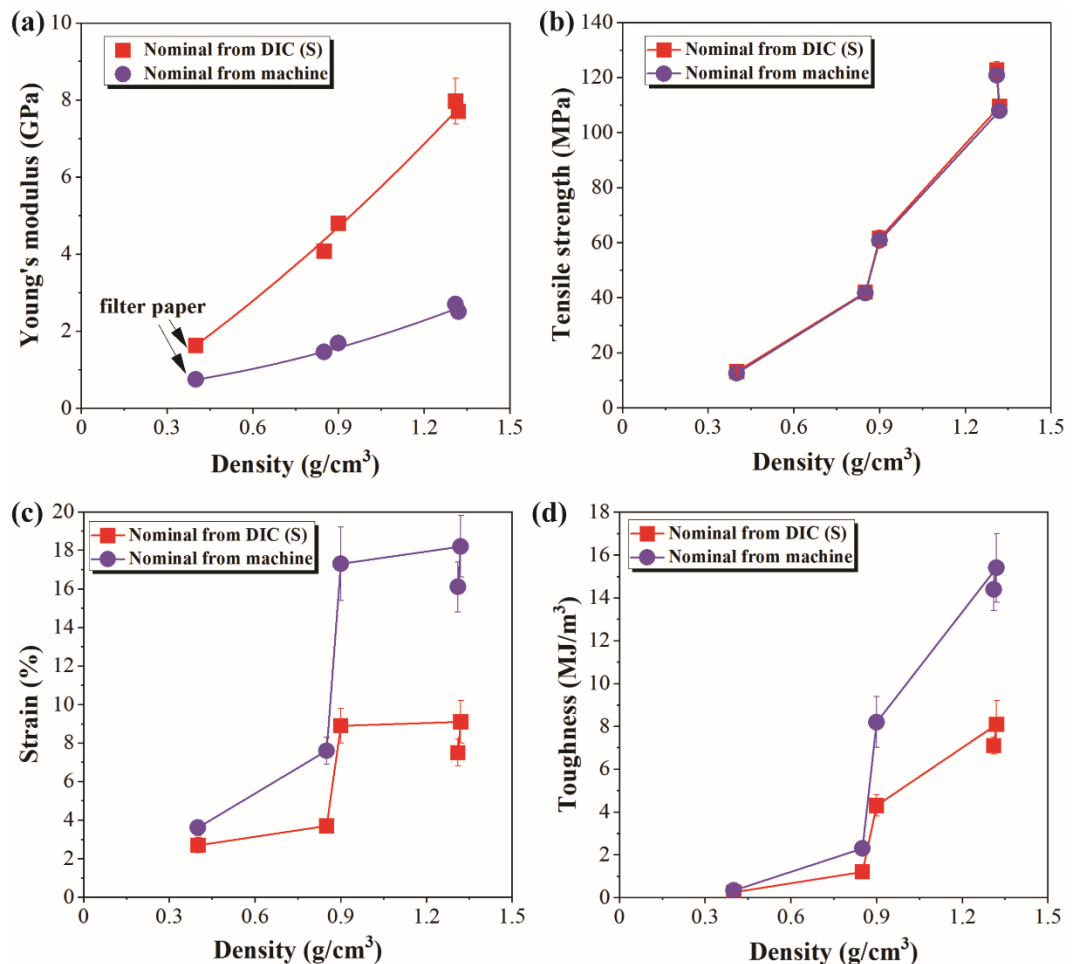
420 Finally, Figure 8e compares the nominal stress-strain curve directly derived  
 421 from the machine (machine approach) with that derived from stereovision and  
 422 averaged over the surface S (local approach). Here the difference is significant: the  
 423 strain at failure determined with machine approach is twice higher than that  
 424 determined with DIC. With nominal tensile strength being almost the same,

425 Young's modulus calculated with the local approach will be much higher than that  
 426 calculated from machine approach. We remind that the latter provides results with  
 427 the systematic error arising from the equipment input.

### 428 3.3.2 Tensile properties of ACCs

429 Young's modulus, tensile strength, strain at maximal stress and toughness were  
 430 calculated from nominal and true stress-strain curves (Figure S1, Supporting  
 431 Information) derived from the machine and local approaches, the latter using  
 432 stereovision system and averaged over the surface S. All mechanical characteristics  
 433 of the filter paper and ACCs are given in Table S1, their dependence on material  
 434 density is shown in Figure 9 and on the impregnation time in Figure S2.

435



436

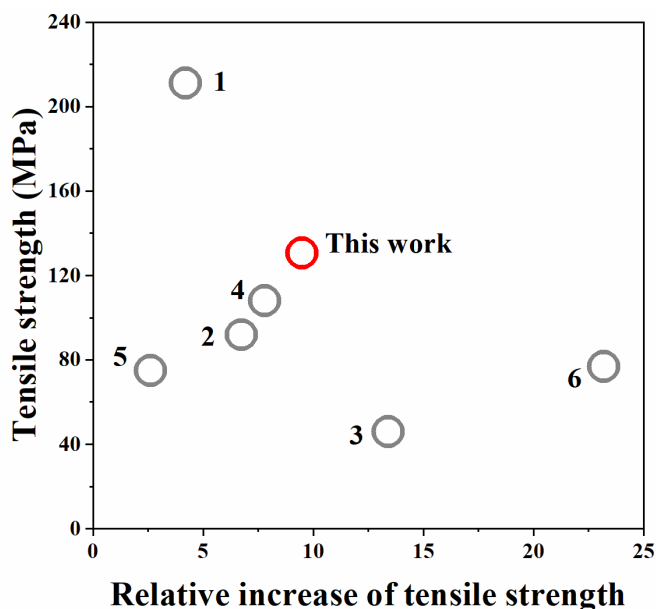
437 **Fig. 9** Young's modulus, tensile strength, strain at maximal stress and toughness of  
 438 the filter paper and ACCs as a function of density. When errors are not visible, they  
 439 are within the size of the symbol. The lines are given to guide the eye

440 The increase in ACC density, which corresponds to the increase of  
441 impregnation time, leads to a strong increase of Young's modulus, independent of  
442 the method used to determine it (Figure 9a). All values calculated from nominal  
443 stress-strain curves via a local approach using stereovision are much higher than  
444 those calculated from nominal ones via machine approach, as expected from Figure  
445 8e. We also plotted Young's modulus as a function of crystallinity (Figure S3);  
446 modulus decrease with crystallinity increase shows that the crystallinity does not  
447 play an important role here as it is the presence of pores and heterogeneities that  
448 control mechanical properties. It has been demonstrated in the previous studies that  
449 density plays the essential role in the mechanical performance of ACCs (Korhonen  
450 et al. 2019; Chen et al. 2020a); an adequate comparison with literature can thus be  
451 made only for the materials either of the same density or for the specific values of  
452 mechanical characteristics. Unfortunately, the density of ACC is not always  
453 reported. To the best of our knowledge, for paper-based isotropic all-cellulose  
454 composites, only the study from Piltonen et al. (Piltonen et al. 2016) reported  
455 density values. The calculated specific strength and modulus values obtained in this  
456 work are listed in Table S2 in the Supporting Information and compared with those  
457 reported by Piltonen et al. (Piltonen et al. 2016). Considering that the type of  
458 approach (machine or contact or non-contact extensometer) is rarely specified, the  
459 comparison of moduli values with the results obtained in literature becomes even  
460 more delicate.

461 Similar to the Young's modulus, tensile strength and toughness increase with  
462 density increase. Interestingly, the strain at break also increases, from 4 to 9%, the  
463 latter corresponding to the ACC with a density of around  $0.9 \text{ g/cm}^3$  (impregnation  
464 time 10 min); at higher density, the strain at break remains on the same level. A  
465 certain porosity improves material ductility.

466 Figure 8 and 9 show that while Young's modulus calculated from nominal  
467 stress-strain curves using a local approach is higher than that calculated using the  
468 machine approach, the opposite was obtained for the strain at maximum stress and  
469 toughness. A lower toughness obtained from local approach is due to much lower  
470 nominal strains at maximum stress as compared to those obtained via machine  
471 approach. Tensile strength values did not depend on the approach used within the  
472 errors.

473 Overall, a simple strategy of filter paper impregnation with ionic liquid for 30-  
474 60 min allowed increasing the tensile strength by almost 10 times, of Young's  
475 modulus by 5 times and of toughness by 25 times as compared to the initial filter  
476 paper. In order to make an adequate comparison with literature results, the  
477 properties of the starting material should be considered. In our case, the nominal  
478 tensile strength values calculated from the local approach and from machine  
479 approach are similar. Supposing this is the case for ACCs published in other works,  
480 the results on various isotropic ACCs can be put together. As presented in Figure  
481 10, Sirviö et al. (Sirviö et al. 2017) obtained a very high increase of nominal tensile  
482 strength of dissolving pulp-based ACCs, up to 24 times, but the absolute value of  
483 tensile strength was only around 76 MPa, most probably because of the low  
484 mechanical properties of the starting material. Nishino and Arimoto (Nishino and  
485 Arimoto 2007) reported a filter paper-based ACC with a nominal highest tensile  
486 strength of 211 MPa, but the initial filter paper was much stronger, with tensile  
487 strength around 50 MPa. In the current study the tensile strength of the initial filter  
488 paper was around 13 MPa. The comparison of the best values of tensile strength vs  
489 its increase as compared to the strength of the initial paper is shown in Figure 10.  
490



491

492 **Fig. 10** A comparison of maximal tensile stress and of the increase of maximal  
493 tensile stress as compared to the starting filter paper for isotropic paper-based ACCs

494 (1, Nishino and Arimoto 2007; 2, Duchemin et al. 2009; 3, Piltonen et al. 2016; 4,  
495 Wei et al. 2020; 5, Han and Yan 2010; 6, Sirviö et al. 2017)

496

## 497 **4 Conclusions**

498 All-cellulose composites were made via controlled impregnation with ionic  
499 liquid, [EMIM][OAc]. First, the properties of the composites (density, porosity,  
500 crystallinity, cellulose II fraction, transmittance, haze and morphology) were  
501 investigated as a function of impregnation time. The results showed that cellulose  
502 was dissolved during the first 5 minutes, and further evolution of properties was  
503 due to the distribution of dissolved phase within the pores.

504 Tensile testing was conducted using different methods to obtain the specimen  
505 elongation: i) data directly taken from machine sensors and ii) using digital image  
506 correlation technique and local approach. The latter excludes the errors related to  
507 the stiffness of the tensile testing machine itself. Although the nominal tensile  
508 strength values from DIC and machine are similar, the nominal Young's modulus,  
509 strain at maximal stress and, as a consequence, toughness, are very different. This  
510 must be taken into account when comparing results from different literature sources.  
511 ACC fabrication strategy using in this work resulted in the increase of tensile  
512 strength, Young's modulus and toughness by almost 10, 5 and 25 times,  
513 respectively, as compared to the initial filter paper.

514

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521

522 **Declarations**

523

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526 Oyj

527

528 **Conflicts of interest:** not applicable

529 **Availability of data and material:** data can be provided upon request

530 **Code availability:** not applicable

531

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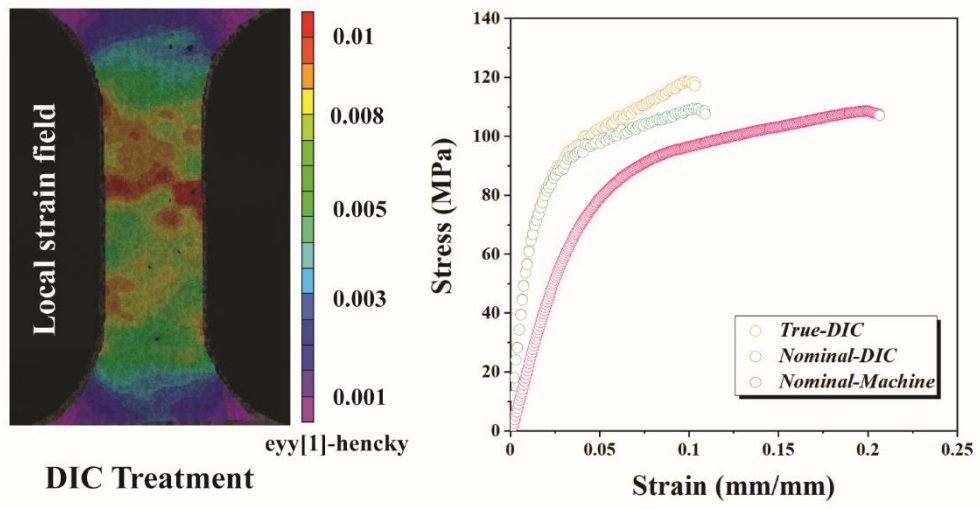
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611

### TOC Image



612