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1 **Influence of water ageing on the mechanical properties of flax/PLA non-woven composites**

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7 **Abstract**

8 Flax fibres are widely used in the automotive sector to reinforce polyolefins, such as for
9 dashboard and interior door panels. A promising option is poly-(lactid) (PLA), as it leads to
10 higher mechanical properties and offers an additional end-of-life scenario following recycling:
11 industrial composting. However, like other composite systems such as flax/polyolefin, flax/PLA
12 composites are also sensitive to water. Here, a non-woven flax/PLA composite is aged under
13 several conditions (50% RH/75% RH/98% RH/Immersion) until saturation. After ageing, all
14 samples are reconditioned at 50% RH, and their residual properties are assessed. The presence
15 of a critical relative humidity between 75% and 98% is highlighted, above which, increases in
16 moisture content irreversibly decrease the composite's mechanical properties. After ageing at
17 98% RH and in immersion, tangent modulus was reduced by 23.0 and 33.8% and ultimate
18 strength by 26.7 and 37.4%, respectively, compared to reference materials. This decrease is
19 mainly due to microstructure evolution in the form of increasing porosity. This microstructure
20 evolution is induced by the swelling of flax fibres, which generates high local stresses, above
21 what PLA can withstand. As a result, micro-cracks appear in the matrix, responsible for
22 reduction in mechanical properties.

23 **Keywords** : Biocomposites ; Flax fibres ; Non-woven ; Degradation ; Microstructure ; Moisture

24 **1 Introduction**

25 Thanks to their light weight [1] and their good mechanical properties [2], flax fibres can be
26 drop-in alternatives to glass fibres as composite material reinforcements in the automotive
27 area [3]. In addition, using thermoplastics as matrices reduces the composite's environmental
28 impacts, especially thanks to recycling [4], which is a potential end-of-life solution for
29 circularity. However, one of the bottlenecks for wider applications is the sorption behaviour of
30 flax composites, especially when considering stringent validation standards of the automotive
31 industry, which impose the test of materials across a large range of humidity and temperature
32 conditions [5].

33 An elementary flax fibre, not embedded in a matrix, has a moisture content of 6% at 50%
34 relative humidity (RH) and reaches 18% at 98% RH [6]. Flax sorption behaviour follows Park's
35 model [7,8], divided into three sorption mechanisms, depending on the relative humidity. The
36 first part follows Langmuir's sorption, where water molecules attach on specific sites of
37 interactions. The second is described by Henry's sorption, where water uptake evolves linearly
38 with the relative humidity, and the final stage occurring at high relative humidity is the
39 clustering of water molecules in the remaining free spaces. Combining these three phenomena
40 leads to a sigmoidal relation between the relative humidity and the moisture content in the
41 flax fibres [6]. Interestingly, this phenomenon presents a hysteresis loop meaning that the
42 water content of flax is not the same at a given relative humidity depending on if it is in the
43 dynamic state of sorption or desorption [6]. Furthermore, this water uptake induces radial
44 swelling of the flax fibre, correlating linearly with the hygro-expansion coefficient, measured to
45 be $1.14 \epsilon/\Delta m$ by Le Duigou et al. [9].

46 The moisture uptake in a composite is mainly due to flax fibres' water sorption behaviour and

47 the presence of a fibre/matrix interface [10], even for a hydrophilic matrix (PHBV) [11]. The
48 sigmoidal sorption/desorption behaviour is also observed at the composite level [5]. For non-
49 woven flax/PP composite (50wt%), Gager et al. [5] report a moisture content of 2.6% at 50%
50 RH and 8% at 98% RH. The volume fraction of fibres impacts the moisture sorption of the
51 composites [12]. However, the classical rule of mixture cannot predict the moisture uptake of
52 the composites at high relative humidity. It appears coherent with experimental values at 75%
53 RH but overestimates them at 98% RH [12]. This deviation at high relative humidity is
54 explained by El Hachem et al. [12] by the containment effect of the matrix on the flax fibres,
55 limiting their moisture uptake potential. Indeed, flax swelling is observed at the composite
56 scale at a lower amplitude, as the matrix constrains fibre displacement [13].

57 This moisture uptake induces a decrease in stiffness and ultimate strength of the composite
58 [5,10,14]. The origin of this decrease is still discussed in the literature [15–17], and several
59 phenomena appear to be involved. It is reported for thermoset flax composites that cracks
60 appear in the matrix [14,17], inducing debonding at the flax/matrix interface [14,15,17] and
61 flax fibre damage [15,17,18]. All these phenomena are reported to be linked with the swelling
62 of flax fibres inside the composite. However, there is no consensus because the phenomena
63 observed varies depending on the ageing conditions, the experimental methods, and the flax
64 composite mesostructure such as porosity, fibre volume fraction, fibre individualisation and
65 fibre orientation. As an example, Chilali et al. [19] observed that the presence of sealed edges,
66 inducing a preferential water diffusion direction, impacts the sorption kinetics and the ageing
67 behaviour. Indeed, they suggest several damage mechanisms depending on the type of
68 diffusion.

69 This paper focuses on the hygroscopic ageing of flax/PLA non-woven composite through its
70 mesostructure and mechanical property evolution. Several hygroscopic conditions are

71 investigated (50% RH / 75% RH / 98% RH) as well as immersion ageing. The sorption kinetics
72 are followed through weight monitoring, and the residual composite mechanical properties
73 are measured. The mechanical properties of flax cell walls and matrix after ageing are also
74 investigated at microscale thanks to AFM Peakforce measurements in mechanical mode (AFM-
75 PF-QNM). Finally, the structure of the composite is examined through density measurement
76 and SEM observation.

77 **2 Materials and methods**

78 2.1 Materials

79 2.1.1 Raw materials

80 An industrial non-woven flax/PLA preform of 350 g/m² with a flax weight fraction of 40%, was
81 manufactured on a needle-punching industrial line (Ecotechnilin, Yvetot, France). The non-
82 woven has a preferred fibre direction. Indeed, the machine direction has slightly more
83 oriented fibres in these industrial non-wovens [20]. The raw materials used are scutched flax
84 tows and INGEO™ PLA fibres. Thanks to the needle-punching line, flax and PLA fibres are
85 commingled together, leading to the non-woven preform.

86 2.1.2 Composite manufacturing

87 Composite manufacturing is done through an optimised thermo-compression cycle of eight
88 minutes using a hydraulic press LabTech Scientific 50T (Labtech, Samutprakarn, Thailand)
89 press, set at 200°C. This processing cycle is presented in a previous study [21]. Eight plies of
90 200x200 mm are stacked together and then dried at 40°C under vacuum for 24h. During the
91 lay-up step, the specific orientation of the preforms is maintained. Therefore, thermo-
92 compression leads to a composite with a preferential orientation of fibres, identical to the
93 preform.

94 Next, dog-bone samples, according to the ISO 527-4 standard, are cut from the 2 mm thick

95 composite plates using a milling machine. The centre part of the dog bone has a width of 8
 96 mm, a length of 45 mm and a thickness of 2 mm. The edges of the samples were not sealed to
 97 be consistent with industrial applications. Thus, after cutting, flax fibres appear accessible in
 98 the edges. Furthermore, the milling process damages the edges by initiating defects, which are
 99 likely to influence the ageing response of the composite.

100 2.2 Methods

101 2.2.1 Ageing protocol

102 Once manufactured, samples are stored in a controlled humidity chamber at 50% RH. Once the
 103 weight is stabilised, five samples are dried for 48h in an oven at 105°C and weighted. The initial
 104 moisture content of samples, obtained through the mean of the five values, is 2.6 ± 0.1 %. The
 105 remaining samples are separated into five batches. One stays in the 50% RH chamber until
 106 the end of the experiments and is called the 50_RH_ref batch. Others undergo humidity ageing
 107 (also called vapour ageing) at 50%, 75% or 98% RH thanks to humidity chambers
 108 (corresponding batches are labelled 50_RH/ 75_RH/ 98_RH) or immersion ageing in distilled
 109 water (corresponding batch is called Immersion). Ageing is conducted over a period of six
 110 weeks. The humidity in the chambers is controlled thanks to saturated salt solutions. The salt
 111 used and the exact relative humidity condition, controlled using testo 174H captors (Testo Inc.,
 112 West Chester, USA), are presented in Table 1.

113

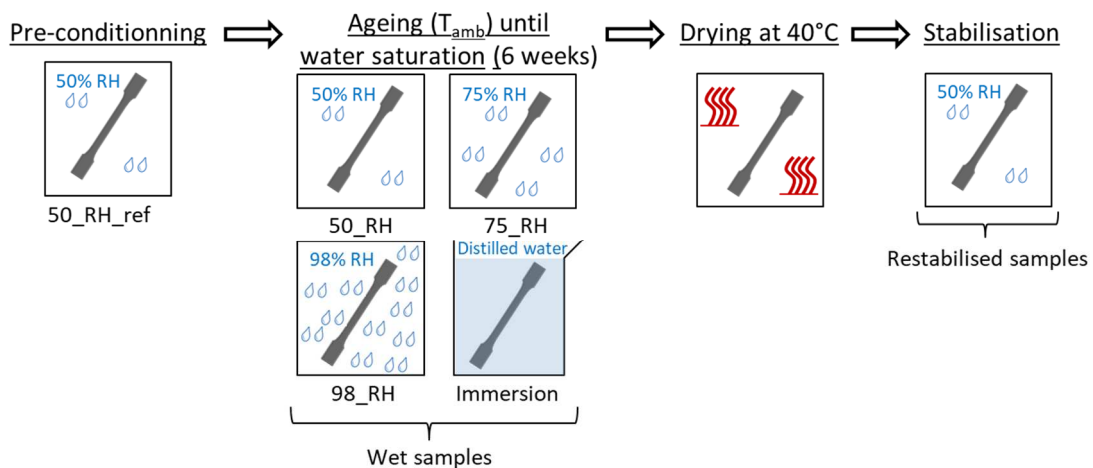
114 **Table 1.** Salt used for conditioning the chambers and the exact relative humidity condition
 115 induced by them.

	Temp. [°C]	50% RH	75% RH	98% RH
Mean value [%]	23.3 ± 2.2	55.7 ± 2.9	77.2 ± 1.9	99.7 ± 0.8
Salt used	/	$\text{Mg}(\text{NO}_3)_2$	NaCl	K_2SO_4

116

117 Five samples of each batch are regularly weighted to obtain the weight evolution. After six
118 weeks, once their weight stabilises, the 50_RH / 75_RH / 98_RH / Immersion samples are dried
119 at 40°C until stabilisation. This drying step allows avoiding the hysteresis consideration of flax
120 fibre sorption [6]. Finally, all samples are stabilised again at 50% RH. This ageing protocol is
121 summarized in Figure 1. The difference between the 50_RH_ref and the 50_RH batches
122 remains in the drying and restabilisation step, which are not applied to the 50_RH_ref
123 samples. All the ageing protocol is done at room temperature. In the following discussions,
124 wet samples (or wet state) will refer to the samples in saturated state during ageing. The
125 restabilised samples (or restabilised state) will refer to the samples that have undergone
126 ageing, drying and restabilisation at 50% RH.

127



128

129 **Figure 1.** Schematic representation of the ageing protocol applied to a flax/PLA non-woven
130 composite with a fibre volume fraction of 36%.

131

132 2.2.2 Water content

133 As described before, samples are regularly weighted using a Fisherbrand™ (Fisher Scientific
134 SAS, Illkirch Cedex, France) scientific high precision scale having a precision of 10^{-4} g. The
135 sampling depends on the stage of composite sorption, being narrow at the beginning of the
136 sorption phenomenon. The moisture content at a given time ($M_c(t)$) is calculated from the
137 weight evolution using equation (1).

$$M_c(t) = \frac{W(t) - W_{dry}}{W_{dry}} \quad (\text{Equ.1})$$

138 Where $W(t)$ is the sample weight at time t and W_{dry} is its dry weight. The dry weight of each
139 sample is calculated equal to 97.4% of the initial mass of the samples as the initial moisture
140 content was measured to be 2.6%. It avoids the drying step for samples before ageing, as it
141 impacts the materials [22].

142 The sorption kinetics of the samples during ageing is discussed using Fick's law [11], equation
143 (2), where D_{diff} is the diffusion coefficient, and h is the sample thickness. The initial moisture
144 content and the moisture content at saturation are $M_{c,init}$ and M_{∞} , respectively. They are
145 extracted from the experimental data for each ageing condition.

$$M_c(t) = (M_{\infty} - M_{c,init}) \cdot \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp \frac{-\pi^2 \cdot (2n+1)^2 \cdot D_{diff} \cdot t}{h^2} \right) + M_{c,init} \quad (\text{Equ.2})$$

146 The diffusion coefficient (D_{diff}) is calculated for all experimental points in the linear part of
147 the experimental curves ($M_c(t) < 0.5M_{\infty}$) using equation (3). The mean diffusion coefficient is
148 used to implement Fick's law, equation (2).

$$D_{diff} = \pi \cdot \frac{h^2}{16 \cdot t} \cdot \left(\frac{M_c(t) - M_{c,init}}{M_{\infty}} \right) \quad (\text{Equ.3})$$

149 2.2.3 Mechanical characterisation through tensile tests

150 A universal Instron (Instron, Norwood, Massachusetts, USA) tensile machine is used with a
151 10kN load cell. The tensile test is based on the ISO 527-4 standard, using a cross-head speed of
152 1 mm/min. The elongation of the samples is measured with an Instron extensometer having a
153 gauge length of 25 mm. The stiffness is calculated between 0.02% and 0.1%. At least nine
154 samples are tested, and the mean value is extracted. Standard deviations are used as errors.
155 The tensile tests are only done on restabilised samples.

156 2.2.4 Density measurement

157 The density was obtained through a hydrostatic balance using ethanol as immersion liquid,
158 leading to the density of the composites. Samples for density measurement are cut from the
159 central part of the dog bone samples (2 x 8 x 45 mm) thank to a circular saw as it is the part
160 loaded in the measurement of mechanical properties. This extraction is done on restabilised
161 samples. Density results are given as mean values of at least five samples.

162 Thanks to the apparent density of the composite (ρ_c), the volume fraction of porosity (V_p) of
163 each batch is estimated using equation (4). The weight fraction of fibres W_f are 40% here. The
164 density of PLA (ρ_{PLA}) and flax (ρ_{flax}) are taken respectively as 1.24 and 1.5 gcm⁻³ [1]. This flax
165 density value was measured at room temperature and 50RH. The flax fibres were extracted
166 from unidirectional preforms made for composite applications.

$$V_p = 1 - \left(\frac{1 - W_f}{\rho_{PLA}} + \frac{W_f}{\rho_{flax}} \right) \cdot \rho_c \quad (\text{Equ.4})$$

167 The assumption of an unchanged fibre density during ageing is taken. The porosity induced by
168 manufacturing will be considered as matrix pores, and the porosity due to ageing will be
169 referred to as defects, or specifically matrix micro-cracks or interface decohesion zones.

170 2.2.5 SEM

171 Samples are observed thanks to a JEOL (Jeol, Tokyo, Japan) SEM (JSM-IT500HRSEM) at an
172 acceleration voltage of 3 kV. For transverse section observation, sample preparation consists
173 of embedding them into an epoxy matrix, polishing and gold-coating thanks to a sputter coater
174 (Edward Scancoat6). For flax/PLA interface observation, samples underwent a brittle fracture
175 under nitrogen before being sputter coated. Any surface degradation was observed, skipping
176 the embedding step as polishing is not desirable.

177 2.2.6 Biochemical analysis

178 Biochemical analysis is done on the immersion leachate to quantify the polysaccharides
179 released by the composite. Before undergoing biochemical analysis, the leachate was
180 centrifuged (3min at 800 rpm). Three samples of supernatants (500 μ L) were collected. First, 2-
181 déoxy-D-ribose is added before samples are hydrolysed (2h at 120°C). Then, the uronic acid
182 (UA) concentration was determined by an automated m-hydroxybiphenyl method [23].
183 Additionally, the neutral sugar concentration was analysed as their alditol acetate derivatives
184 [24] by GC gas chromatography (PerkinElmer, Clarus 580, Shelton, CT, USA) equipped with a
185 DB 225 capillary column (J&W Scientific, Folsom, CA, USA) at 205°C, with H₂ as the carrier gas.

186 2.2.7 AFM

187 A Multimode 8 AFM instrument (Bruker, Billerica, Massachusetts, USA) was used in PF-QNM
188 imaging mode. This mode is based on the recording of force-distance curves at a high rate (2
189 kHz) for a limited maximum load (200 nN here), and thus limited indentation depth (of the
190 order of a nanometre here), while the tip scans the surface of the sample thus allowing to
191 make topography maps. The indentation modulus is obtained from the unloading part of the
192 force-distance curve using an appropriate contact model. We used a DMT model here, which
193 corresponds to the Hertz contact model (small indentation depth compared to the tip apex

194 radius) modified to take into account the adhesion force (mainly due to water capillarity in our
195 case) between the tip and the sample surface [25]. The indentation modulus obtained is
196 similar to that obtained by nanoindentation measurements but with the required resolution to
197 study mechanical gradients within and between cell wall layers [26]. RTESPA-525 (Bruker)
198 silicon probe with a spherical tip apex was used here. Its spring constant (between 136 and
199 177 N/m) was calibrated using the Sader method (<https://sadermethod.org/>), and the tip
200 radius adjusted between 20 and 80 nm on an aramid sample having a comparable indentation
201 modulus to flax fibre cell walls. Image resolution of 384×384 pixels was achieved, and a peak
202 force amplitude between 50 and 100 nm was set for indentation modulus measurements. This
203 variety of amplitude depends on the roughness of the region investigated.

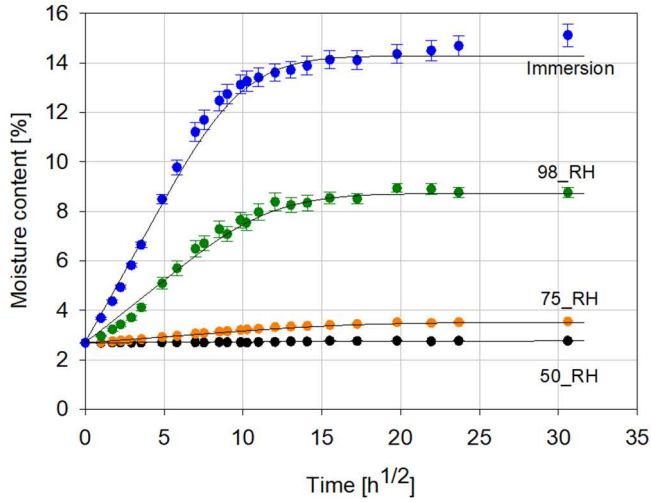
204 Only the reference, the 98_RH and the immersion batches were investigated in regards to the
205 mechanical properties, the density results and the SEM observation. AFM samples of 2 mm³
206 are extracted from the middle of the centre part of the dog bones. It avoids edge influence.
207 They are embedded into agar resin (Agar Scientific, Stansted, UK) and cut thanks to an
208 ultramicrotome (Leica Ultracut R). Four images, including of flax fibres and PLA, were used for
209 each reference to obtain the mean indentation modulus of the reinforcement and the matrix.
210 The samples were analysed in a perpendicular plane of the direction with the predominant
211 orientation of fibres (machine direction of the preform). For flax fibres, which are highly
212 anisotropic, elliptical fibre cross-sections were not selected to avoid the risk of fibre
213 misorientation.

214 **3 Results and discussion**

215 3.1 Moisture content evolution

216 The moisture content at saturation of the composite stored at 50% RH is 2.6 ± 0.1 %. As
217 expected for flax composite, the moisture sorption at room temperature follows Fick's law

218 [18,27] (pseudo-Fickian behaviour for immersion), as presented in Figure 1. The parameters
 219 used for Fick's law are extracted from the experimental curves and are given in Table 2.



220

221 **Figure 2.** Moisture content evolution of a non-woven flax/PLA composite (Wf=40%) under
 222 several ageing conditions. The dark lines correspond to Fick's laws extrapolation. The
 223 experimental curves are used to obtain the diffusion coefficients and the moisture content at
 224 saturation.

225

226 **Table 2.** Parameters used to calculate Fick's law, depending on the ageing condition.

	50_RH	75_RH	98_RH	Immersion
$D_{diff} \cdot 10^{-6}$ [mm ² /s]	0.56	0.72	1.53	2.15
M_{∞} [%]	2.77	3.52	8.72	14.275

227

228 The moisture contents at saturation after each ageing step can be observed in Figure 2. No
 229 clear saturation is reached in the case of immersion. Before discussing the results, note that
 230 the stabilised moisture content of flax fibres is measured by Hill et al. [6] to be 18% at 95% RH.

231 The water uptake of virgin PLA under immersion at 25°C was measured by Deroiné et al. [28]
232 to be $0.59 \pm 0.03\%$. This low moisture sorption is explained by the high glass transition
233 temperature of PLA (60°C) [29]. As our flax/PLA composite uptakes $15.12 \pm 0.46\%$ after 38 days
234 ($30 \text{ h}^{1/2}$) of moisture under immersion at room temperature, it can be concluded that flax
235 fibres and/or composite microstructure (matrix pores/defects induced by ageing) are
236 principally responsible for moisture uptake. As a consequence, PLA moisture sorption is not
237 considered in any further detail in this work.

238 Besides a slightly higher moisture content at saturation, the moisture uptake behaviour of
239 50_RH and 75_RH are similar, as observed in Table 3. The moisture uptake appears to be more
240 critical for the 98_RH and immersion samples. The sorption behaviour of flax fibres can explain
241 this. It has been reported by Gouanvé et al. [8] that the mechanism of sorption of flax fibres
242 evolves after a relative humidity close to 80%. Water molecules are absorbed on specific
243 interaction sites or randomly adsorbed by flax, and thereafter, the water molecules cluster in
244 the interstice and porosity of flax fibres, such as lumen or cell wall micropores [8]. Such
245 micropores have been observed by Melelli et al. [30] on flax kink bands, where the flax
246 structure is more heterogeneous and presents significant cavities compared to intact cell walls.
247 This phenomenon is also observed for composites [5], where the matrix pores and the
248 interfaces (matrix/fibres or fibres/fibres) are other places for potential water clustering.

249 Regarding the drying and restabilisation step, all batches return to a moisture content slightly
250 higher than their initial moisture content of $2.6 \pm 0.1\%$, except the immersion one.

251 Interestingly, the 98_RH samples lose more water during the drying step, meaning it has
252 potentially a higher free/bonded water ratio than the 75_RH and 50_RH batches.

253

254 **Table 3.** Moisture content in non-woven flax/PLA composite (Wf=40%) at each ageing step for
 255 all the ageing conditions. Index a, b, c highlight statistical groups determine by comparative t-
 256 tests (p-value > 0.05 in a same group).

		50_RH	75_RH	98_RH	Immersion
Water content at saturation [-]	ageing	2.77 ± 0.01 %	3.55 ± 0.04 %	8.76 ± 0.21 %	15.12 ± 0.46 %
	drying	1.46 ± 0.04 %	1.59 ± 0.05 %	1.17 ± 0.11 %	0.24 ± 0.07 %
	restabilisation	2.72 ± 0.02 % ^a	2.88 ± 0.03 % ^b	2.86 ± 0.09 % ^b	1.94 ± 0.05 % ^c

257

258 The difference between mean water content at restabilisation is checked with t-tests. It
 259 appears that statistically, only 75_RH and 98_RH have an identical mean value. In the case of
 260 immersion, the moisture content after ageing and restabilisation is lower than the initial
 261 moisture content.

262 3.2 Leaching phenomenon

263 The difference of water uptake for immersed samples is mainly due to a decrease in the
 264 sample weight, distorting the moisture content value. Considering that the moisture content
 265 of the immersed samples after stabilisation should be similar to other ageing conditions (ca
 266 2.7-2.9%), this weight loss equals ca 0.8-1.0%.

267 This decrease can be induced by a leaching phenomenon already reported in the literature
 268 [31]. It is confirmed by a change in the colour of the leachate during immersion ageing. Some
 269 polysaccharides of the flax are dissolved and released in the surrounding water. The total mass
 270 of samples immersed is 40 g in one litre of distilled water. Thus, considering leaching as the
 271 only origin of the mass evolution (taken equals to 0.9%), the weight loss should induce a sugar
 272 concentration of 360 µg/mL. However, thanks to biochemical analysis of the leachate, the total
 273 sugar concentration only equals 25.7 µg/mL. This concentration includes 18.9 µg/mL of neutral
 274 sugars and 6.8 µg/mL of uronic acids. The detailed biochemical analysis of the leachate is given

275 in Table 4.

276 **Table 4.** Biochemical analysis of the leachate obtained after flax/PLA non-woven composite
277 immersion ageing. Rha = Rhamnose, Fuc= Fucose, Ara= Arabinose, Xyl= Xylose, Man=Mannose,
278 Gal=Galactose, Glc=Glucose; U.A. = Uronic acids. N/A refers to undetected sugars.

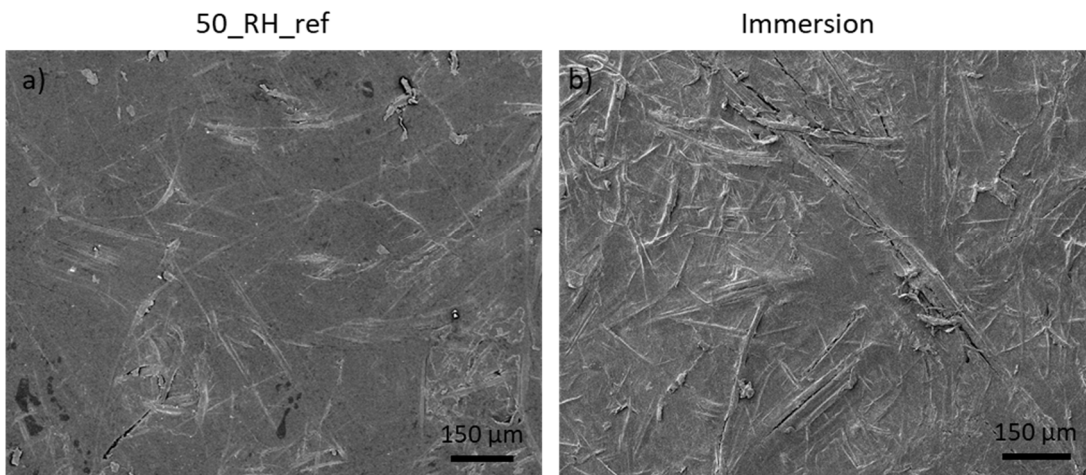
	Rha	Fuc	Ara	Xyl	Man	Gal	Glc	U.A.
Concentration [$\mu\text{g}/\text{mL}$]	4.6 ± 1.6	N/A	N/A	N/A	N/A	5.2 ± 1.7	9.1 ± 4.4	6.8 ± 0.3

279

280 As dissolved polysaccharides alone cannot explain all the weight loss, PLA degradation due to
281 fibre swelling at the surface is assumed to have a role [32]. The surface degradation is
282 observed through SEM in Figure 3. Interestingly, the composite manufacturing process
283 exposes flax fibres on the surface (face and edge) of unaged composites, see Figure 3. These
284 fibres are a preferential path for water molecules, influencing the sorption kinetics observed in
285 Figure 2.

286 3.3 Surface degradation

287 Additionally, an increase in degradation is observed qualitatively from the reference to
288 immersion samples (see Figures 3.a, 3.b). Indeed, the surface roughness increases, highlighting
289 the contribution of flax fibres swelling due to surface degradation. Additionally, cracks are
290 reported close to the fibres, confirming PLA damaged by flax swelling.

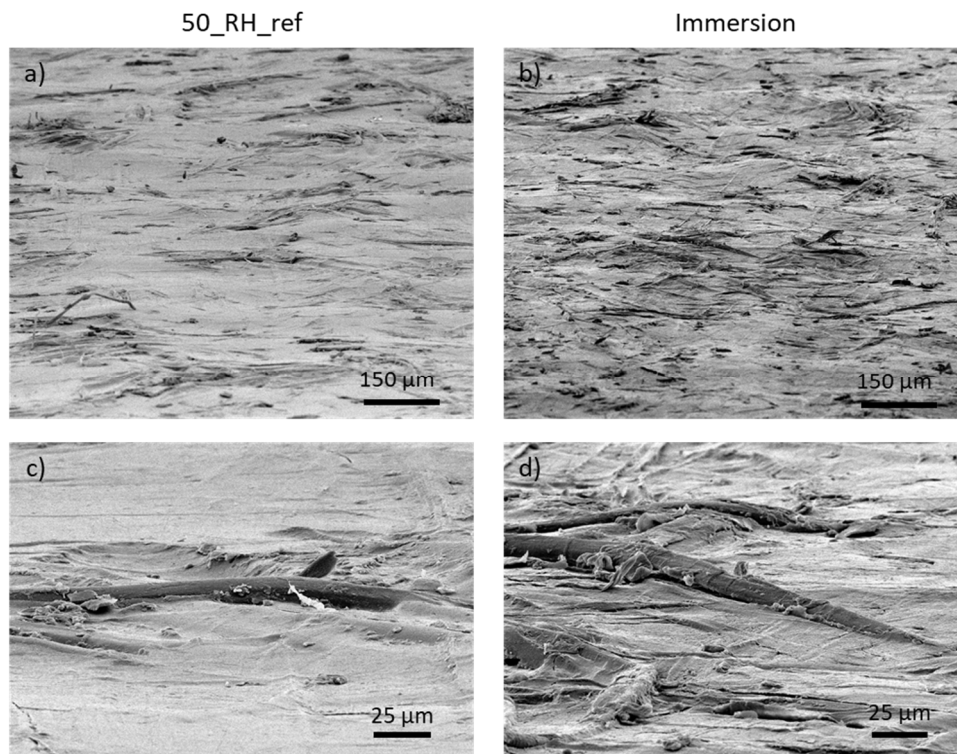


291

292 **Figure 3.** Perpendicular SEM observation of the surface degradation for 50_RH_ref (a) and
 293 immersion (b) samples, focussing on the role of flax fibre swelling.

294

295 The surface degradation is more evident through tilted observation of the surfaces,
 296 highlighting the presence of flax fibres exposed at the surface, responsible for the higher
 297 roughness of the immersed samples. At a lower scale, as seen in Figures 4.c, 4.d, the reference
 298 sample presents few exposed fibres at the composite face/edge, which are still surrounded by
 299 PLA (see Figure 4.c). This is due to the manufacturing process which does not include the
 300 presence of extra PLA layer on the edges. The number of exposed flax fibres in the immersion
 301 samples appear higher, and they are locally detached from the PLA as gaps are present (see
 302 Figure 4.d). They can even be uncoupled from PLA in some cases. It highlights the surface
 303 degradation and liberation of PLA micro-particles, explaining also the weight loss.



304

305 **Figure 4.** Tilt SEM observation of surface degradation for 50_RH_ref (a & c) and immersion (b
 306 & d) samples. a) & b) are global views of the surface aspect, c) & d) focus on the aspect of
 307 exposed flax fibres.

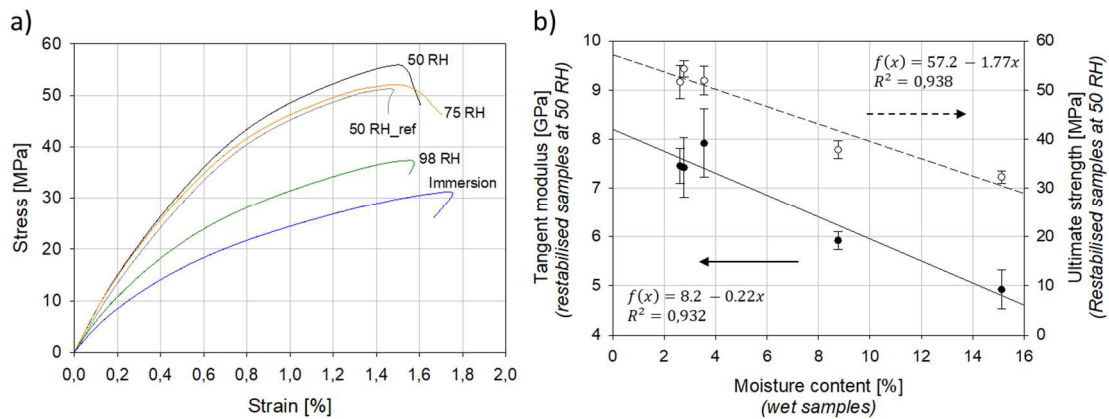
308

309 3.4 Tensile properties

310 By testing the mechanical properties of restabilised samples, their irreversible alteration
 311 induced by water sorption is assessed. The tensile behaviours are represented in Figure 4.a
 312 and the mechanical properties are summarised in Table 5. The 50_RH and 75_RH samples do
 313 not present significant differences with the 50_RH_ref batch, as they present similar tensile
 314 behaviour (Figure 4.a). That means the drying step (40°C until stabilisation) does not impact
 315 the reference composite, and ageing at 75% RH does not induce irreversible change in the
 316 flax/PLA composite. However, a decrease in stiffness and strength are observed for the 98_RH
 317 and immersion batches (Figure 4. b)), with a stiffness decrease of 20.3% for 98_RH and 33.4%

318 for immersion. It agrees with the moisture uptake of wet samples, which is much higher for
 319 98_RH and immersion than for the three undamaged batches.

320



321

322 **Figure 5.** a) Tensile behaviour of flax/PLA composite (Wf=40%) after ageing under several
 323 conditions, drying and restabilisation at 50% RH (restabilised state), b) Influence of moisture
 324 content at saturation (wet state) on the tensile properties of the flax/PLA composite after
 325 ageing, drying and restabilisation at 50% RH (restabilised state).

326

327 Interestingly, the decrease in mechanical properties of restabilised samples appears to directly
 328 depend on the moisture content in the wet state (mainly due to the damage created by the
 329 water uptake), as reported in Figure 4.b. These trends approach a linear correlation, with a
 330 decrease factor of 1.77 MPa/% for strength and 0.22GPa/% for the modulus. This linearity
 331 might be due to the progressive increase of defects inside the composite induced by the
 332 moisture content. These linear decreases were also observed for an injected PLA/flax
 333 immersed in seawater [33], and an increase in defects in the composite was assumed.

334 Interestingly, the strain of the composite remains around 1.6 – 1.8% (Table 5) even for 98_RH

335 and immersed samples, which is in the same range as the failure strain of the flax fibre, $2.1 \pm$
336 0.5% [34]. Thus, composite behaviour is still fibre dominated even after ageing. The decrease
337 appears similar to fibre volume reduction, indicated a loss of interface and therefore a loss of
338 stress transfer ability from fibre.

339 It highlights the existence of a critical relative humidity between 75% RH and 98% RH (see
340 Figure 5), where flax composites present irreversible damage. The moisture content of flax
341 composites is described by a sigmoid [5,8] as the water starts to sorb at specific sites of
342 interaction, then in non-specific sites before clustering micro-pores become present in flax
343 fibres (lumen or kink-bands). A relative humidity close to 80% RH induces a drastic increase in
344 water content in flax fibres and therefore inside the composite. This relative humidity is
345 probably the limit to not reach to avoid irreversible damage in the composite, but its exact
346 value may depend on the matrix mechanical behaviour. This critical relative humidity can be
347 observed using more relative humidity ageing between 75% RH and 98% RH. Additionally, it
348 will help to identify more precisely the nature of the trend. The dry states (lower than 2.6%)
349 can result in different damage mechanisms, leading to another modification of mechanical
350 properties not highlighted by the presented trend Figure 5.).

351 Interestingly, the water molecules change from the gas phase to the liquid phase when the
352 saturation pressure of water is reached. It occurs at the physical limits of relative humidity of
353 99.9%. For the flax/PLA non-woven composite, the moisture content jumps from 9% to 15% by
354 switching from 98% RH to immersion ageing. Therefore, the moisture content range of 9% to
355 15% is not reachable. However, the impact of immersion on tensile properties appears to align
356 with vapour ageing impact, as observed in Figure 4.b. The shortcut of immersion as
357 accelerated vapour ageing should be used carefully as the water molecules are not in the same
358 state. Thus, ageing mechanisms could be different between vapour and immersion conditions.

359 The latter is expected to be harsher.

360

361 **Table 5.** Tensile properties of flax/PLA composite (Wf=40%) after ageing under several
362 conditions, drying and reconditioning at 50% RH (restabilised state). The pure PLA values are
363 extracted from a previous study [35] and measured on unaged INGEO™ PLA samples.

	50_RH_ref	50_RH	75_RH	98_RH	Immersion	Pure PLA (unaged)
Tangent modulus [GPa]	7.4 ± 0.3	7.4 ± 0.6	7.9 ± 0.7	5.9 ± 0.2	4.9 ± 0.4	3.4 ± 0.1
Ultimate strength [MPa]	51.6 ± 3.3	54.3 ± 1.6	51.9 ± 3.0	37.8 ± 1.8	32.3 ± 1.3	37.6 ± 0.8
Strain at failure [%]	1.5 ± 0.2	1.5 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	1.8 ± 0.3	2.6 ± 0.4

364

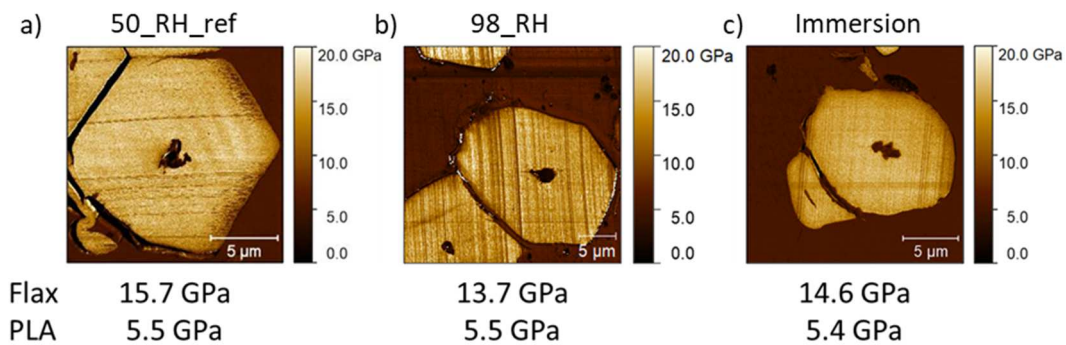
365 The amount of water uptake is the origin of composite degradation. Two hypotheses have to
366 be verified. First, contact with water can decrease the mechanical properties of the flax fibres
367 and the matrix. Indeed, the mechanical properties of elementary flax fibres depend on the
368 surrounding relative humidity [23], with a decrease in strength of ca. 15% and an increase of
369 ca. 25% of strain switching from 46% to 85% RH. Second, the composite structure can
370 deteriorate through decohesion of the flax and matrix or by creating matrix micro-cracks
371 induced by flax swelling and shrinkage. The combination of both phenomena will induce
372 connected defects. For example, the decohesion at the interface creates a gap between the
373 flax and the matrix. These gaps could be linked together by the micro-cracks present in the
374 matrix. The reduction in composite density can be used to quantify the volume of these
375 structural defects.

376 3.5 Evolution of flax cell wall and matrix stiffness in the composite

377 As expressed previously, one hypothesis is that ageing impacts the properties of flax and/or

378 the matrix. Therefore, their mechanical properties are assessed through AFM measurement on
379 the reference and the two impacted batches. Figure 5 presents the indentation modulus
380 mapping used for one measurement, whereas Table 6 presents the averaged indentation
381 modulus for flax and PLA matrix.

382



383

384 **Figure 6.** AFM indentation stiffness map for one fibre of flax/PLA composite after a) no ageing
385 (50_RH_ref), b) moisture ageing at 98% RH, c) immersion ageing with distilled water.

386

387 The evolution of constituent mechanical properties is measured at microscale level.^{b,b} First,
388 the mechanical properties of PLA do not evolve during ageing, with a constant indentation
389 modulus value of ca. 5.5 GPa. Thus, there is no local recrystallisation of PLA. This is expected as
390 PLA's stiffness is relatively insensitive to immersion ageing at 25°C [28]. Indeed, Deroiné et al.
391 [28] reported, for virgin PLA aged six months in distilled water at 25°C, no decrease in
392 mechanical properties at the macro-scale and only a small chemical evolution with a decrease
393 of number-averaged molecular weight from 75,000 g/mol (unaged) to 66,300 g/mol.

394

395 **Table 6.** Impact of the ageing condition on the indentation stiffness of flax fibres cell walls and
 396 PLA in the composite. It is investigated at the micro-scale level through AFM-QNM
 397 measurements.

	50_RH_ref	98_RH	Immersion
Flax fibre indentation modulus [GPa]	15.3 ± 1.0	13.4 ± 1.8	13.9 ± 0.9
PLA indentation modulus [GPa]	5.5 ± 0.1	5.4 ± 0.3	5.4 ± 0.2

398

399 For the flax cell wall (the layer S2 of the secondary cell wall), a slight decrease appears
 400 between the reference and the impacted samples. The impacted samples (98_RH and
 401 immersion) are considered statistically identical, as a t-test gives a probability of similarity
 402 equals to 63%. However, due to the close value between the reference and the impacted
 403 samples, their standard deviation and the operator influence on the selection of the fibres, it
 404 can be concluded that flax cell walls present similar mechanical properties whatever the
 405 ageing condition used. Note that these values are slightly lower than the indentation modulus
 406 usually obtained in the literature using AFM, being between 17-22 GPa [36].

407 Interestingly, this stable indentation modulus does not agree with Le Duigou et al.'s [31]
 408 results from nanoindentation measurements on immersed unidirectional flax/PLA composite.
 409 Indeed, they observed a 40% decrease in nanoindentation modulus after four weeks,
 410 compared to a 10% decrease (without considering the standard deviation) after six weeks in
 411 this study. They explain the decrease of the mechanical properties by the solubilisation of
 412 uronic acids, playing a role in transferring loads in the second wall (S2) of the flax fibres [31].
 413 They observed a ratio of 2.5 between the uronic acids released and the neutral sugars. Thanks
 414 to the biochemical analysis, this ratio is calculated to be 0.36 in our leachate, supporting the
 415 unchanged mechanical properties of the flax fibres in the immersed samples.

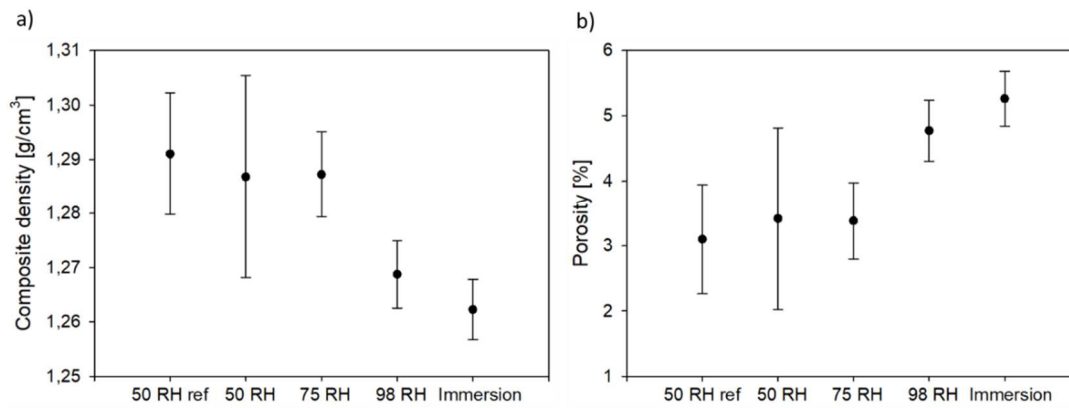
416 The difference between both experiments can be explained by the difference in flax preform
417 and manufacturing process. Le Duigou et al. [31] used a vacuum film stacking method to
418 manufacture flax/PLA unidirectional composite at a fibres weight fraction of 50%. This
419 manufacturing method leads to lower compaction than the thermo-compression due to low
420 pressure (≈ 0.95 bar) [37] and potentially modify flax fibres composition as it requires the
421 severe manufacturing condition of 180°C for 1 hour. In addition, the unidirectional orientation
422 of fibres leads to easier leaching than random orientation as fibre percolation in the composite
423 is higher for unidirectional. Finally, they used a magnetic stirrer, which may increase the
424 leaching phenomenon.

425 Thus, the evolution of flax cell walls and PLA's mechanical properties cannot explain the
426 decrease in stiffness observed at the composite scale. Therefore, the second hypothesis
427 relating to the evolution in composite microstructure (and density) should be investigated as it
428 may be responsible for mechanical property evolution.

429 3.6 Composite density evolution

430 The structural modification of the composite through ageing is potentially due to the
431 decohesion phenomenon or micro-cracks generation in the matrix, both being related to flax
432 fibre swelling. These mechanisms are directly linked to the composite density, as they modify
433 its structure by damaging the interfaces for the first one and creating matrix micro-cracks for
434 the second. The density measurement is presented in Figure 6.a). The porosity estimated is
435 presented in Figure 6.b), considering constant flax and matrix density. However, the
436 assumption of a constant flax density is debatable as the moisture uptake and swelling
437 phenomena can modify flax fibre structure (not observed here by AFM), where the leaching
438 phenomenon (immersed samples only) modifies its biochemical composition.

439



440

441 **Figure 7.** Evolution of the a) composite density and b) porosity of restabilised samples after
 442 different ageing conditions. The porosity is calculated assuming ageing does not modify the
 443 PLA nor flax density.

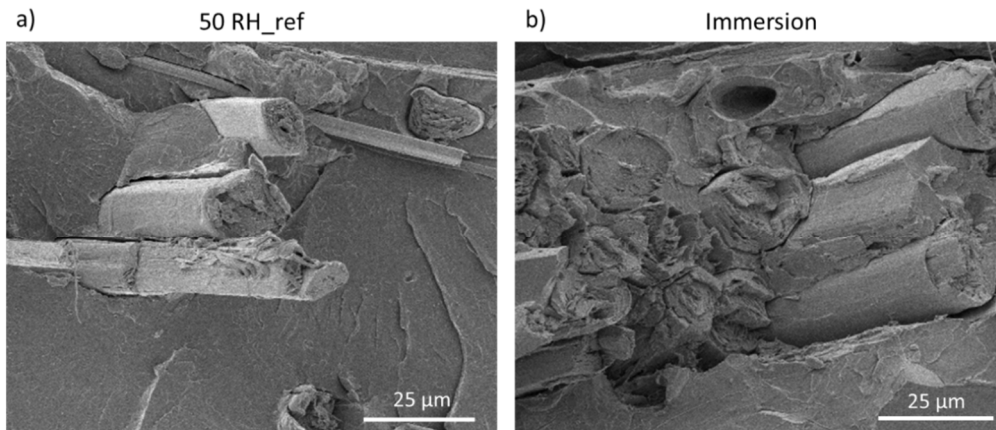
444

445 Nevertheless, the results fall in line with the mechanical properties evolution as the batches
 446 with low density present the lowest mechanical properties. Indeed, the porosity appears to be
 447 similar for the 50_RH_ref / 50_RH / 75_RH samples, increasing for 98_RH and Immersion
 448 samples (see Figure 6.b). Thus, ageing induces a modification of the inner structure of the
 449 composite. The origin of the structural modification needs further investigations to understand
 450 its influence on mechanical properties.

451 3.7 Interface decohesion

452 First, interface cohesion is checked through SEM observation on cryo-fractured samples. The
 453 obtained pictures are presented in Figure 7, presenting flax fibres in the normal direction of
 454 the fracture. If a damage is observed, a physical decohesion can be identified. The embedded
 455 length should not be considered here as these samples are observed before any tensile test.

456



Cryogenic failure for interface consideration

457

458 **Figure 8.** Interface observation by SEM of flax/PLA composite after a failure of the sample
 459 under cryogenic condition, a) observation of the reference and b) observation of the most
 460 damaged batches, being the immersion one. No decohesion is observed after an immersion
 461 ageing as damage is present.

462

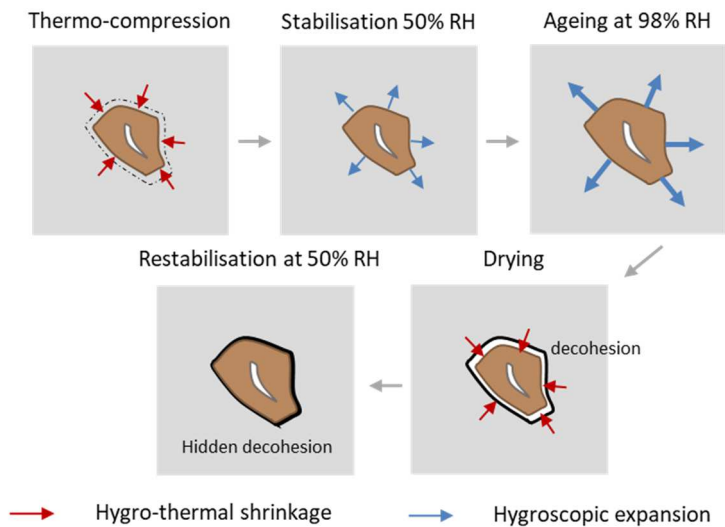
463 No significant decohesion at the flax/matrix or the flax/flax interfaces could be observed for
 464 reference or aged flax/PLA composite. There are two explanations, the first being that the
 465 interface is not damaged during ageing. One possibility is that fibres embedded within the PLA
 466 in the core of the sample are not subjected to water uptake nor swelling. However, this is
 467 unrealistic as the randomness of the preform induces interconnectivity of the flax fibres,
 468 percolating the open edges in contact with the environment.

469 The second more realistic explanation is a damaged interface, but this could not be observed.
 470 This damage can be due to chemical modification (leaching [31]) or hidden physical
 471 decohesion. During the thermo-compression process, the flax fibres have a low water content
 472 due to the high temperature. Thus, the flax fibres in the 50_RH_ref composite are already
 473 constrained. In addition to the hygroscopic stress, some residual stresses due to the thermal

474 history of the polymer and flax fibres are present. In addition, flax fibres act as nucleating
475 agents for the PLA, creating a transcrystalline layer around the fibres [38]; presence of water in
476 the interface region, can also induce local hydrolysis of the PLA matrix.

477 During the ageing, the flax fibres swell enough to overcome the matrix's yield point locally and
478 irreversibly deform the matrix. The drying step allows the flax fibres to retract as their water
479 content decrease, damaging the interface and releasing the internal residual stresses. Through
480 the restabilisation at 50% RH, the flax fibres are now free to swell, as the matrix did not
481 constrain it, and fill the gap previously created, hiding the decohesion. This phenomenon,
482 schematised in Figure 8, should not significantly modify the composite's density.

483



484

485 **Figure 9.** Schematic explanation of the formation of hidden decohesion due to the alternation
486 of shrinkage and expansion of flax fibres inside the composite. Inspired from [9].

487

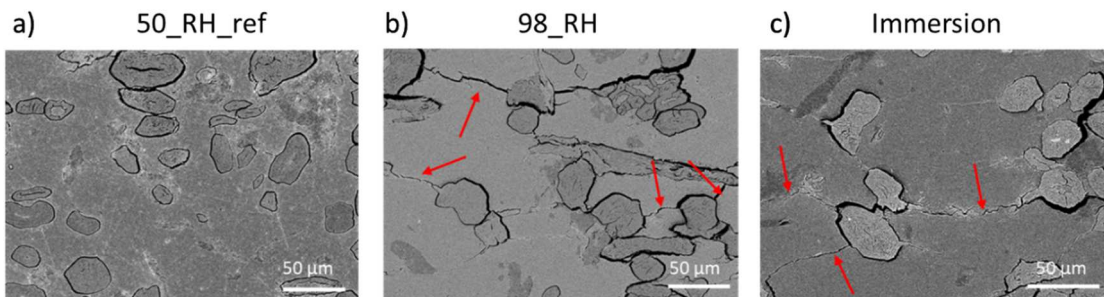
488 These potential damages at the interface can explain the decrease of the mechanical

489 properties of flax/PLA composite as the stress transfer between reinforcement and matrix.
490 Consequently, the reinforcement of flax fibres is less efficient, inducing a decrease in the
491 modulus and the ultimate strength of the composite without any increase in its ultimate strain.

492 3.8 Micro-cracks generation in the matrix

493 The swelling of the fibres during ageing has another consequence in the composite structure.
494 As observed in Figure 10, the aged composite presents micro-cracks inside the matrix, initiated
495 at the matrix/fibre interfaces. It suggests that the stresses applied locally by the swelled flax
496 fibres to the matrix are higher than the ultimate strength of the matrix. Therefore, the
497 presence of these micro-cracks decreases the mechanical properties of the composites.
498 Indeed, they act as defects, lowering the ultimate strength of the composite but also reducing
499 the apparent stiffness of the matrix.

500



501

502 **Figure 10.** SEM observation of flax/PLA composite after a) no ageing, b) ageing at 98% RH, c)
503 an immersion ageing. The observations are perpendicular to the direction of the sample. The
504 red arrows focus on the presence of matrix micro-cracks. The samples are polished.

505

506 As a first approach, the stiffness of a random non-woven composite (E_{NW}) is estimated thanks

507 to $E_{NW} = \frac{3}{8} \cdot E_{UD,lon gi} + \frac{5}{8} \cdot E_{UD,transv}$, where $E_{UD,lon gi}$ and $E_{UD,transv}$ are the longitudinal and
508 transversal stiffness of an equivalent unidirectional composite, respectively. The matrix
509 stiffness is the predominant parameter of the unidirectional transversal stiffness [39]. Thus,
510 the apparent matrix stiffness reduction due to micro-cracks directly decreases the transversal
511 stiffness of an equivalent unidirectional composite, and so does the non-woven composite
512 stiffness. In addition, a higher number of matrix micro-cracks might induce a lower apparent
513 matrix stiffness. It has been observed in Figure 4.b) that the tensile stiffness of a dry sample
514 depends on its moisture uptake in the wet state. As the number of micro-cracks should
515 increase with higher moisture uptake (due to higher flax swelling), the generation of matrix
516 micro-cracks is responsible for the decrease in the tensile stiffness of aged non-woven flax/PLA
517 composites. Thus, these matrix micro-cracks decrease the composite strength but also its
518 stiffness.

519 The fact that immersion ageing influences mechanical properties in line with vapour ageing
520 indicates that the main damage mechanisms are mutual to immersion and vapour ageing. It
521 can be the matrix micro-cracks or the hidden decohesion. The leaching phenomenon is
522 discarded as it is specific to immersed samples.

523 Note that these micro-cracks were observed on epoxy embedded and polished samples (with
524 water). The friction induced by polishing and water sorption at the surface could have been
525 responsible for these cracks. However, the reference samples did not present micro-cracks.
526 This gives confidence that these micro-cracks are created during ageing and not during the
527 sample preparation. A CT-scan analysis could avoid this damaging effect and confirm the
528 presence of the micro-cracks due to ageing. Such analysis could give additional information
529 such as the number of matrix micro-cracks, their connectivity and their geometry.

530 Furthermore, it can confirm the link between the number of matrix micro-cracks, the water

531 uptakes at the wet state and the tensile mechanical properties of the dry sample. However,
532 that needs a high resolution as such micro-cracks have a thickness of no more than a few
533 micrometres.

534 **4 Conclusion**

535 The evolution of the microstructure and the development of damage in a flax non-woven
536 composite subjected to water ageing (at 50% RH / 75% RH / 98% RH / immersion) was
537 investigated. The ageing conditions selected aimed to understand the first degradation step of
538 a flax/PLA non-woven composite. The ageing process was monitored by following the
539 composite's moisture content over six weeks and waiting for stabilisation in their weight
540 before being dried and restabilised at 50% RH. Interestingly, ageing at 75% RH did not impact
541 the mechanical properties nor the composite structure. On the other hand, samples aged at
542 98% RH and immersion for six weeks presented a significant uptake of water, decreasing the
543 strength and stiffness of the composites significantly.

544 A deeper analysis was conducted to better understand the ageing mechanisms. AFM
545 investigation in peak-force mode revealed that the flax fibre cell walls and the PLA appeared to
546 keep their initial indentation moduli. Thus, any composite softening was due to an evolution of
547 the composite's structure, confirmed by increased porosity for the two impacted batches. The
548 interface was observed thanks to the cryogenic failure of aged samples. No damage, including
549 signs of decohesion of matrix and fibre, was observed. This may probably be due to the
550 restabilisation step and the free swelling of fibres, closing ('hiding') debonding regions created
551 by ageing. It appeared that the porosity increase was due to the creation of transverse micro-
552 cracks induced by flax fibres swelling. That confirmed that the swelling of the fibres was
553 responsible for the structural evolution of the composite, hidden decohesion or matrix micro-
554 crack generation. These structural evolutions impacted the tensile properties of the flax/PLA

555 non-woven composite by decreasing its ultimate strength and stiffness.

556 On the one hand, investigating more relative humidity conditions in the range of 75RH and
557 98RH can help identify the presence of a critical relative humidity at which mechanical
558 properties and structure start to get significantly affected. Additionally, extending these
559 experimental investigations of flax/PLA non-woven composites with various fibres volume
560 fractions could lead to additional clues on the degradation mechanisms. Furthermore, using
561 cyclic tensile loading cycles could give information on the role of interfacial defects on the
562 composite mechanical behaviour. Finally, the effect of protecting the edges and the surface by
563 a thin PLA layer could be scientifically interesting as it is expected to reduce the sorption
564 kinetics, even if it is not realistic industrially speaking, unless for example using thermal
565 methods for machining (such as laser cutting).

566

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570

571 **References**

- 572 [1] M. Le Gall, P. Davies, N. Martin, C. Baley, Recommended flax fibre density values for
573 composite property predictions, *Industrial Crops and Products*. 114 (2018) 52–58.
574 <https://doi.org/10.1016/j.indcrop.2018.01.065>.
- 575 [2] A. Lefeuvre, A. Bourmaud, C. Morvan, C. Baley, Tensile properties of elementary fibres of
576 flax and glass: Analysis of reproducibility and scattering, *Materials Letters*. 130 (2014)
577 289–291. <https://doi.org/10.1016/j.matlet.2014.05.115>.
- 578 [3] J. Holbery, D. Houston, Natural-fiber-reinforced polymer composites in automotive
579 applications, *JOM*. 58 (2006) 80–86. <https://doi.org/10.1007/s11837-006-0234-2>.
- 580 [4] F. Bensadoun, B. Vanderfeesten, I. Verpoest, A.W. Van Vuure, K. Van Acker,

- 581 Environmental impact assessment of end of life options for flax-MAPP composites,
582 Industrial Crops and Products. 94 (2016) 327–341.
583 <https://doi.org/10.1016/j.indcrop.2016.09.006>.
- 584 [5] V. Gager, A. Le Duigou, A. Bourmaud, F. Pierre, K. Behloui, C. Baley, Understanding the
585 effect of moisture variation on the hygromechanical properties of porosity-controlled
586 nonwoven biocomposites, Polymer Testing. 78 (2019).
587 <https://doi.org/10.1016/j.polymertesting.2019.105944>.
- 588 [6] C.A.S. Hill, A. Norton, G. Newman, The water vapor sorption behavior of flax fibers—
589 Analysis using the parallel exponential kinetics model and determination of the
590 activation energies of sorption, Journal of Applied Polymer Science. 116 (2010) 2166–
591 2173. <https://doi.org/10.1002/app.31819>.
- 592 [7] S. Alix, E. Philippe, A. Bessadok, L. Lebrun, C. Morvan, S. Marais, Effect of chemical
593 treatments on water sorption and mechanical properties of flax fibres, Bioresource
594 Technology. 100 (2009) 4742–4749. <https://doi.org/10.1016/j.biortech.2009.04.067>.
- 595 [8] F. Gouanvé, S. Marais, A. Bessadok, D. Langevin, M. Métayer, Kinetics of water sorption
596 in flax and PET fibers, European Polymer Journal. 43 (2007) 586–598.
597 <https://doi.org/10.1016/j.eurpolymj.2006.10.023>.
- 598 [9] A. le Duigou, J. Merotte, A. Bourmaud, P. Davies, K. Belhouli, C. Baley, Hygroscopic
599 expansion: A key point to describe natural fibre/polymer matrix interface bond strength,
600 Composites Science and Technology. 151 (2017) 228–233.
601 <https://doi.org/10.1016/j.compscitech.2017.08.028>.
- 602 [10] A. Regazzi, S. Corn, P. Ienny, J.-C. Bénézet, A. Bergeret, Reversible and irreversible
603 changes in physical and mechanical properties of biocomposites during hydrothermal
604 aging, Industrial Crops and Products. 84 (2016) 358–365.
605 <https://doi.org/10.1016/j.indcrop.2016.01.052>.
- 606 [11] W.V. Srubar, C.W. Frank, S.L. Billington, Modeling the kinetics of water transport and
607 hydroexpansion in a lignocellulose-reinforced bacterial copolyester, Polymer. 53 (2012)
608 2152–2161. <https://doi.org/10.1016/j.polymer.2012.03.036>.
- 609 [12] Z. El Hachem, A. Céline, G. Challita, M.-J. Moya, S. Fréour, Hygroscopic multi-scale
610 behavior of polypropylene matrix reinforced with flax fibers, Industrial Crops and
611 Products. 140 (2019) 111634. <https://doi.org/10.1016/j.indcrop.2019.111634>.
- 612 [13] T. Joffre, E.L.G. Wernersson, A. Miettinen, C.L. Luengo Hendriks, E.K. Gamstedt, Swelling
613 of cellulose fibres in composite materials: Constraint effects of the surrounding matrix,
614 Composites Science and Technology. 74 (2013) 52–59.
615 <https://doi.org/10.1016/j.compscitech.2012.10.006>.
- 616 [14] M. Assarar, D. Scida, A. El Mahi, C. Poilâne, R. Ayad, Influence of water ageing on
617 mechanical properties and damage events of two reinforced composite materials: Flax–
618 fibres and glass–fibres, Materials & Design. 32 (2011) 788–795.
619 <https://doi.org/10.1016/j.matdes.2010.07.024>.
- 620 [15] G. Koolen, J. Soete, A.W. van Vuure, Interface modification and the influence on damage
621 development of flax fibre – Epoxy composites when subjected to hygroscopic cycling,
622 Materials Today: Proceedings. 31 (2020) S273–S279.
623 <https://doi.org/10.1016/j.matpr.2020.01.183>.

- 624 [16] T. Cadu, L. Van Schoors, O. Sicot, S. Moscardelli, L. Divet, S. Fontaine, Cyclic hygrothermal
625 ageing of flax fibers' bundles and unidirectional flax/epoxy composite. Are bio-based
626 reinforced composites so sensitive?, *Industrial Crops and Products*. 141 (2019) 111730.
627 <https://doi.org/10.1016/j.indcrop.2019.111730>.
- 628 [17] L. Van Schoors, T. Cadu, S. Moscardelli, L. Divet, S. Fontaine, O. Sicot, Why cyclic
629 hygrothermal ageing modifies the transverse mechanical properties of a unidirectional
630 epoxy-flax fibres composite?, *Industrial Crops and Products*. 164 (2021) 113341.
631 <https://doi.org/10.1016/j.indcrop.2021.113341>.
- 632 [18] A. Le Duigou, A. Bourmaud, P. Davies, C. Baley, Long term immersion in natural seawater
633 of Flax/PLA biocomposite, *Ocean Engineering*. 90 (2014) 140–148.
634 <https://doi.org/10.1016/j.oceaneng.2014.07.021>.
- 635 [19] A. Chilali, M. Assarar, W. Zouari, H. Kebir, R. Ayad, Effect of geometric dimensions and
636 fibre orientation on 3D moisture diffusion in flax fibre reinforced thermoplastic and
637 thermosetting composites, *Composites Part A: Applied Science and Manufacturing*. 95
638 (2017) 75–86. <https://doi.org/10.1016/j.compositesa.2016.12.020>.
- 639 [20] N. Martin, P. Davies, C. Baley, Evaluation of the potential of three non-woven flax fiber
640 reinforcements: Spunlaced, needlepunched and paper process mats, *Industrial Crops and
641 Products*. 83 (2016) 194–205. <https://doi.org/10.1016/j.indcrop.2015.10.008>.
- 642 [21] D. Pantaloni, D. Shah, C. Baley, A. Bourmaud, Monitoring of mechanical performances of
643 flax non-woven biocomposites during a home compost degradation, *Polymer
644 Degradation and Stability*. 177 (2020) 109166.
645 <https://doi.org/10.1016/j.polymdegradstab.2020.109166>.
- 646 [22] C. Baley, A. Le Duigou, A. Bourmaud, P. Davies, Influence of drying on the mechanical
647 behaviour of flax fibres and their unidirectional composites, *Composites Part A: Applied
648 Science and Manufacturing*. 43 (2012) 1226–1233.
649 <https://doi.org/10.1016/j.compositesa.2012.03.005>.
- 650 [23] A. Thuault, S. Eve, D. Blond, J. Bréard, M. Gomina, Effects of the hygrothermal
651 environment on the mechanical properties of flax fibres, *Journal of Composite Materials*.
652 48 (2014) 1699–1707. <https://doi.org/10.1177/0021998313490217>.
- 653 [24] A.B. Blakeney, P.J. Harris, R.J. Henry, B.A. Stone, A simple and rapid preparation of alditol
654 acetates for monosaccharide analysis, *Carbohydrate Research*. 113 (1983) 291–299.
655 [https://doi.org/10.1016/0008-6215\(83\)88244-5](https://doi.org/10.1016/0008-6215(83)88244-5).
- 656 [25] K.L. Johnson, J.A. Greenwood, An Adhesion Map for the Contact of Elastic Spheres,
657 *Journal of Colloid and Interface Science*. 192 (1997) 326–333.
658 <https://doi.org/10.1006/jcis.1997.4984>.
- 659 [26] A. Melelli, O. Arnould, J. Beaugrand, A. Bourmaud, The Middle Lamella of Plant Fibers
660 Used as Composite Reinforcement: Investigation by Atomic Force Microscopy,
661 *Molecules*. 25 (2020) 632. <https://doi.org/10.3390/molecules25030632>.
- 662 [27] W. Wang, M. Sain, P.A. Cooper, Study of moisture absorption in natural fiber plastic
663 composites, *Composites Science and Technology*. 66 (2006) 379–386.
664 <https://doi.org/10.1016/j.compscitech.2005.07.027>.
- 665 [28] M. Deroiné, A. Le Duigou, Y.-M. Corre, P.-Y. Le Gac, P. Davies, G. César, S. Bruzaud,
666 Accelerated ageing of polylactide in aqueous environments: Comparative study between

- 667 distilled water and seawater, *Polymer Degradation and Stability*. 108 (2014) 319–329.
 668 <https://doi.org/10.1016/j.polymdegradstab.2014.01.020>.
- 669 [29] G. Francois, B. Stéphane, D. Guillaume, F. Pascale, C. Emmanuelle, G. Jeff, G. Régis, G.
 670 Matthieu, H. Arnaud, L. Fabienne, others, Pollution des océans par les plastiques et les
 671 microplastiques Pollution of oceans by plastics and microplastics, *Techniques de*
 672 *l'Ingenieur*. (2020) BIO9300. <https://archimer.ifremer.fr/doc/00663/77471/>.
- 673 [30] A. Melelli, S. Durand, O. Arnould, E. Richely, S. Guessasma, F. Jamme, J. Beaugrand, A.
 674 Bourmaud, Extensive investigation of the ultrastructure of kink-bands in flax fibres,
 675 *Industrial Crops and Products*. 164 (2021) 113368.
 676 <https://doi.org/10.1016/j.indcrop.2021.113368>.
- 677 [31] A. Le Duigou, A. Bourmaud, C. Baley, In-situ evaluation of flax fibre degradation during
 678 water ageing, *Industrial Crops and Products*. 70 (2015) 204–210.
 679 <https://doi.org/10.1016/j.indcrop.2015.03.049>.
- 680 [32] T. Bayerl, M. Geith, A.A. Somashekar, D. Bhattacharyya, Influence of fibre architecture on
 681 the biodegradability of FLAX/PLA composites, *International Biodeterioration &*
 682 *Biodegradation*. 96 (2014) 18–25. <https://doi.org/10.1016/j.ibiod.2014.08.005>.
- 683 [33] A. Le Duigou, P. Davies, C. Baley, Seawater ageing of flax/poly(lactic acid) biocomposites,
 684 *Polymer Degradation and Stability*. 94 (2009) 1151–1162.
 685 <https://doi.org/10.1016/j.polymdegradstab.2009.03.025>.
- 686 [34] C. Baley, A. Bourmaud, Average tensile properties of French elementary flax fibers,
 687 *Materials Letters*. 122 (2014) 159–161. <https://doi.org/10.1016/j.matlet.2014.02.030>.
- 688 [35] D. Pantaloni, L. Ollier, D.U. Shah, C. Baley, E. Rondet, A. Bourmaud, Can we predict the
 689 microstructure of a non-woven flax/PLA composite through assessment of anisotropy in
 690 tensile properties?, *Composites Science and Technology*. 218 (2022) 109173.
 691 <https://doi.org/10.1016/j.compscitech.2021.109173>.
- 692 [36] O. Arnould, D. Siniscalco, A. Bourmaud, A. Le Duigou, C. Baley, Better insight into the
 693 nano-mechanical properties of flax fibre cell walls, *Industrial Crops and Products*. 97
 694 (2017) 224–228. <https://doi.org/10.1016/j.indcrop.2016.12.020>.
- 695 [37] V. Popineau, A. Céline, M. Le Gall, L. Martineau, C. Baley, A. Le Duigou, Vacuum-Bag-Only
 696 (VBO) Molding of Flax Fiber-reinforced Thermoplastic Composites for Naval Shipyards,
 697 *Appl Compos Mater*. (2021). <https://doi.org/10.1007/s10443-021-09890-2>.
- 698 [38] S. Garkhail, B. Wieland, J. George, N. Soykeabkaew, T. Peijs, Transcrystallisation in PP/flax
 699 composites and its effect on interfacial and mechanical properties, *J Mater Sci*. 44 (2009)
 700 510–519. <https://doi.org/10.1007/s10853-008-3089-9>.
- 701 [39] I.M. Daniel, O. Ishai, *Engineering mechanics of composite materials*, 2nd ed, Oxford
 702 University Press, New York, 2006.
 703

704 **Figures captions**

705 **Figure 1.** Schematic representation of the ageing protocol applied to a flax/PLA non-woven

706 composite with a fibre volume fraction of 36%.

707 **Figure 2.** Moisture content evolution of a non-woven flax/PLA composite ($W_f=40\%$) under
708 several ageing conditions. The dark lines correspond to Fick's laws extrapolation. The
709 experimental curves are used to obtain the diffusion coefficients and the moisture content at
710 saturation.

711 **Figure 3.** Perpendicular SEM observation of the surface degradation for 50_RH_ref (a) and
712 immersion (b) samples, focussing on the role of flax fibre swelling.

713 **Figure 4.** Tilt SEM observation of surface degradation for 50_RH_ref (a&c) and immersion
714 (b&d) samples. a) & b) are global views of the surface aspect, c) & d) focus on the aspect of
715 exposed flax fibres.

716 **Figure 5.** a) Tensile behaviour of flax/PLA composite ($W_f=40\%$) after ageing under several
717 conditions, drying and restabilisation at 50% RH (restabilised state), b) Influence of moisture
718 content at saturation (wet state) on the tensile properties of the flax/PLA composite after
719 ageing, drying and restabilisation at 50% RH (restabilised state).

720 **Figure 6.** AFM indentation stiffness map for one fibre of flax/PLA composite after a) no ageing
721 (50_RH_ref), b) moisture ageing at 98% RH, c) immersion ageing with distilled water.

722 **Figure 7.** Evolution of the a) composite density and b) porosity of restabilised samples after
723 different ageing conditions. The porosity is calculated assuming ageing does not modify the
724 PLA nor flax density.

725 **Figure 8.** Interface observation by SEM of flax/PLA composite after a failure of the sample
726 under cryogenic condition, a) observation of the reference and b) observation of the most
727 damaged batches, being the immersion one. No decohesion is observed after an immersion

728 ageing as damage is present.

729 **Figure 9.** Schematic explanation of the formation of hidden decohesion due to the alternation
730 of shrinkage and expansion of flax fibres inside the composite. Inspired from [9].

731 **Figure 10.** SEM observation of flax/PLA composite after a) no ageing, b) ageing at 98% RH, c)
732 an immersion ageing. The observations are perpendicular to the direction of the sample. The
733 red arrows focus on the presence of matrix micro-cracks. The samples are polished.

734

735 **Tables Captions**

736 **Table 1.** Salt used for conditioning the chambers and the exact relative humidity condition
737 induced by them.

738 **Table 2.** Parameters used to calculate Fick's law, depending on the ageing condition.

739 **Table 3.** Moisture content in non-woven flax/PLA composite (Wf=40%) at each ageing step for
740 all the ageing conditions.

741 **Table 4.** Biochemical analysis of the leachate obtained after flax/PLA non-woven composite
742 immersion ageing. Rha = Rhamnose, Fuc= Fucose, Ara= Arabinose, Xyl= Xylose, Man=Mannose,
743 Gal=Galactose, Glc=Glucose; U.A. = Uronic acids. N/A refers to undetected sugars.

744 **Table 5.** Tensile properties of flax/PLA composite (Wf=40%) after ageing under several
745 conditions, drying and reconditioning at 50% RH (restabilised state). The pure PLA values are
746 extracted from a previous study [35] and measured on unaged INGEO™ PLA samples.

747 **Table 6.** Impact of the ageing condition on the indentation stiffness of flax fibres cell walls and
748 PLA in the composite. It is investigated at the micro-scale level through AFM-QNM

749 measurements.