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1 **Property changes in plant fibres during the processing of bio-based composites**

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20

21 **Abstract**

22

23 Over the past decades, the use of plant fibre reinforced composites has increased significantly

24 due to their many attractive attributes such as high specific strength and modulus, wide

25 availability, low cost and high environmental credibility compared to their synthetic counterparts.

26 These attributes are especially attractive for lightweight applications in automotive, marine,

27 aerospace and sporting goods sectors. This growth is expected to continue in the future. To

28 improve the design and performance of bio-based composites, an improved understanding of

29 processing-structure-property relations in such bio-based composites is required, **the fibres**

30 being the key component of the composite to obtain performing properties. This is due to the  
31 sensitivity of the constituent plant fibres to mechanical stress (pressure), temperature, water  
32 and other parameters. The purpose of this review is to critically synthesise literature on the  
33 impact of composites processing steps on plant fibre cell wall structure and properties. The  
34 impact of plant fibre composites processing steps from the polymer impregnation stage right  
35 through to the end-of-life recycling stage is reviewed. Additionally, mechanical, morphological  
36 and hygroscopic properties of plant fibres are considered in conjunction with process times,  
37 temperature and shear rate. This review will aid process and product designers to develop new  
38 performing plant fibre composite products, taking into account the process parameters to select  
39 the most optimised process and (their effects on) plant fibres. Considering how fibre properties  
40 change with biocomposites processing steps is indeed essential to understanding the links  
41 between the micro and macro scales, and to be able to design optimised plant fibre composite  
42 materials.

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44

45 **Keywords:** Plant fibres; Processing; Time; Temperature; Water sorption; Mechanical properties

46

47

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61

### 62 1. Introduction

63 Plant fibres have been an integral part of the 'fabric' of human history. Their use in ropes or  
64 clothing dates back several tens of thousands of years (Kvavadze et al., 2009). Among the  
65 latter, flax (*Linum Usitatissimum L.*) and hemp (*Cannabis Sativa*) fibres were originally cultivated  
66 by the advanced civilizations of the Fertile Crescent; they are now the two most produced plant  
67 fibres in Europe (Bourmaud et al., 2018). Over time, their uses have widened and for the past  
68 twenty years, they have been of particular interest in the field of technical materials, in the form  
69 of plant fibre composites.

70 Plant fibre reinforced composites are becoming an important area of development for a large  
71 number of industries. This is particularly the case in the transport, marine and construction  
72 sectors. These fibres have important environmental advantages, good specific mechanical  
73 properties and are often available at a viable cost (Bourmaud et al., 2018). They offer a credible  
74 alternative to synthetic fibres such as glass fibres for semi-structural applications. In the context  
75 of impoverishment and the decline of fossil-based resources available to our civilization, their  
76 use addresses a real societal and industrial challenge, driven by a regulatory framework that  
77 promotes the use of bio-based, recyclable, biodegradable or lighter materials, and therefore  
78 creating a less negative environmental impact (Mohanty et al., 2018).

79 To produce these bio-based composites, the plant fibres are processed with thermoplastic or  
80 thermoset matrices by extrusion, injection, compression moulding, and also by the emerging  
81 process of fused deposition moulding (3D printing), amongst various other techniques. During  
82 these material transformation processes, the plant fibres are subject to thermomechanical  
83 stresses that are not benign to the integrity of plant fibre cell walls (Bourmaud and Baley, 2010).  
84 While the mechanical properties of synthetic fibres (such as glass or carbon fibres) may only be  
85 slightly impacted by process stages (Shah and Clifford, 2015), this is not the case for plant cell  
86 walls made of cellulose but also of non-cellulosic polymers, many of which have low thermal

87 stability (Siniscalco et al., 2018). In addition, they have a very specific architecture and structure  
88 that can be significantly altered by the mechanical stresses involved in conventional composites  
89 tools (Berzin et al., 2014). These structural modifications have a significant impact on the  
90 dimensions of the fibres, and therefore on their aspect ratio (length/diameter) which strongly  
91 conditions their reinforcement ability (G Ausias et al., 2013). Similarly, lengths of synthetic fibres  
92 are drastically affected by shear rate and process parameters (Bourmaud and Baley, 2007). In  
93 addition, structural modifications of the constituent polymers, induced by thermomechanical  
94 stresses, will have an impact on their architecture, degree of crystallinity, chain length, but also  
95 on inter-polymer bonds and on the overall parietal structure of plant fibres (Placet, 2009). These  
96 different impacts, whether morphological or structural, will modify the mechanical behaviour of  
97 the reinforcing fibres (Gourier et al., 2014). They can also have a major influence on the water  
98 absorption capacity of the principally hydrophilic non-cellulosic cell wall polymers, which will  
99 have consequences on the quality of multi-scale interfaces (polymer-fibre, fibre-fibre or between  
100 layers of a fibre) and therefore on the performance and durability of the resulting composites  
101 (Hill et al., 2009).

102 Thus, at both the fibre and composite scale, it is desirable to take into account all the relevant  
103 parameters that can alter the integrity of the plant fibres during all the processing stages.  
104 Whether during the drying, extrusion, compression, injection phase or even during a resin  
105 infusion process, the plant fibre must be considered as an evolutionary object whose structure  
106 and performance changes according to the process parameters used. This data is also  
107 important for mechanical modelling purposes as the properties of the fibres used as inputs into  
108 such models should be those following mechanical and thermal exposures, and not those of  
109 virgin fibres as the latter may no longer be valid model inputs. For example, the input  
110 permeability during flow process modelling should not be unsaturated permeability (alone), but  
111 rather saturated permeability that is a function of time, and incorporates effects of changing  
112 pressure and temperature during impregnation and curing, changing fibre structural properties  
113 (such as stiffness) as they get 'wet' and are being compacted, as well as any dimensional  
114 changes (e.g. swelling) of fibres due to resin absorption. Similarly, any micro-mechanical or  
115 finite element modelling should employ inputs of fibre geometry (vis. length, diameter, aspect

116 ratio, orientation) or structural properties (e.g. stiffness, strength, failure strain) based not on the  
117 virgin reinforcement form (e.g. pellets for injection/extrusion moulding) alone, but rather, make  
118 an effort to account for property changes due to the various processing steps.

119 In this critical review, an overview of these phenomena is provided. Firstly, the main thermal  
120 and mechanical parameters involved during a plant fibre composite processing transformation  
121 stage will be detailed. This will bear in mind the choice of the family and characteristics of the  
122 polymer matrix and the specific processing method. Secondly, the impacts of the plant fibre  
123 composite processing methods on the morphology of plant fibres are analysed. Following a  
124 detailed description of the architecture and composition of the fibres, the damage and rupture  
125 mechanisms occurring at the fibre scale, alongside the dimensional consequences on the fibre  
126 object is discussed. In addition, the effect of multiple re-processing cycles (injection recycling)  
127 on fibre property changes will also be elucidated. Thirdly, the impact of the plant fibre composite  
128 processing method and temperature on the mechanical performance of plant cell walls, in  
129 relation to the changes in their structure, as well as the hygroscopic behaviour of the plant fibres  
130 is discussed. The final section of this review will be a concluding analysis that will identify and  
131 account the key parameters to be defined when producing biocomposites and the compromise  
132 to be found between time, pressure, shear rate, and exposure temperature. Consideration will  
133 also be given to the choice of the nature of the fibres and the need (or not) to develop specific  
134 processing tools. We clarify here that the scope of this review does not include exploring the  
135 changes in properties of composites; rather the (changes in properties of) plant fibre  
136 reinforcements themselves are the subject of this review.

137

138

## 139 **2. Choice of temperature and shear rate for plant fibre composite materials processing**

140

141 Depending on the processing method chosen, which is largely determined by the nature of the  
142 polymer, its viscosity and its processing temperature, the thermal and mechanical stresses on  
143 the materials will vary greatly. They will impact both the polymer and the fibres, plant fibres  
144 being particularly sensitive to temperature but also to the exposure time. In this section, the

145 temperature and time ranges to which materials are subjected to during processing will be  
146 discussed. In addition, a parallel will be established with the shear rates, which are also very  
147 varied depending on the nature of the polymer used but especially on the processing technique.

148 When using a plant fibre composite, the temperature is highly dependent on the process used  
149 and the nature of the matrix. In general, the constituents of plant fibres (particularly amorphous  
150 polysaccharides) begin to degrade and lose their native properties above 200°C (Velde and  
151 Baetens, 2001). But for some, such as pectins, the glass transition occurs at much lower values  
152 (around 50°C), leading to a change in behaviour of the constituent cell wall polymer and  
153 premature change in fibre performance. For more details on the impact of temperature on the  
154 performance and structure of plant fibres, the reader is invited to refer to section 4.a of this  
155 review.

156 The first parameter to consider is the choice of the polymer matrix, which will in turn determine  
157 the temperature undergone by the plant walls during the transformation process. The use of  
158 matrices with low process temperatures is then of major interest (Liang et al., 2010). This is of  
159 course possible with thermosetting resins, but also with thermoplastic matrices, which also offer  
160 a wide processing temperature window. In addition, many low melting temperature  
161 thermoplastics, such as poly-(butylene succinate) (PBS) (Teramoto et al., 2004), poly-  
162 (caprolactone) (PCL) (Berzin et al., 2014) or poly-(lactid) (PLA) (Duc et al., 2014) are also  
163 compostable, which is an additional advantage when the reinforcement is also compostable  
164 (Pantaloni et al., 2020). Bourmaud et al. (A. Bourmaud et al., 2015) found for composites  
165 injected and reinforced with flax fibre that the choice of matrix had an impact on the mechanical  
166 performance of the reinforcements, with fibres impregnated at 140°C with PBS being  
167 significantly less impacted than those embedded in PLA at 190°C. Thus, the process  
168 temperature is important because of its impact on the performance of the fibres as well as its  
169 influence on the rheological flow properties of the polymer. A rise in temperature generally leads  
170 (except in special cases) to a decrease in the viscosity of the resin, which will be important for  
171 the quality of the final impregnation. Indeed, due to the complexity of the plant fibre  
172 reinforcements, the presence of fibre bundles (Coroller et al., 2013), preforms made of twisted  
173 (Baets et al., 2014) or sometimes treated yarns, impregnation can be impeded and high fluidity

174 is preferable to obtain quality impregnation and thereby minimize porosity in the composite  
175 materials.

176 With regards to plant fibres, the choice of a suitable temperature that allows for better fibre  
177 impregnation is a key consideration. A compromise must therefore be found between possible  
178 fibre degradation and resin impregnation quality. This link between temperature, structural  
179 defects and viscosity has been studied in depth on PP/flax composites by Ramakrishnan et al.  
180 (Ramakrishnan et al., 2019). They have shown that the increase in pressure during  
181 compression moulding, temperature, and forming time allows for better impregnation but also a  
182 reduced porosity content. However, if the temperature and exposure time are too high, fibre  
183 degradation occurs, causing the release of volatile organic compounds and consequently an  
184 increase in porosity. The authors showed that although the composite stiffness is only slightly  
185 affected by these variations, tensile strength is substantially diminished. A low temperature is  
186 recommended as this allows for satisfactory porosity values to be obtained while also protecting  
187 the plant fibres. This relationship between time and temperature has also been studied at the  
188 composite scale by Liang et al. (Liang et al., 2015) on poly-(amide 11) composites reinforced  
189 with woven flax preforms. A decrease in composite performance with an increase in  
190 temperature and process time was observed; a 64% decrease in tensile **strength** of the material  
191 was measured with an increase in processing temperature from 230°C to 250°C and process  
192 time from 2 to 5 minutes. These conclusions are in line with those of Ramakrishnan et al.  
193 (Ramakrishnan et al., 2019). In addition to temperature, time also has a major impact and these  
194 various works show that a compromise is necessary to obtain parts of suitable quality. This is  
195 true for a compression moulding process, as well as for extrusion and injection moulding. By  
196 varying the nature of the extrusion tools and therefore the residence times of the flax fibres in a  
197 composite extruded and then injected with a poly(propylene) matrix (PP), Doumbia et al.  
198 (Doumbia et al., 2015) showed a decrease in the performance of the mechanical properties of  
199 the materials, which can be explained by a decrease in the rigidity of the flax fibres measured  
200 by nano-indentation. The choice of a process is often dictated by economic production  
201 constraints, but when several variables require consideration, it is **appealing to** select them



202 according to the residence time, which can vary from a few hundredths of a second to a few  
203 minutes depending on the process (Fig. 1).

204

205 **Figure 1**

206

207 Depending on the processes and materials used, despite set temperatures appropriate for the  
208 use of plant fibres, self-heating can occur; the latter can be caused by the exothermic nature of  
209 the resin in the case of thermosetting matrices but also by energy dissipation during major  
210 shearing operations. This is particularly true in extrusion **where** conjugates and single threads  
211 are used. This phenomenon also occurs commonly in injection at the mould thresholds which  
212 are intended to fluidize the material under the effect of pressure but which also **causes**  
213 significant increases in its temperature. On PCL-extruded hemp fibre PCL blends, Beaugrand et  
214 al. (Beaugrand and Berzin, 2013) found self-heating between 3°C and 67°C depending on the  
215 screw rotation speed, for a barrel temperature imposed at 100°C. This strong difference shows  
216 how difficult it is to control the real process conditions and above all the need to adapt the  
217 machine parameters to the plant fibres in order to limit both the self-heating of the parts and the  
218 shear rate, although the latter is necessary to homogenize the compounds and reinforcement  
219 homogeneity.

220 Depending on the processes considered, shear rates vary considerably; Figure 1 summarizes  
221 the stress ranges that can be encountered in the various tools used to transform plant fibre  
222 composites.

223 Numerical tools exist to model the energy supplied to plant fibres during a process stage (with  
224 particular attention to the extrusion process). These design assistance tools make it possible to  
225 control the parameters during a process stage and **thereby maintain plant cell wall integrity** as  
226 much as possible to generate materials with optimized performance.

227 To limit temperature and shear rate, one way is to use softer moulding stages such as  
228 thermocompression (Liang et al., 2015), **thermoforming** (Bhattacharyya et al., 2003),

229 compression with induction heating (Ramakrishnan et al., 2019), 3D printing (Duigou et al.,  
230 2016) or automated fibre deposition (Baley et al., 2016; McGregor et al., 2017). As can be seen  
231 in Figure 1, they generally reduce pressure or time significantly; however, in the case of powder  
232 impregnation, 3D printing or automated deposition (Badouard et al., 2019; Baley et al., 2016),  
233 initial porosity rates are often high and require the implementation of an additional thermal  
234 consolidation stage. Infusion or thermocompression processes also have their advantages in  
235 terms of moderate shear rate but they are often carried out with thermosetting resins that offer  
236 good impregnation but also require longer processing times. For example, a complete curing  
237 stage of a flax epoxy composite can take between 2 and 8 hours, while it will only take 7 to 8  
238 minutes in the case of PLA-flax (Liang et al., 2015). Moreover, thermosetting matrices are not  
239 easily recyclable, which is an environmental contradiction when it comes to plant fibre  
240 composites.

241

### 242 **3. Impact of process on plant fibre morphology**

#### 243 **3.1. Initial morphology of plant fibres**

244 **This section discusses the initial morphology of natural and extracted plant fibres, prior to being**  
245 **subjected to any biocomposites processing step.** Fibres are ubiquitous in vascular plants and  
246 are found in various organs including stems, leaves, seeds, and roots. Indeed, the structure and  
247 properties of a fibre are governed by their growth and development process ('ontogenesis' in  
248 biology = 'processing' in technology) as well as their function in the plant (Shah, 2013).

249 For the materials community, fibres are loosely referred to as long cells or bundles of cells.  
250 They include i) sclerenchyma fibres in dicotyledon stems, such as phloem fibres of flax and  
251 hemp, ii) fibres around vascular bundles in monocotyledon stems and leaves, such as bamboo  
252 and sisal, respectively, iii) trichomes and mesocarp of seeds, such as cotton and coir,  
253 respectively, iv) and xylem fibres, such as tracheids (Bourmaud et al., 2018; Leuwin, 2007). Of  
254 course, in botanical terms, fibres have a tighter definition: a fibre is an individual cell that  
255 belongs to the sclerenchyma, and has characteristics including elongated shape (high aspect  
256 ratio), thick secondary cell wall, tapered ends, and structure-supporting role in the plant (Esau,

257 1953; Gorshkova et al., 2012; Mokshina et al., 2018; Van Dam and Gorshkova, 2003). Many  
258 other classifications of fibres exist, such as primary and secondary fibres, but no classification is  
259 sufficiently all-encompassing to exclusively capture the diversity (Van Dam and Gorshkova,  
260 2003). For the purposes of this wide review, we will use the looser definition frequently adopted  
261 in the plant fibre composite materials community. Figure 2 illustrates structural properties  
262 (length, diameter, aspect ratio) and mechanical properties (stiffness, strength) of a range plant  
263 fibres, commonly used for composites reinforcement.

264 In terms of ontogenesis, fibres typically develop through three key stages (Bourmaud et al.,  
265 2018; Gorshkova et al., 2012): i) initiation, to up to around 30µm length and 3-5 µm thickness, ii)  
266 elongation, by up to more than 1000-fold in length and 10-fold in thickness, and iii) further  
267 specialisation (vis. cell wall thickening). Of course, environmental and agronomical factors  
268 would have compounded effects on plant - and therefore fibre - growth, however such effects  
269 are not the focus of this section.

270

271

## Figure 2

272

273 During the elongation growth phase, fibres increase substantially in length, but also, albeit to a  
274 lesser degree, in width. The resulting aspect ratio ( $l/d$ ) of a fibre is a governing geometric  
275 parameter of mechanical properties (Legland and Beaugrand, 2013), with high aspect ratios  
276 correlating to high stiffness and strength (Fig. 2) (Bourmaud et al., 2018; Mukherjee and  
277 Satyanarayana, 1986; Pickering and Rowell, 2008; Shah, 2013). However, the **aspect ratio of**  
278 fibre elements is also dependent on its form: if it exists as an elementary fibre (idioblast) or in  
279 bundles. Although bundles may have comparable lengths, they also have much higher  
280 diameters leading to substantially reduced aspect ratios. Most non-bast fibres have a shorter  
281 elongation phase and exist in large bundles (Leuwin, 2007; Van Dam and Gorshkova, 2003)  
282 leading to smaller aspect ratios (Fig.2). Indeed, even secondary phloem bast fibres, which grow  
283 in the secondary (cambial) meristem, have (up to an order of magnitude) shorter lengths, aspect  
284 ratios and mechanical properties in comparison to primary phloem bast fibres that grow in the

285 primary (apex) meristem (Gorshkova et al., 2012). This is because secondary phloem fibres  
286 grow in already formed tissue, while primary phloem fibre cells undergo coordinated growth,  
287 thereby developing at the same rate as the surrounding soft tissues (Bourmaud et al., 2018).  
288 Moreover, the embedding of fibres in the surrounding tissues to form bundles affects the ease  
289 of extraction of these fibres (Van Dam and Gorshkova, 2003) through retting, decortication,  
290 scutching and hackling. These processes further influence fibre aspect ratio, as well as impart  
291 defects (Hughes, 2012), leading to a further deterioration in fibre mechanical properties.

292 Secondary cell wall thickening is also an important growth phase, particularly in phloem and  
293 xylem fibres (Bourmaud et al., 2018; Gorshkova et al., 2012). Indeed, ratio of cell wall thickness  
294 to lumen diameter, referred to as luminal porosity, is also an important geometric parameter  
295 influencing fibre mechanical properties; larger cell wall thickness and lower luminal porosity  
296 correlate to higher strength and stiffness (Pickering and Rowell, 2008; Shah, 2013). As there is  
297 significant heterogeneity in dimensional characteristics of natural fibres, the luminal porosity  
298 may also vary along the length of the fibres (Beaugrand et al., 2017) and therefore may  
299 influence the fracture mechanics.

300

301

### Figure 3

302

303 It is not just the cell wall thickening process in this third growth phase that is important, but also  
304 the emerging biochemical composition and the structural organisation of the fibre (Fig. 3).

305 Secondary cell wall thickening involves the formation of thick, sometimes lignified, secondary  
306 cell wall layers with properties substantially better than the primary cell wall. The principal cell  
307 wall polysaccharides are cellulose, hemicellulose, with pectin-rich middle lamella adjoining the  
308 fibre cells. In addition, the lignin, a polyphenolic polymer, is non homogeneously distributed over  
309 the cell wall structure with a reported enrichment in the middle lamella and primary cell wall. To  
310 a lesser extent, proteins are also part of the cell wall as some of them are playing a structural  
311 role, and are well known to act as the cytoskeleton of the cell, which impact on the plant cell  
312 remodelling (Wasteneys and Galway, 2003). The cellulose content, and in particular, cellulose

313 crystallinity are the key biochemical parameters influencing mechanical properties (Bledzki and  
314 Gassan, 1999; Pickering and Rowell, 2008; Shah, 2013). Cellulose crystallinity is higher for  
315 structure-supporting bast fibres and decreases with reducing structural requirements, as in leaf  
316 and seed fibres. The S2 secondary cell wall, the thickest of the cell wall layers (Fig.3),  
317 dominates the structural behaviour of a plant fibre cell (Bledzki and Gassan, 1999; Leuwin,  
318 2007). The cell wall layer is comprised of cellulose microfibrils that helically orient at specific  
319 microfibril angle (MFA) to the fibre axis, and are held together by amorphous hemicellulose and  
320 lignin polymers. The MFA of the S2 cell wall is the key structural organisation parameter  
321 influence fibre mechanical properties. Bast fibres have low MFA ( $<10^\circ$ ), leaf fibres moderate  
322 MFA ( $10-25^\circ$ ) and seed fibres have high MFA ( $30-50^\circ$ ) leading to their corresponding  
323 mechanical properties of high, moderate and low stiffness (Figure 2), but low, moderate and  
324 high elongation at failure (Gorshkova et al., 2012; Shah, 2013).

325 The initial morphology and properties of plant fibres evolve through their extraction phases, and  
326 subsequent processing into polymer reinforcing fibre composites. Henceforth, we explore the  
327 main premise of this review paper, the evolution in fibre morphology and properties from an  
328 initial stage through the various processing methods employed to produce plant fibre composite.

329

### 330 **3.2. Breakage mechanism during a process stage**

331 As an introduction, we must recall that it seems unrealistic to demand for a description of one  
332 sole prevalent breakage mechanism, due to the large panel of stress modes generated by the  
333 multiple processes and stages in use. One can expect that according to the process used, the  
334 dominant mechanical stress will vary between shear, impact, compression, tension and wear.  
335 Hence, it would be a very challenging task to generalise 'the' breakage mechanism that is  
336 sufficiently malleable to adequately describe the effects of all the plant fibre composites process  
337 stages used for plant fibres.

338

339

**Figure 4**

340

341 Along this line of thought, it is relevant to compare the different processes. To conduct an  
342 empirical comparison of the severity of dedicated processes is not a trivial task. Some have  
343 already embraced this challenge with noticeable success when comparing effects of vacuum-  
344 assisted resin transfer moulding (VARTM), pultrusion and extrusion-injection moulding (Haag et  
345 al., 2017).

346 Establishing a relationship between process intensity and breakage is fundamental for natural  
347 fibres. Due to their natural biochemical anisotropy and composite poly-laminate structure  
348 (Barber and Meylan, 1964), a dynamic succession of predominant breakages mechanisms is  
349 observed, which take place in a more or less coordinated fashion according to the process  
350 scale and duration (Fig. 4, illustration of the decohesion-delamination of individual fibre in a  
351 bundle).

352 Understanding and predicting process-induced damage mechanisms will enable better control  
353 of fibre length. Indeed, longer fibres with high aspect ratio (Pickering et al., 2016) may improve  
354 composite mechanical performance (G Ausias et al., 2013; Beaugrand and Berzin, 2013). Many  
355 works on natural fibre are inspired from previous studies on synthetic glass fibres (Shon and  
356 White, 1999). Process-induced damage affects the structural geometry of the fibre, the latter  
357 being characterized by its aspect ratio (Grishanov et al., 2006; Nyström et al., 2007). Moreover,  
358 improvement in thermoplastic composite strength is reported with increasing fibre aspect ratio  
359 (Beaugrand and Berzin, 2013). Notably, the more individualised the fibres are (see Fig.4), the  
360 higher the aspect ratio. The resulting decohesion from process stresses may expose various  
361 surface chemicals, but also substantially increases the specific surface area on offer for  
362 interfacial adhesion.

363 This hypothesis is not new and is supported by research in the field of pulp and paper. Indeed  
364 with wood fibres, which are relatively short in length and rather homogeneous in dimension  
365 compared to plant fibres, this community has understood that the breakage mechanisms of the  
366 bundles and individual fibres of wood are governed by the refining intensity (e.g. torque), which

367 also leads to specific desirable technical characteristic of the pulps and products thereof  
368 (Padovani et al., 2019).

369 Among processes that induce damage, an arguably aggressive process is milling (Mayer-Laigle  
370 et al., 2020). The fibre milling process may lead to plant fibre particles less than a few  $\mu\text{m}$  in  
371 length (see Fig 5, d), and of non-elongated shape (aspect ratio lower than 10). Extrusion with a  
372 co-malaxor system, single- or twin-screw, is yet another harsh process (Doumbia et al., 2015).  
373 Many reports are available on the impact of single-screw profiles on a batch of natural fibres (El-  
374 Sabbagh, 2014). The rich literature on this topic is explained by the economic implication of this  
375 research for the current plant fibre composite sector, given that the twin-screw process is the  
376 main industrial process for incorporating lignocellulosic fibres into polymers (Antoine Gallos et  
377 al., 2017) and it may offer a numerical damage descriptor for a common scale unit. Indeed,  
378 using this approach, one is able to scale the fibre breakage observed, depict it in terms of  
379 damage mechanisms (Castellani et al., 2017), and even model the progressing mechanisms for  
380 twin screw (Berzin et al., 2017) or extrusion-injection moulding (Albrecht et al., 2018).

381 Technically, mechanistic models of evolution-simulation for lignocellulosic fibre breakage are  
382 based on observations, such as through static (Le Moigne et al., 2013) and dynamic (Le Duc et  
383 al., 2011) methods, quantification by morphometric measurements from 2D image analysis  
384 (Hamdi et al., 2015) (Hamdi et al. 2015 CPA), and even 3D particle volumes from X-ray  
385 tomography (Hamdi et al., 2018).

386

387 **Figure 5**

388

389 One recent breakthrough in plant fibre breakage understanding is a breakage classification  
390 based on fatigue, fragility or where peeling behaviour is present (Castellani et al., 2017). The  
391 study used a setup of four batches of fibres of botanical origin and proposed correlations  
392 between breakages, intrinsic fibre properties, and biochemical composition. Lignin, a  
393 recalcitrant polyphenolic polymer, seems to be strongly involved in the breakage behaviour.  
394 Regarding the morphometry of the fibre elements, it seems to be a first order criteria for

395 breakage mechanisms. A breakage index of lignocellulosic fibres was defined by Berzin et al.  
396 (Berzin et al., 2017). The authors report a strong influence of the initial dimensions of the fibre  
397 elements: longer fibres are more susceptible to length breakage (i.e. more susceptible to a  
398 decrease in length) rather than decohesion of bundles (which result in decrease of diameter).  
399 Note, for instance, that there is much variation between miscanthus and hemp. Figure 5 gives a  
400 schematic representation of the plant fibre-breakage mechanisms during a process stage along  
401 with a kinetic of reduction of both the length and the diameter of the fibre elements. At the  
402 beginning of the process stage, both the rate of decohesion (mostly longitudinal break) and  
403 fragmentation (due to transverse break), are high but not identical. Several types of damages  
404 are often visible at the surface of the fibre elements (Fig 5) like surface flaws (vestiges of  
405 residual middle lamella, primary cell wall). And along with the process, there is an enrichment of  
406 fine elements according to the duration or severity (Fig 5). The kinetics of breakages have been  
407 measured for fibres of various origin, but the influence of central cavity (*vis. lumen*) (Fig.3),  
408 which is often considered a defect, is *not usually* considered in breakage predictions due to  
409 technical considerations. More generally, the ratio between respective area of cell wall and  
410 lumen is known to be important in the rupture properties of fibre elements (Lucas et al., 1997).  
411 The filling of *these* lumen by polymer can *occur* during the hot melt processing for thermoplastic  
412 based composites. This filling can *significantly* increase the strength of the composites  
413 (Mohanty et al.). The lumen *may be* partially or totally filled with the polymer *depending on*  
414 parameters *such as* the *lumen/cell wall size* ratio, the viscosity of the matrix and the process  
415 parameters. Reported lumen filling values range from 5 to 50% for wood fibers (Mohanty et al.,  
416 2005), whereas *such data is unavailable for* bast fibres.

417 For annual plant fibres, the heterogeneity of the morphometries (Legland and Beaugrand,  
418 2013), biochemical compositions and macromolecular cell wall organisations have discouraged  
419 many researchers to propose breakage mechanisms during a process stage. Indeed, these  
420 fibre elements are often organised as bundles, rarely as individual fibres, in an industrial lot.  
421 These fibre elements, comprising fibrils, macrostructural defects such as kink bands, and a  
422 myriad of broken parts, are often called 'fines' (see Fig 5). The overall challenge is in i) the  
423 technical description and the labelling of the morphometric features, and ii) relating the



424 functional properties (mechanical/thermal) of each of those micron features and in explaining an  
425 homogenised property at the composite scale.

426 Fines are defined as particles of length smaller than 200µm (Mayer-Laigle et al., 2020), though  
427 these fines can be underestimated due to technical detection limits. Fines are known to have an  
428 impact on rheological and even mechanical properties of plant fibre composites, particularly  
429 when they are highly concentrated (Bourmaud et al., 2019).

430 The damage mechanism during a process stage does not necessarily mean 'breakage' that  
431 leads to division of the fibre elements in at least two bodies. Indeed, there are also damage-  
432 induced defects, like compression zone, kink band, and fibrillation (Fig 5), that are even more  
433 difficult to assess in comparison to decohesion and rupture. Indeed, they require more focused  
434 instruments for visualisation, such as microscopy techniques (optical or electronic). Arguably,  
435 these are defects or weakness points that could initiate further breakage mechanisms. In  
436 fibrillation, often part of the fibre sub-layer remains, i.e. there is partial delamination. They could  
437 enhance paper properties, whereas their positive contribution in plant fibre composites is more  
438 questionable and rather difficult to quantify by direct observation (Padovani et al., 2019). The  
439 kink bands are submicronic damages present in natural fibres and could drive failure, as  
440 observed in hemp fibres (Beaugrand et al., 2017). They are naturally present in stems  
441 (Thygesen et al., 2011) but their content increases drastically with the decortication process  
442 (hackling/scutching) where the fibre bundles are extracted from the plant. Kink bands are zones  
443 of disorganisation of crystalline cellulose in the cell wall, and span across the full diameter of the  
444 fibre elements. Recent work investigated by (Beaugrand et al., 2017) reported some crack  
445 bridging between two adjacent kink bands, thanks to the propagation of the main crack via the  
446 fibre lumen (Beaugrand et al., 2017). Lumen porosity and empty space between fibres are often  
447 viewed as defects (Madsen and Lilholt, 2003; Shah et al., 2016) (Madsen CST 2003, Shah et al  
448 Cellulose 2016); the smaller they are, the higher the mechanical properties of the technical fibre  
449 (Fuentes et al., 2017; Müssig and Stevens, 2010). In addition, the surface defects (crack, pith,  
450 notch) are often forgotten, however it has been shown using finite element simulation and high-  
451 resolution X-ray microtomography that they contribute significantly to the development of severe  
452 damage evolution (Guessasma and Beaugrand, 2019), as well as the fibre ends. Finally, it

453 seems useful to highlight that in terms of damage rate, the development of damage growth is  
454 often related to the presence of localized or diffused damage sites (Andersons and Joffe, 2011;  
455 Gourier et al., 2017; Guessasma and Beaugrand, 2019).

456

### 457 **3.3. Impact of process on plant fibre diameter and aspect ratio: focus on recycling.**

458 Processing of thermoplastic composites generally cause a drastic reduction in the length of the  
459 plant fibres, especially after an extrusion stage (Albrecht et al., 2018; Beaugrand and Berzin,  
460 2013; Berzin et al., 2014; Subasinghe et al., 2015). The **diameters of the fibres** are also reduced  
461 during this transformation phase. The design of the processing screws in an injection moulding  
462 machine or single- or twin-screw extruder influences the final dimensions, morphology and  
463 properties of the fibre, and consequently affects the properties of the resulting fibre reinforced  
464 composite. Indeed, different screw designs may generate very different shearing and mixing  
465 conditions during the process. Generally, to attain homogeneity and good dispersion of fibres in  
466 the composites, twin-screw extruders are favored. Buss co-mixers can also be an efficient  
467 alternative (Shon and White, 1999). Doumbia et al. (Doumbia et al., 2015) compare the  
468 transformation of flax-PP following processing through a Buss co-malaxor and by twin screw  
469 extrusion; they show that individualisation was more efficient with the co-malaxor but the latter  
470 induces shorter fibre lengths. It is, nevertheless, recommended that fibre individualization and  
471 dispersion are promoted. This is due to their positive effect on the resulting composite material's  
472 tensile strength and modulus, as demonstrated on flax (Doumbia et al., 2015) and kenaf (Sallih  
473 et al., 2014) fibre composites; better dispersion leads to homogenization and also possible  
474 penetration of resin into hollow cores of plant fibres especially for high lumen-size fibres such as  
475 kenaf. A 2D simulation comparison between single-screw and twin-screw extruders (Connelly  
476 and Kokini, 2007) has shown better spreading of fibres/particles through mixing by twin-screw  
477 extruders.

478 The screw profile is also an important factor to be considered. The screws can be tailored with  
479 multiple block elements of various shapes for specific functions such as conveying and mixing (A  
480 Gallos et al., 2017). Based on the shaped elements used for the screw profile, fibres will be

481 subject to different residence times by using conveyors or reverse elements. The evolution in bast  
482 fibre lengths during processing through various screw elements was recently studied by X-ray  
483 microtomography (Hamdi et al., 2018), revealing that the shaped profile of the screw has a strong  
484 influence on fibre length. The use of reverse screw elements increases the shear rate and the  
485 severity of the process (Gogoi et al., 1996). Shearing increases with mixing or kneader elements  
486 (Berzin et al., 2017), as reported for bast fibre, and also short wood fibre (Dickson et al., 2020);  
487 inducing a drastic reduction in the length of the fibres (Teuber et al., 2016). The screw profile  
488 also influences the final properties of composites. For instance, it has been demonstrated that  
489 the screw profile can be used to substantially improve the exfoliation of organoclay in PP  
490 (Lertwimolnun and Vergnes, 2007), and the mechanical properties of short glass fibre reinforced  
491 polypropylene composites (Lekube et al., 2019). Aside from the screw configuration itself, several  
492 other extruder parameters can be optimised, such as the feed rate or screw speed.

493 Depending on the nature of the fibres, their behaviour may vary during an extrusion or injection  
494 stage. Originally, fibres are assembled into bundles in plants (Bourmaud et al., 2015) and these  
495 bundles may still be present after one or more transformation cycles in a composite material.  
496 However, their ability to divide depends on the cohesion of these bundles and the nature of the  
497 middle lamellae, and in particular their lignin content. Thus, jute bundles, made of very cohesive  
498 short fibres, will be difficult to individualise (Tanguy et al., 2018), which will be detrimental to  
499 maintaining a good aspect ratio. In contrast, flax fibres, already highly individualised during  
500 scutching, can be almost elementarised at the end of an extrusion or injection stage (Oksman et  
501 al., 2009). This has also been demonstrated on hemp by Peltola et al. (Peltola et al., 2011).

502 **The concentration of fibres can affect fibre morphology but also viscosity and overall rheology of**  
503 **the melt blend during moulding or extrusion stage**; and several models have tried to describe  
504 and quantify this phenomenon. These models use numerical simulation software (e.g.  
505 Cadmould® and MoldFlow®) and determine fibre interaction coefficients (Albrecht et al., 2018)  
506 that reflect the adhesion forces between the fibres within fibre bundles. When the volume  
507 fraction (and thereby concentration) of plant fibre increases, the fibre lengths and diameters  
508 decrease, as shown for wood (Teuber et al., 2016) and flax (Puglia et al., 2008). These trends  
509 were confirmed experimentally by Ausias et al. (G. Ausias et al., 2013). They observed a

510 substantial decrease in flax fibre length with increasing fibre content following extrusion or  
511 injection molding. They also noted a slight decrease in the aspect ratio at low fibre contents. A  
512 threshold fibre content of 30%-vol. was highlighted, indicating the estimated critical aspect ratio.  
513 This critical aspect ratio depends on fibre intrinsic characteristics, matrix properties and quality  
514 of fibre/matrix adhesion. **These changes in fibre morphology induced by changes in fibre**  
515 **volume fraction significantly impact the viscosity and rheology of polymers and consequently the**  
516 **flow behaviour in processing tools; this decrease in compound viscosity may be an advantage**  
517 **for industrial users, especially considering the high initial mixing viscosity resulting from the**  
518 **presence of the notable plant fibre components (Bourmaud et al., 2016; Dombia et al., 2015).**

519 By applying successive injection cycles after this compounding, these evolutions will naturally  
520 continue with particular characteristics related to the nature and the structure of the  
521 reinforcements. A distinction can be made here between i) fibres originating from the supporting  
522 tissues which have initial lengths of a few tens of mm and high aspect ratio (case of flax and  
523 hemp), and ii) shorter fibres, such as cell walls of wood, which are naturally short and are  
524 generally incorporated in the form of powder or flour because of their extraction method or their  
525 origin (sawmill waste, for example). Figure 6 shows the evolution in length distribution of flax  
526 fibres from an initial length of ca. 2 mm after successive cycles of compounding and injection  
527 within a PLLA-PBS matrix (Bourmaud et al., 2016). We observe a steady decrease in fibre  
528 length with recycling steps; as the injection cycles continue, the decrease in length continues to  
529 reach a threshold value from the fourth cycle. Interestingly, we have been able to demonstrate a  
530 correlation, on PA11-flax composites (Gourier et al., 2017), between the inter-defect distances  
531 and the final lengths of the same fibres after recycling; Indeed, as shown by Le Duc et al. (Le  
532 Duc et al., 2011), the break of fibres during compounding preferentially occurs in the kink band  
533 zones.

534 This strong decrease in length after compounding has already been observed on flax, hemp  
535 and even sisal and kenaf fibres (Bourmaud and Baley, 2009, 2007; Dickson et al., 2014; Le  
536 Duigou et al., 2008; Subasinghe et al., 2015). This has also been observed on synthetic fibres  
537 such as glass. Due to the different structure of the fibre plants, the observations are different for  
538 changes in diameters and therefore in aspect ratio ( $L/D$ ). Regarding glass fibres, one can note a

539 significant decrease in this form factor ( $L/D$ ) with the number of cycles due to the shear rate of  
540 the injection process.

541

542 **Figure 6**

543

544 This decrease is caused by the constant reduction in the length of the fibres associated with the  
545 fact that their diameter remains constant throughout the injection cycles. Indeed, glass fibres  
546 are initially individualized within the compound. The behaviour of plant fibres is different. These  
547 fibres are initially present in the plant in the form of bundles which can contain several tens of  
548 fibres. After recycling, these bundles will divide, which will cause a reduction in the diameters of  
549 the reinforcements. In parallel, fibre lengths decrease but this decrease is less marked than for  
550 glass fibres (Bourmaud and Baley, 2007). The combination of these two decreases (length and  
551 diameter) leads to a relative stabilization of the aspect ratios as can be seen in Figure 6, for flax  
552 fibre elements.

553 One can notice that the aspect ratio obtained on plant fibres are relatively low compared to  
554 those of glass fibres - 13.0 and 10.5 for hemp and sisal against 54.0 for the glass after an  
555 injection cycle (Bourmaud and Baley, 2007). This can lead to a lower reinforcement quality. This  
556 factor must be taken into account in the realization of future compounds where the emphasis  
557 will be on the dispersion of the elementary fibres in order to favour performing aspect ratios.

558 Works have also been carried out on composites reinforced with wood flour (Beg and Pickering,  
559 2008; Dickson et al., 2014; Soccalingame et al., 2015). Given the specific morphology of these  
560 reinforcements, it is sometimes difficult to define a length and a diameter, these are therefore  
561 mostly defined by a single dimension. Even if the geometry of these reinforcements is  
562 noticeable, it remains modest and the wood particles very quickly reach a floor value given their  
563 initial geometrical characteristics which are already small. By working with wood fibres extracted  
564 by methods that better preserve the lengths, it is possible to approach the trends observed for  
565 flax and hemp fibres, the fibres then maintaining a significant aspect ratio over the cycles

566 (Dickson et al., 2014). However, these extraction processes require the use of heavy  
567 mechanical and chemical equipment and the environmental impacts must be considered in  
568 parallel.

569 After compounding and injection, the plant reinforcements are embedded into a polymer matrix.  
570 If it is possible to extract them from the latter chemically in order to study their morphologies, it  
571 is not possible to carry out tensile tests because of their short lengths and especially the impact  
572 of the solvents on the integrity of the plant walls. In addition, the nanoindentation allows to  
573 obtain an estimate of the stiffness and hardness of the plant cell walls by working on cross-  
574 sections of injected parts. Figure 6 illustrates the evolution in mechanical properties measured  
575 by nanoindentation (Bourmaud et al., 2016) of flax fibres after injection cycles in a PLLA-PBS  
576 matrix. These images show that in this specific case the surface morphologies and the  
577 geometries of the indents are similar, evidencing no major structural differences, contrary to  
578 what can be observed, for example, between two species of plant cell walls (Tanguy et al.,  
579 2016). We can note an important difference between the performances of the virgin fibres and  
580 after a process cycle, this being particularly marked for the hardness which exhibits a significant  
581 drop after compounding.

582 As was pointed out by the wood community (Eder et al., 2012), the nanoindentation modulus is  
583 representative of the behaviour of cellulose microfibrils (especially when the microfibrillary  
584 angles are weak as it is the case for flax or reaction wood) whereas the hardness is much more  
585 sensitive to changes linked to the matrix polysaccharide. This is mainly due to its method of  
586 calculation, based on a theoretical contact area which can be modified in the event of alteration  
587 of this matrix. Thus, the large drop in hardness after a process cycle reveals a probable  
588 alteration of the pectins and hemicellulose constituting the matrix of the S2 wall. This was also  
589 demonstrated by tensile tests on heated fibres (Gourier et al., 2014) or by nanoindentation by  
590 studying the effect of an injection cycle on the mechanical performance of flax cell walls  
591 (Bourmaud and Baley, 2010).

592 Similar tests were carried out on PP-wood compounds (Soccalingame et al., 2015; Stanzl-  
593 Tschegg et al., 2009). The observations are different, especially for the hardness whose value

594 tends to increase with the recycling cycles. This contradictory phenomenon can be explained by  
595 the nature of the wood cell walls which, contrary to flax, constitute a large part of lignin and  
596 xylan. It has been demonstrated (Yin et al., 2011) that in the case of wood, partial crosslinking  
597 of the cellulose-xylan-lignin system could occur after a thermal stage, this phenomenon has  
598 been exploited to develop stabilization treatments for the walls such as wood refining.

599 In spite of these morphological and mechanical **changes** of the reinforcing plant fibres, bio-  
600 based composites have stable mechanical performances after recycling, even if caveats are  
601 made based on the nature of matrix; some such as PLA may be more sensitive to shear rate  
602 and hydrolysis. In this case, a significant decrease in the stress at break of the composite  
603 appears after a few cycles (Le Duigou et al., 2008). In case of use of a polyolefin or PA11 matrix  
604 (Gourier et al., 2017), the values of Young's modulus and strength at break are mostly stable  
605 after several process cycles. This is mainly due to the good stability of the fibres' aspect ratio  
606 but also to a relatively stable fibre-matrix adhesion compared to the one between PP and glass  
607 fibres. The latter benefits from optimized sizing but this sizing loses efficiency with subsequent  
608 process cycles. Moreover, one can notice that recycled PP offers also good recycling behaviour  
609 and enables to manufacture reliable plant fibre composites, even after several process cycles  
610 (Bourmaud et al., 2011).

611 At the same time, due to the smaller size of the fibrous elements but also the alteration of the  
612 chain length of the matrix, the plant fibre composite viscosity is generally considerably reduced  
613 after recycling. This point does not constitute a disadvantage, in particular for applications  
614 requiring high fluidity such as injection moulding. Thus, all these elements ensure that the plant  
615 fibre composites generally present useful properties after recycling, the main limit being their  
616 collection and the waste separation, which is not yet really implemented mainly because of the  
617 low volumes available. The increase in market shares in the automotive sector must be a trigger  
618 for taking their end-of-life into account.

619

620

621 **4. Impact of process on plant fibre properties**

#### 622 4.1. Impact of the temperature at the single fibre scale

623 As discussed previously, important morphological or mechanical degradations of the plant cell  
624 walls may occur during a process stage, with significant decreases in length but also in terms of  
625 mechanical performance. Shear rate and pressure are responsible for a large part of this  
626 damage but temperature, by modifying structure of fibre constitutive polymers must also be  
627 considered. As evidenced by Subasinghe et al. (Subasinghe et al., 2015), extrusion  
628 temperature has an impact on fibre length and also on fibre ultrastructure and properties. The  
629 temperature regime undergone by the cell walls induces a significant decrease in the properties  
630 of these walls which is accentuated with the rise in temperature, either due to the choice of the  
631 matrix or self-heating (often uncontrolled) (Beaugrand and Berzin, 2013) induced by the shear  
632 rate within the process tools and especially the extrusion screws. This last point still requires  
633 work to be done: the temperatures really experienced by the fibres are poorly known and often  
634 underestimated, even when approximated using modelling software (Berzin et al., 2014).

635 Sometimes, thermal treatment is used; this is especially the case for wood fibres with regards to  
636 the torrefaction process (Pushkin et al., 2015; Volfson et al., 2015). The purpose of torrefaction  
637 is to modify the chemical composition of wood filler in order to improve its compatibility with  
638 polymers, particularly polyolefin matrices. In these two works, the effect of torrefaction (soft  
639 pyrolysis (200–300°C) in inert atmosphere) on the samples of hardwood (birch) and softwood  
640 (pine) has been compared. The authors observed strong differences between the torrefied  
641 samples between 225 and 250°C, mainly due to the specific behaviour of hemicellulose  
642 constituents. A significant decrease in the xylose content was observed at a temperature of  
643 250°C whereas mananes were more resistant to degradation. Thus, an important modification  
644 in hemicelluloses was reported. Interestingly, the content of cellulose remained stable up to  
645 250°C and the crystallinity rate increased in torrefied samples. Moreover, the  
646 lignin/carbohydrate ratio gradually increased with the temperature of treatment, probably due to  
647 both carbohydrate decomposition and the formation of new aromatic clusters due to  
648 thermochemical reactions. This last point is considered to be very promising for the forthcoming  
649 plant fibre composite blends, lignin being an interesting promoter of adherence, especially with  
650 polyolefin matrices (Graupner et al., 2014).



651 Temperature may also negatively impact the cell walls properties and performances. Plant  
652 fibres are mainly composed of cellulose but also of non-cellulosic polymers, which for flax are  
653 mainly pectins and hemicelluloses. Research works have shown that the first polymers to be  
654 affected by a thermal stage are these non-cellulosic polymers and in particular pectin; cellulose  
655 does not start to degrade until about 200°C (Gourier et al., 2014). This assessment is confirmed  
656 by several literatures. For example, Paris et al. (Paris et al., 2005) have studied spruce and pine  
657 heating between 35 °C and 250 °C, these authors highlight the evaporation of water and  
658 dehydration with slight depolymerization, but no change in cellulose microfibrils. In addition,  
659 Zollfrank and Fromm (Zollfrank and Fromm, 2009) have studied wood pyrolysis between 200 °C  
660 and 300 °C. In the range of 200°C–250 °C, they demonstrate at first a degradation of polyoses  
661 but only a disorientation of cellulose micro-fibrils away from the fibre axis; a significant evolution  
662 in cellulose structure appears only near 250 °C.

663 At the cell wall scale, nanoindentation or AFM Peak Force technology are powerful tools to  
664 study and monitor local mechanical properties of plant cell walls. The review of Eder et al. (Eder  
665 et al., 2012) thoroughly synthesis advantages and drawbacks of such investigations, mainly on  
666 wood. Other authors have investigated the impact of temperature through this route. For  
667 example Li et al. (Li et al., 2015) studied the mechanical properties of bamboo cell walls in order  
668 to link the indentation modulus and hardness with an increase in temperature. Zickler et al.  
669 (Zickler et al., 2006) studied the behaviour of pyrolysed spruce wood as a function of high  
670 temperature up to 2,400°C. They evidenced significant variations depending on the temperature  
671 range. Stanzl-Tschegg et al. (Stanzl-Tschegg et al., 2009) highlighted a slight increase of the  
672 indentation modulus with temperature but a significant increase of the hardness. This increase  
673 can be explained by a cross-linking reaction of lignin and xylan (Yin et al., 2011) and is specific  
674 of xylan type fibres (Mikshina et al., 2013). This result was confirmed by (Soccalingame et al.,  
675 2015). These authors observed wood cell wall hardening as a function of recycling cycles, the  
676 number of cycles resulting in substantial cumulated heating time (Fig.7).

677 Similar work on thermoplastic composites reinforced with flax fibres has shown different results  
678 by using nanoindentation (Bourmaud et al., 2015; Dombia et al., 2015; Gourier et al., 2017; Le  
679 Duigou et al., 2016). Flax cell walls, not lignin-rich, are considered as gelatinous cell walls,

680 generally show a decrease in their mechanical performance with temperature and process  
681 stages. The nature of its constitutive non-cellulosic polymers make it more heat sensitive than  
682 more lignified plant walls such as wood or kenaf (Fig. 7). These results were confirmed by  
683 Siniscalco et al. (Siniscalco et al., 2018) with AFM PeakForce measurements in a range of  
684 temperatures from room to 250°C.

685

686

### Figure 7

687

688 Observations at the cell wall scale are confirmed on elementary fibres. Gassan and Bledzki  
689 (Gassan and Bledzki, 2001) evidenced that tensile properties of jute and flax fibres start to be  
690 affected by temperature at around 170°C but time must also be considered. In their case an  
691 exposition time of 8 min was considered. Gourier et al. (Gourier et al., 2014), have checked the  
692 performance of the elementary flax fibres after an 8-min heating stage between room  
693 temperature and 250°C. A strong decrease in mechanical performance was observed above  
694 210°C with a reduction in modulus of 10% and strength of 30%. This decrease is mainly  
695 attributed to the degradation of the non-cellulosic matrix and not to the cellulose itself, as  
696 previously underlined. This evolution of non-cellulosic parietal polymers induces a decrease into  
697 the slipping ability of cellulose macro-fibrils and a more brittle behaviour of single fibres.  
698 Consequently a progressive drop in strain and also strength is observed. As explained in  
699 section 2 of this review, time needs also to be considered; Baley et al. (Baley et al., 2012) report  
700 a significant decrease in tensile properties of flax fibres after 12 hours at 105°C; this  
701 temperature is moderate but, conjugated with time, has approximatively the same impact as 8  
702 min at 210°C.

703

704

#### 705 **4.2. Impact of process on hygroscopic behaviour of the fibre**

706 The reliability and long-term durability of plant fibres is influenced by their structure (microfibrillar  
707 angle, the fibre diameter, fibre surface characteristics) and chemical composition (vis. cellulose,

708 hemicellulose and lignin content). Similarly, the performance of plant fibres as reinforcements  
709 also largely depends on operating environments (temperature and humidity) and the presence  
710 of surface defects and the hydrophilic nature of fibres itself (Faruk et al., 2012) (Faruk, et al.,  
711 2012). The cell walls of plant fibres are predominantly made up of a number of layers including  
712 a primary wall (the first layer deposited during cell development) and the secondary wall (S),  
713 which comprises of three sub-layers (S1, S2 and S3) as depicted in Figure 3.

714 Bast fibres such as hemp, flax, jute and kenaf need to be separated from their barks. In this  
715 process, fibrous and non-fibrous materials are separated using different processes such as  
716 retting and scutching. These process stages have significant effects on the chemical  
717 composition, cellulose structure (Mayer-Laigle et al., 2020) and overall fibre quality. Moreover,  
718 the chemical composition is influenced by the weather, growing conditions and processing  
719 techniques used, potentially generating variability in plant fibres properties. Consequently, the  
720 low maturity of plant cell walls, which manifest with large lumen sizes, as well as defects, such  
721 as kink bands, potentially initiated by aggressive extraction stages, are responsible for increase  
722 in water sensitivity of plant fibres. Despite several attractive attributes, some of the drawbacks  
723 of these fibres include high moisture uptake and moisture gain potential leading to weak fibre-  
724 matrix or fiber layer-layer interface and lower mechanical properties compared to their synthetic  
725 counterparts such as carbon and glass fibres. Thus, defects on the fibre surfaces, as depicted  
726 in Figure 5.a or 5.b, can easily be introduced during process stages hence will significantly  
727 influence the overall mechanical properties, as well as act as hot spots for moisture absorption  
728 (Le Duc et al., 2011; Placet et al., 2014).

729 Manufacturing process has a major role to play in moisture absorption behaviour. Void content  
730 in composite materials largely depend on the manufacturing methods employed. In addition to  
731 their complex structures, the void contents of natural fibre reinforced composites for example  
732 are influenced by manufacturing methods and the processing parameters used. For example, if  
733 hand lay-up, a commonly used lower-cost composites manufacturing technique, is used to  
734 fabricate the composite laminates, there are inherently higher void contents. Moreover, this  
735 technique cannot accommodate high fibre volume fraction. Whereas, if resin transfer moulding  
736 (RTM) techniques are used, then there will be less void content. Manufacturing process also

737 influences the wettability of reinforcements. When there is not enough resin to wet the fibres,  
738 there is chance of having high void content. Therefore, composites manufactured by the hand  
739 lay-up method absorb more moisture than parts produced from the RTM method. It is well  
740 accepted that high void content will promote higher moisture ingress due to higher diffusion  
741 coefficients (Celino et al., 2014; Chilali et al., 2017). Additionally, if composites for example are  
742 manufactured using the compression moulding process, then the processing parameters such  
743 as compaction pressure and temperature will significantly influence void content. If the applied  
744 compaction pressure is high, voids may increase as the individual fibre can be pressed and  
745 elongated and defects can be created, and in such a situation overall mechanical properties  
746 decrease and moisture ingress can increase.

747 Advanced manufacturing techniques such as autoclave and out-of-autoclave (OoA) play an  
748 important role in void formation and represent promising routes for plant fibre composites  
749 development. In autoclave manufacturing, voids for example can be brought to an acceptable  
750 level. It is suggested that without application of vacuum, by increasing cure temperature, voids  
751 can be reduced. However, by increasing cure pressure, voids can form. There are various  
752 factors that influence void formation in autoclave processes, including surface roughness,  
753 humidity and ply orientation (Mehdikhani et al., 2019). Alternatively, OoA process such as  
754 vacuum bag only (VBO) and vacuum assisted resin transfer moulding (VARTM), have been  
755 used in the last few decades due to expensive and high energy requirements of the autoclave  
756 process. Low capital investment, lower consumable costs, and improved energy efficiency are  
757 considered attractive attributes of OoA curing process. Literature suggests that OoA production  
758 of large parts has void contents of less than 2% (Mehdikhani et al., 2019) but (Grunenfelder and  
759 Nutt, 2010) concludes that the autoclave process can suppress void formation while for the OoA  
760 process, void volume fractions (void growth) increased exponentially as a function of moisture  
761 and humidity. It is true that void content and moisture content are an interlinked phenomenon.  
762 Consequently, the use of these moulding processes can be suitable for plant fibre composite  
763 materials processing, provided that the moisture content of the plant cell walls is controlled  
764 beforehand.

765 Indeed, plant fibre reinforced polymer composites are affected by humidity. During their service  
766 life, plant fibre composites may be exposed to extreme weather conditions. Such conditions  
767 could affect the structure of composites by disrupting the bonds between the fibres and the  
768 matrix, which in turn can reduce mechanical properties.

769 Here, it is worth noting that fibre volume fraction influences the moisture uptake percentages  
770 and diffusion coefficient (rate of moisture uptake). It is well-accepted that void content and  
771 service conditions such as humidity and extreme service conditions affect the moisture  
772 absorption behaviour of natural fibre composites. Similarly, moisture contents in the fibre  
773 (hydrophilic) promotes void contents. Additionally, fibre aspect ratio, thickness of composites  
774 and fibre orientation equally play an important role in moisture absorption of plant fibre  
775 composites (Gager et al., 2019; Réquillé et al., 2018). Void formation can be attributed to both  
776 moisture contents of the matrix and the reinforcements. Void fraction can increase significantly  
777 with increased moisture/humid environments during manufacturing. It is well established that  
778 voids in composites can severely degrade the mechanical properties, especially in the case of  
779 natural fibre composites. These are the key concerns for these reinforcements to be used fully  
780 in structural composites as reinforcements.

781 Study of water absorption and its influence on various properties is of great interest. Plant fibre  
782 reinforced composites especially have a natural tendency to absorb moisture in extreme  
783 hygroscopic conditions. Extensive studies have been carried out by (Akil et al., 2009;  
784 Almansour et al., 2017; Dhakal et al., 2007; Errajhi et al., 2005; Hu et al., 2010) on the influence  
785 of water on the various mechanical properties of different composite materials. The reported  
786 work by (Dhakal et al., 2007) for example on the effects of room and elevated temperature on  
787 hemp fibre reinforced unsaturated polyester suggests that the temperature has a significant  
788 effect on the tensile and flexural properties. Their findings highlighted that the moisture  
789 absorption was directly proportional to fibre volume fraction. Their work further concluded that  
790 the water absorption patterns of hemp/UP composites were illustrating Fickian behaviour at  
791 room temperature and displaying non-Fickian behaviours at elevated temperature.

792 The work carried out by (Hu et al., 2010) explored the effect of moisture absorption on short  
793 jute fibre reinforced PLA composites manufactured using a hydrothermal setup. In that study,  
794 they reported the changes at a microstructure level due to moisture ingress. They also linked  
795 the changes in mechanical properties due to weak fibre matrix interface due to moisture  
796 absorption. Similarly, the work undertaken by (Almansour et al., 2017) reported the moisture  
797 absorption behaviour of flax fibre reinforced vinyl ester composites and basalt fibre hybridised  
798 composites. Their work highlighted that basalt fibre hybridisation improved the water repellence  
799 of flax/vinyl ester composites significantly.

800

801 **Figure 8**

802

803 The diffusion mechanisms and the effect of geometric dimensions and the fibre orientation are  
804 further illustrated in Figure 8 (Chilali et al., 2017). It can be seen that the degradation of  
805 interfacial adhesion due to moisture absorption is significant which will significantly reduce the  
806 mechanical properties. This reduction in strength further continues due to the swelling and  
807 debonding of the fibres (Dhakal et al., 2013).

808 From the above discussions and review, one can arrive upon three key factors through which  
809 water causes changes and degradation to the fibre and composites structure and a significant  
810 reduction in overall mechanical performance. The factors are as follows:

- 811 • Water molecules diffuse through the microscopic gaps (micro-pores) between  
812 polymer chains in the fibre and the composites.
- 813 • The flaws (void and defects) and gaps pave the way for capillary transport  
814 between the fibres and the matrix.
- 815 • Swelling of the reinforced fibres, especially plant fibres, causes expansion of  
816 the micro-cracks in the matrix leading to debonding.

817 Additionally, moisture diffusion into the plant fibre composite involves displacement of water  
818 molecules from a region of high concentration to a region of lower concentration (Assarar et al.,

819 2011). This diffusion is further exacerbated through poor wetting of the fibre and surface defects  
820 leading to mechanical fatigue (Wang et al., 2006).

821 Considering the above-mentioned three key factors, moisture absorption related behaviours  
822 could be assigned into one of the following categories:

- 823 • Linear Fickian behaviour: after an initial increase due to weight gain resulting  
824 from moisture absorption, gradual equilibrium is achieved.
- 825 • Non-Fickian behaviour: after an initial increase due to weight gain resulting from  
826 moisture absorption, no equilibrium is achieved.
- 827 • Two-stage sorption: In this scenario, both Fickian and non-Fickian behaviours  
828 are observed which includes both the linear and plateau regions.

829

830

## 831 **5. Concluding discussion**

832 Through this review, we were able to highlight various major points related to the **use and**  
833 **transformation** of plant fibres as composites reinforcements. We have studied the impact of  
834 transformation processes on the mechanical performance, water absorption and also micro-  
835 scale morphology of plant fibre reinforcements. We have mainly focused on extrusion and  
836 injection processes involving thermoplastics. These allow, given the nature of the short fibre  
837 reinforcements used, a study of the morphology of the fibres. In addition, their thermoplastic  
838 nature also makes it possible to carry out recyclability studies, **the latter being an essential**  
839 **argument in** the development of future plant fibre composite materials. **It is not possible to**  
840 **design optimally performing bio-based composite materials without knowledge and**  
841 **understanding of the constituent components (vis. Fibres and matrix), and especially the**  
842 **changes in fibre properties through composite processing steps given the temperature, stress,**  
843 **moisture and time sensitive nature of plant fibres.**

844 Given the thermal sensitivity of plant fibres, the choice of matrix is essential. The thermoplastic  
845 family offers a wide range of materials with shaping temperatures suitable for plant fibres,

846 whether or not the polymers are compostable. Process time is also a major factor; from a  
847 morphological or mechanical point of view, it plays a key role in the evolution of fibre properties.  
848 A temperature indication is only useful if the exposure time is specified. A lower temperature but  
849 with a significantly longer exposure time period is often synonymous with damage to plant walls  
850 that is at least as severe as in the case of a higher temperature over shorter time period. This  
851 thermal exposure time can be modulated by paying attention to the choice of the  
852 implementation process. There are processes by induction, fibre placement or electric field that  
853 can significantly reduce the thermal exposure times of the fibres. However, they are often  
854 expensive and not always compatible with production constraints, and may require a  
855 consolidation stage. Another option to reduce **exposure time** is to choose low-viscosity polymers  
856 to facilitate fibre impregnation.

857 The latter differs according to the nature of the fibres considered; thus, plant fibres are generally  
858 classified into gelatinous cell walls (flax, hemp, nettle) or lignified walls (wood, sisal, kenaf, jute).  
859 The nature of their parietal constituents differs and so does their behaviour on thermal  
860 exposure. Local hardness or stiffness tests generally show an increase in mechanical  
861 performances for lignified walls while mechanical performance decreases with thermal exposure  
862 for gelatinous fibres. This is explained in the literature by a cross-linking of the xylane and lignin  
863 compounds with a heating stage. It is therefore possible, depending on the temperatures  
864 considered, to select fibres that will have a more stable mechanical behaviour, or even  
865 improved performance with heating.

866 In addition to mechanical performance, the hygroscopic behaviour and morphology of the fibres  
867 are affected by the transformation processes. The nature of the processes and the pressures  
868 involved will have a direct impact on the quality of the parts, their porosity rate and therefore the  
869 accessibility of water to the fibres. For example, injection moulding, or autoclave moulding for  
870 thermosetting materials, will achieve a very low porosity rate and a much higher durability, the  
871 action of water being limited in this case. The porosity and quality of the interface between the  
872 fibres and the matrix are the main damage source when using materials under variable or  
873 severe environmental conditions. From a morphological point of view, plant fibres evolve  
874 considerably in length and diameter, especially when high shear injection or extrusion



875 processes are used. The decrease in length can quickly reach 90% for fibrous elements a few  
876 mm long but given their assembly in bundles in the plant, their diameter also decreases which  
877 allows their shape factor ( $L/D$ ) to evolve. This is particularly interesting when cycles multiply,  
878 compared to glass fibres for example. Thus, plant fibre composite materials generally exhibit  
879 stable mechanical performance after recycling, due to the low evolution of the aspect ratio of  
880 their reinforcements.

881 Changes in fibre properties observed at the microscopic scale are generally caused by  
882 parameters that are difficult to control, such as stress during growth due to weather conditions.  
883 However, they have an impact on a macroscopic scale for composite materials; understanding  
884 the origin of the properties is thus a valuable aid to avoid damage during the industrial  
885 processing of plant fibres. Being the main cause of damage in plant fibres, even before their  
886 use, control of the transformation processes into plant fibre composites is a major challenge for  
887 their growing industrial development. It is necessary to respect the fibres from the moment the  
888 parts are manufactured. The availability of a range of processes and reinforcements allows  
889 relevant choices to be made and the best selection of exposure and processing times,  
890 temperatures, pressures and shear rates, as well as the nature of the reinforcements, to obtain  
891 the material best suited to the specifications. Taking these factors into account is imperative to  
892 take full advantage of the extraordinary performance of these natural materials.

893

894

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902 **Bibliography**

903

904 Akil, H.M., Cheng, L.W., Mohd Ishak, Z.A., Abu Bakar, A., Abd Rahman, M.A., 2009. Water  
905 absorption study on pultruded jute fibre reinforced unsaturated polyester composites.  
906 *Compos. Sci. Technol.* 69, 1942–1948.

907 Albrecht, K., Osswald, T., Baur, E., Meier, T., Wartzack, S., Müssig, J., 2018. Fibre Length  
908 Reduction in Natural Fibre-Reinforced Polymers during Compounding and Injection  
909 Moulding—Experiments Versus Numerical Prediction of Fibre Breakage. *J. Compos. Sci.*  
910 2, 20–37. doi:10.3390/jcs2020020

911 Almansour, F.A., Dhakal, H.N., Zhang, Z.Y., 2017. Effect of water absorption on Mode I  
912 interlaminar fracture toughness of flax/basalt reinforced vinyl ester hybrid composites.  
913 *Compos. Struct.* 168, 813–825. doi:https://doi.org/10.1016/j.compstruct.2017.02.081

914 Andersons, J., Joffe, R., 2011. Estimation of the tensile strength of an oriented flax fiber-  
915 reinforced polymer composite. *Compos. Part A Appl. Sci. Manuf.* 42, 1229–1235.  
916 doi:10.1016/j.compositesa.2011.05.005

917 Assarar, M., Scida, D., Mahi, A. El, Poilâne, C., Ayad, R., 2011. Influence of water ageing on  
918 mechanical properties and damage events of two reinforced composite materials: Flax-  
919 fibres and glass-fibres. *Mater. Des.* 32, 788–795.  
920 doi:https://doi.org/10.1016/j.matdes.2010.07.024

921 Ausias, G., Bourmaud, A., Coroller, G., Baley, C., 2013. Study of the fibre morphology stability  
922 in polypropylene-flax composites. *Polym. Degrad. Stab.* 98, 1216–1224.  
923 doi:http://dx.doi.org/10.1016/j.polymdegradstab.2013.03.006

924 Ausias, G., Bourmaud, A., Coroller, G., Baley, C., 2013. Study of the fibre morphology stability  
925 in polypropylene-flax composites. *Polym. Degrad. Stab.* 98, 1216–1224.  
926 doi:10.1016/j.polymdegradstab.2013.03.006

927 Badouard, C., Traon, F., Denoual, C., Mayer-Laigle, C., Paës, G., Bourmaud, A., 2019.  
928 Exploring mechanical properties of fully compostable flax reinforced composite filaments  
929 for 3D printing applications. *Ind. Crops Prod.* 135, 246–250.  
930 doi:https://doi.org/10.1016/j.indcrop.2019.04.049

931 Baets, J., Plastria, D., Ivens, J., Verpoest, I., 2014. Determination of the optimal flax fibre  
932 preparation for use in unidirectional flax–epoxy composites. *J. Reinf. Plast. Compos.* 33,  
933 493–502. doi:10.1177/0731684413518620

934 Baley, C., Goudenhoft, C., Gibaud, M., Bourmaud, A., 2018. Flax stems: from a specific  
935 architecture to an instructive model for bioinspired composite structures. *Bioinspir.*  
936 *Biomim.* 13, 026007. doi:10.1088/1748-3190/aaa6b7

937 Baley, C., Kervoëlen, A., Lan, M., Cartié, D., Le Duigou, A., Bourmaud, A., Davies, P., 2016.  
938 Flax/PP manufacture by automated fibre placement (AFP). *Mater. Des.* 94.  
939 doi:10.1016/j.matdes.2016.01.011

940 Baley, C., Le Duigou, A., Bourmaud, A., Davies, P., 2012. Influence of drying on the mechanical  
941 behaviour of flax fibres and their unidirectional composites. *Compos. Part A Appl. Sci.*  
942 *Manuf.* 43. doi:10.1016/j.compositesa.2012.03.005

943 Barber, N., Meylan, B., 1964. The Anisotropic Shrinkage of Wood. A Theoretical Model.  
944 *Holzforsch. - Int. J. Biol. Chem. Phys. Technol. Wood* 18, 146–156.  
945 doi:10.1515/hfsg.1964.18.5.146

946 Beaugrand, J., Berzin, F., 2013. Lignocellulosic fiber reinforced composites: Influence of  
947 compounding conditions on defibrization and mechanical properties. *J. Appl. Polym. Sci.*  
948 128, 1227–1238. doi:10.1002/app.38468

949 Beaugrand, J., Guessasma, S., Maigret, J., 2017. Does the green revolution relies on defected  
950 natural fibers? *Sci. Rep.* Submitted.

951 Beg, M.D.H., Pickering, K.L., 2008. Reprocessing of wood fibre reinforced polypropylene  
952 composites. Part I: Effects on physical and mechanical properties. *Compos. Part A Appl.*  
953 *Sci. Manuf.* 39, 1091–1100. doi:10.1016/j.compositesa.2008.04.013

954 Berzin, F., Beaugrand, J., Dobosz, S., Budtova, T., Vergnes, B., 2017. Lignocellulosic fiber  
955 breakage in a molten polymer. Part 3. Modeling of the dimensional change of the fibers  
956 during compounding by twin screw extrusion. *Compos. Part A Appl. Sci. Manuf.* 101, 422–  
957 431. doi:https://doi.org/10.1016/j.compositesa.2017.07.009

958 Berzin, F., Vergnes, B., Beaugrand, J., 2014. Evolution of lignocellulosic fibre lengths along the  
959 screw profile during twin screw compounding with polycaprolactone. *Compos. Part A Appl.*

960 Sci. Manuf. 59, 30–36. doi:10.1016/j.compositesa.2013.12.008

961 **Bhattacharyya, D., Bowis, M., Jayaraman, K., 2003. Thermoforming woodfibre–polypropylene**  
962 **composite sheets. Compos. Sci. Technol. 63, 353–365. doi:https://doi.org/10.1016/S0266-**  
963 **3538(02)00214-2**

964 Bledzki, A.K., Gassan, J., 1999. Composites reinforced with cellulose based fibres. Prog.  
965 Polym. Sci. 24, 221–274. doi:10.1016/S0079-6700(98)00018-5

966 Bourmaud, A., Åkesson, D., Beaugrand, J., Le Duigou, A., Skrifvars, M., Baley, C., 2016.  
967 Recycling of L-Poly-(lactide)-Poly-(butylene-succinate)-flax biocomposite. Polym. Degrad.  
968 Stab. 128, 77–88. doi:10.1016/j.polymdegradstab.2016.03.018

969 Bourmaud, A., Baley, C., 2010. Effects of thermo mechanical processing on the mechanical  
970 properties of biocomposite flax fibers evaluated by nanoindentation. Polym. Degrad. Stab.  
971 95. doi:10.1016/j.polymdegradstab.2010.06.022

972 Bourmaud, A., Baley, C., 2009. Rigidity analysis of polypropylene/vegetal fibre composites after  
973 recycling. Polym. Degrad. Stab. 94. doi:10.1016/j.polymdegradstab.2008.12.010

974 Bourmaud, A., Baley, C., 2007. Investigations on the recycling of hemp and sisal fibre  
975 reinforced polypropylene composites. Polym. Degrad. Stab. 92, 1034–1045.  
976 doi:10.1016/j.polymdegradstab.2007.02.018

977 Bourmaud, A., Beaugrand, J., Shah, D., Placet, V., Baley, C., 2018. Towards the design of  
978 high-performance plant fibre composites. Prog. Mater. Sci. 97, 347–408.

979 Bourmaud, A., Corre, Y.-M., Baley, C., 2015. Fully biodegradable composites: Use of poly-  
980 (butylene-succinate) as a matrix and to plasticize l-poly-(lactide)-flax blends. Ind. Crops  
981 Prod. 64, 251–257. doi:10.1016/j.indcrop.2014.09.033

982 Bourmaud, A., Corre, Y.-M.Y.-M., Baley, C., 2015. Fully biodegradable composites: Use of poly-  
983 (butylene-succinate) as a matrix and to plasticize l-poly-(lactide)-flax blends. Ind. Crops  
984 Prod. 64, 251–257. doi:10.1016/j.indcrop.2014.09.033

985 Bourmaud, A., Gibaud, M., Lefeuvre, A., Morvan, C., Baley, C., 2015. Influence of the  
986 morphology characters of the stem on the lodging resistance of Marylin flax. Ind. Crops  
987 Prod. 66, 27–37. doi:10.1016/j.indcrop.2014.11.047

988 Bourmaud, A., Le Duigou, A., Baley, C., 2011. What is the technical and environmental interest

989 in reusing a recycled polypropylene–hemp fibre composite? *Polym. Degrad. Stab.* 96,  
990 1732–1739. doi:<http://dx.doi.org/10.1016/j.polymdegradstab.2011.08.003>

991 Bourmaud, A., Mayer-Laigle, C., Baley, C., Beaugrand, J., 2019. About the frontier between  
992 filling and reinforcement by fine flax particles in plant fibre composites. *Ind. Crops Prod.*  
993 141, 111774. doi:<https://doi.org/10.1016/j.indcrop.2019.111774>

994 Castellani, R., Di Giuseppe, E., Beaugrand, J., Dobosz, S., Berzin, F., Vergnes, B., Budtova, T.,  
995 2017. Lignocellulosic fiber breakage in a molten polymer. Part 1. Qualitative analysis using  
996 rheo-optical observations *Original Research Article Composites Part A: Applied Science*  
997 *and Manufacturing*, Volume 91, Part 1, December 2016, Pages 229-237. *Compos. Part A*  
998 91, 229–237.

999 Celino, A., Freour, S., Jacquemin, F., Casari, P., 2014. The hygroscopic behavior of plant fibers:  
1000 a review. *Front. Chem.* 1. doi:10.3389/fchem.2013.00043

1001 Chilali, A., Assarar, M., Zouari, W., Kebir, H., Ayad, R., 2017. Effect of geometric dimensions  
1002 and fibre orientation on 3D moisture diffusion in flax fibre reinforced thermoplastic and  
1003 thermosetting composites. *Compos. Part A Appl. Sci. Manuf.* 95, 75–86.  
1004 doi:<https://doi.org/10.1016/j.compositesa.2016.12.020>

1005 Connelly, R.K., Kokini, J.L., 2007. Examination of the mixing ability of single and twin screw  
1006 mixers using 2D finite element method simulation with particle tracking. *J. Food Eng.* 79,  
1007 956–969. doi:<https://doi.org/10.1016/j.jfoodeng.2006.03.017>

1008 Coroller, G., Lefeuvre, A., Le Duigou, A., Bourmaud, A., Ausias, G., Gaudry, T., Baley, C., 2013.  
1009 Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional  
1010 composite. *Compos. Part A Appl. Sci. Manuf.* 51, 62–70.  
1011 doi:<http://dx.doi.org/10.1016/j.compositesa.2013.03.018>

1012 Dhakal, H.N., Zhang, Z.Y., Guthrie, R., MacMullen, J., Bennett, N., 2013. Development of  
1013 flax/carbon fibre hybrid composites for enhanced properties. *Carbohydr. Polym.* 96, 1–8.  
1014 doi:<https://doi.org/10.1016/j.carbpol.2013.03.074>

1015 Dhakal, H.N., Zhang, Z.Y., Richardson, M.O.W., 2007. Effect of water absorption on the  
1016 mechanical properties of hemp fibre reinforced unsaturated polyester composites.  
1017 *Compos. Sci. Technol.* 67, 1674–1683.

1018 Dickson, A., Teuber, L., Gaugler, M., Sandquist, D., 2020. Effect of processing conditions on  
1019 wood and glass fiber length attrition during twin screw composite compounding. *J. Appl.*  
1020 *Polym. Sci.* 137, 48551. doi:10.1002/app.48551

1021 Dickson, A.R., Even, D., Warnes, J.M., Fernyhough, A., 2014. The effect of reprocessing on the  
1022 mechanical properties of polypropylene reinforced with wood pulp, flax or glass fibre.  
1023 *Compos. Part A Appl. Sci. Manuf.* 61, 258–267. doi:10.1016/j.compositesa.2014.03.010

1024 Doumbia, A.S., Castro, M., Jouannet, D., Kervoëlen, A., Falher, T., Cauret, L., Bourmaud, A.,  
1025 2015. Flax/polypropylene composites for lightened structures: Multiscale analysis of  
1026 process and fibre parameters. *Mater. Des.* 87. doi:10.1016/j.matdes.2015.07.139

1027 Duc, F., Bourban, P.E., Plummer, C.J.G., Månson, J.-A.E., 2014. Damping of thermoset and  
1028 thermoplastic flax fibre composites. *Compos. Part A Appl. Sci. Manuf.* 64, 115–123.  
1029 doi:10.1016/j.compositesa.2014.04.016

1030 Duigou, A. Le, Castro, M., Bevan, R., Martin, N., 2016. 3D printing of wood fibre biocomposites:  
1031 From mechanical to actuation functionality. *Mater. Des.* 96, 106–114.  
1032 doi:https://doi.org/10.1016/j.matdes.2016.02.018

1033 Eder, M., Arnould, O., Dunlop, J.W.C., Hornatowska, J., Salmen, L., 2012. Experimental  
1034 micromechanical characterisation of wood cell walls. *Wood Sci. Technol.*

1035 El-Sabbagh, A., 2014. Effect of coupling agent on natural fibre in natural fibre/polypropylene  
1036 composites on mechanical and thermal behaviour. *Compos. Part B Eng.* 57, 126–135.  
1037 doi:10.1016/j.compositesb.2013.09.047

1038 Errajhi, O.A.Z., Osborne, J.R.F., Richardson, M.O.W., Dhakal, H.N., 2005. Water absorption  
1039 characteristics of aluminised E-glass fibre reinforced unsaturated polyester composites.  
1040 *Compos. Struct.* 71, 333–336. doi:https://doi.org/10.1016/j.compstruct.2005.09.008

1041 Esau, K., 1953. *Plant Anatomy*. Wiley, New York.

1042 Faruk, O., Bledzki, A., Fink, H.-P., Sain, M., 2012. Biocomposites reinforced with natural fibers:  
1043 2000-2010. *Prog. Polym. Sci.* 37, 1552–1587.

1044 Fuentes, C.A., Willekens, P., Petit, J., Thouminot, C., Müssig, J., Trindade, L.M., Van Vuure,  
1045 A.W., 2017. Effect of the middle lamella biochemical composition on the non-linear  
1046 behaviour of technical fibres of hemp under tensile loading using strain mapping. *Compos.*

1047 Part A Appl. Sci. Manuf. 101, 529–542. doi:10.1016/J.COMPOSITESA.2017.07.017

1048 Gager, V., Duigou, A. Le, Bourmaud, A., Pierre, F., Behlouli, K., Baley, C., 2019. Understanding  
1049 the effect of moisture variation on the hygromechanical properties of porosity-controlled  
1050 nonwoven biocomposites. Polym. Test. 78, 105944.  
1051 doi:<https://doi.org/10.1016/j.polymertesting.2019.105944>

1052 Gallos, A., Paes, G., Legland, D., Allais, F., Beaugrand, J., 2017. Exploring the microstructure  
1053 of natural fibre composites by confocal Raman imaging and image analysis. Compos. Part  
1054 A Appl. Science Manuf. 94, 32–40.

1055 Gallos, A., Paes, G., Legland, D., Allais, F., Beaugrand, J., Paes, G., Legland, D., Allais, F.,  
1056 Beaugrand, J., 2017. Exploring the microstructure of natural fibre composites by confocal  
1057 Raman imaging and image analysis 94, 32–40. doi:10.1016/j.compositesa.2016.12.005

1058 Gassan, J., Bledzki, A.K., 2001. Thermal degradation of flax and jute fibers. J. Appl. Polym. Sci.  
1059 82, 1417–1422. doi:10.1002/app.1979

1060 Gogoi, B., A.J, O., Choudhury, G., 1996. Reverse Screw Element(s) and Feed Composition  
1061 Effects during Twin-Screw Extrusion of Rice Flour and Fish Muscle Blends. J. Food Sci.  
1062 61, 590–595. doi:10.1111/j.1365-2621.1996.tb13165.x

1063 Gorshkova, T., Brutch, N., Chabbert, B., Deyholos, M., Hayashi, T., Lev-Yadun, S., Mellerowicz,  
1064 E.J., Morvan, C., Neutelings, G., Pilate, G., 2012. Plant Fiber Formation: State of the Art,  
1065 Recent and Expected Progress, and Open Questions. CRC. Crit. Rev. Plant Sci. 31, 201–  
1066 228.

1067 Gourier, C., Bourmaud, A., Le Duigou, A., Baley, C., 2017. Influence of PA11 and PP  
1068 thermoplastic polymers on recycling stability of unidirectional flax fibre reinforced  
1069 biocomposites. Polym. Degrad. Stab. 136. doi:10.1016/j.polymdegradstab.2016.12.003

1070 Gourier, C., Le Duigou, A., Bourmaud, A., Baley, C., 2014. Mechanical analysis of elementary  
1071 flax fibre tensile properties after different thermal cycles. Compos. Part A Appl. Sci. Manuf.  
1072 64. doi:10.1016/j.compositesa.2014.05.006

1073 Graupner, N., Fischer, H., Ziegmann, G., Müssig, J., 2014. Improvement and analysis of  
1074 fibre/matrix adhesion of regenerated cellulose fibre reinforced PP-, MAPP- and PLA-  
1075 composites by the use of Eucalyptus globulus lignin. Compos. Part B Eng. 66, 117–125.

1076 doi:10.1016/j.compositesb.2014.05.002

1077 Grishanov, S.A., Harwood, R.J., Booth, I., 2006. A method of estimating the single flax fibre  
1078 fineness using data from the LaserScan system. *Ind. Crops Prod.* 23, 273–287.  
1079 doi:10.1016/j.indcrop.2005.08.003

1080 Grunenfelder, L.K., Nutt, S.R., 2010. Void formation in composite prepregs – Effect of dissolved  
1081 moisture. *Compos. Sci. Technol.* 70, 2304–2309.  
1082 doi:https://doi.org/10.1016/j.compscitech.2010.09.009

1083 Guessasma, S., Beaugrand, J., 2019. Damage Kinetics at the Sub-micrometric Scale in Bast  
1084 Fibers Using Finite Element Simulation and High-Resolution X-Ray Micro-Tomography.  
1085 *Front. Plant Sci.* 10, 194. doi:10.3389/fpls.2019.00194

1086 Haag, K., Padovani, J., Fita, S., Trouvé, J.-P., Pineau, C., Hawkins, S., De Jong, H., Deyholos,  
1087 M.K., Chabbert, B., Müssig, J., Beaugrand, J., 2017. Influence of flax fibre variety and  
1088 year-to-year variability on composite properties. *Ind. Crops Prod.* 98, 1–9.  
1089 doi:10.1016/j.indcrop.2016.12.028

1090 Hamdi, S.E., Delisée, C., Malvestio, J., Beaugrand, J., Berzin, F., 2018. Monitoring the  
1091 Diameter Changes of Flax Fibre Elements during Twin Screw Extrusion Using X-Ray  
1092 Computed Micro-Tomography. *J. Nat. Fibers* 0, 1–12.  
1093 doi:10.1080/15440478.2018.1558149

1094 Hamdi, S.E., Delisée, C., Malvestio, J., Da Silva, N., Le Duc, A., Beaugrand, J., 2015. X-ray  
1095 computed microtomography and 2D image analysis for morphological characterization of  
1096 short lignocellulosic fibers raw materials: A benchmark survey. *Compos. Part A Appl. Sci.*  
1097 *Manuf.* 76, 1–9. doi:10.1016/j.compositesa.2015.04.019

1098 Hill, C.A.S., Norton, A., Newman, G., 2009. The Water Vapor Sorption Behavior of Natural  
1099 Fibers. *J. Appl. Polym. Sci.* 112, 1524–1537. doi:10.1002/app.29725

1100 Hu, R.-H., Sun, M., Lim, J.-K., 2010. Moisture absorption, tensile strength and microstructure  
1101 evolution of short jute fiber/poly lactide composite in hygrothermal environment. *Mater.*  
1102 *Des.* 31, 3167–3173.

1103 Hughes, M., 2012. Defects in natural fibres: their origin, characteristics and implications for  
1104 natural fibre-reinforced composites. *J. Mater. Sci.* 47, 599–609. doi:10.1007/s10853-011-



- 1105 6025-3
- 1106 Kvavadze, E., Bar-Yosef, O., Belfer-Cohen, A., Boaretto, E., Jakeli, N., Matskevich, Z.,  
1107 Meshveliani, T., 2009. 30,000-Year-Old Wild Flax Fibers. *Science* (80- ). 325, 1359.
- 1108 Le Duc, A., Vergnes, B., Budtova, T., 2011. Polypropylene/natural fibres composites: Analysis  
1109 of fibre dimensions after compounding and observations of fibre rupture by rheo-optics.  
1110 *Compos. Part A Appl. Sci. Manuf.* 42, 1727–1737.  
1111 doi:<http://dx.doi.org/10.1016/j.compositesa.2011.07.027>
- 1112 Le Duigou, A., Bourmaud, A., Gourier, C., Baley, C., 2016. Multi-scale shear properties of flax  
1113 fibre reinforced polyamide 11 biocomposites. *Compos. Part A Appl. Sci. Manuf.* 85.  
1114 doi:10.1016/j.compositesa.2016.03.014
- 1115 Le Duigou, A., Pillin, I., Bourmaud, A., Davies, P., Baley, C., 2008. Effect of recycling on  
1116 mechanical behaviour of biocompostable flax/poly(l-lactide) composites. *Compos. Part A*  
1117 39, 1471–1478. doi:10.1016/j.compositesa.2008.05.008
- 1118 Le Moigne, N., van den Oever, M., Budtova, T., 2013. Dynamic and capillary shear rheology of  
1119 natural fiber-reinforced composites. *Polym. Eng. Sci.* 53, 2582–2593.  
1120 doi:10.1002/pen.23521
- 1121 Legland, D., Beaugrand, J., 2013. Automated clustering of lignocellulosic fibres based on  
1122 morphometric features and using clustering of variables. *Ind. Crops Prod.* 45, 253–261.  
1123 doi:10.1016/j.indcrop.2012.12.021
- 1124 Lekube, B.M., Purgleitner, B., Renner, K., Burgstaller, C., 2019. Influence of screw configuration  
1125 and processing temperature on the properties of short glass fiber reinforced polypropylene  
1126 composites. *Polym. Eng. Sci.* 59, 1552–1559. doi:10.1002/pen.25153
- 1127 Lertwimolnun, W., Vergnes, B., 2007. Influence of screw profile and extrusion conditions on the  
1128 microstructure of polypropylene/organoclay nanocomposites. *Polym. Eng. Sci.* 47, 2100–  
1129 2109. doi:10.1002/pen.20934
- 1130 Leuwin, M., 2007. *Handbook of fiber chemistry*, Boca Raton. ed.
- 1131 Li, Y., Yin, L., Huang, C., Meng, Y., Fu, F., Wang, S., Wu, Q., 2015. Quasi-static and dynamic  
1132 nanoindentation to determine the influence of thermal treatment on the mechanical  
1133 properties of bamboo cell walls. *Holzforschung* 69. doi:10.1515/hf-2014-0112

1134 Liang, S., Nouri, H., Lafranche, E., 2015. Thermo-compression forming of flax fibre-reinforced  
1135 polyamide 6 composites: influence of the fibre thermal degradation on mechanical  
1136 properties. *J. Mater. Sci.* 50, 7660–7672. doi:10.1007/s10853-015-9330-4

1137 Lucas, P.W., Tan, H.T.W., Cheng, P.Y., 1997. The toughness of secondary cell wall and woody  
1138 tissue. *Philos. Trans. R. Soc. B-Biological Sci.* 352, 341–352.

1139 Madsen, B., Lilholt, H., 2003. Physical and mechanical properties of unidirectional plant fibre  
1140 composites—an evaluation of the influence of porosity. *Compos. Sci. Technol.* 63, 1265–  
1141 1272. doi:10.1016/S0266-3538(03)00097-6

1142 Mayer-Laigle, C., Bourmaud, A., Shah, D.U., Follain, N., Beaugrand, J., 2020. Unravelling the  
1143 consequences of ultra-fine milling on physical and chemical characteristics of flax fibres.  
1144 *Powder Technol.* 360, 129–140. doi:https://doi.org/10.1016/j.powtec.2019.10.024

1145 McGregor, O.P.L., Duhovic, M., Somashekar, A.A., Bhattacharyya, D., 2017. Pre-impregnated  
1146 natural fibre-thermoplastic composite tape manufacture using a novel process. *Compos.*  
1147 *Part A Appl. Sci. Manuf.* 101, 59–71.  
1148 doi:https://doi.org/10.1016/j.compositesa.2017.05.025

1149 Mehdikhani, M., Gorbatikh, L., Verpoest, I., Lomov, S. V, 2019. Voids in fiber-reinforced polymer  
1150 composites: A review on their formation, characteristics, and effects on mechanical  
1151 performance. *J. Compos. Mater.* 53, 1579–1669. doi:10.1177/0021998318772152

1152 Mikshina, P., Chernova, T., Chemikosova, S., Ibragimova, N., Mokshina, N., Gorshkova, T.,  
1153 2013. Cellulosic Fibres: Role of Matrix Polysaccharides in Structure and Function. *Cellul. -*  
1154 *Fundam. Asp.* 91–112.

1155 Mohanty, A.K., Misra, M., Drzal, L.T., 2005. *Natural Fibers, Biopolymers, and Biocomposites.*  
1156 CRC Press.

1157 Mohanty, A.K., Vivekanandhan, S., Pin, J.-M., Misra, M., 2018. Composites from renewable and  
1158 sustainable resources: Challenges and innovations. *Science (80- )*. 362, 536–542.  
1159 doi:10.1126/science.aat9072

1160 Mokshina, N., Chernova, T., Galinovsky, D., Gorshkov, O., Gorshkova, T., 2018. Key Stages of  
1161 Fiber Development as Determinants of Bast Fiber Yield and Quality. *Fibers* 6.  
1162 doi:10.3390/fib6020020

- 1163 Mukherjee, P.S., Satyanarayana, K.G., 1986. Structure and properties of some vegetable fibres.  
1164 J. Mater. Sci. 21, 51–56. doi:10.1007/BF01144698
- 1165 Müssig, J., Stevens, C., 2010. Industrial application of natural fibres : structure, properties, and  
1166 technical applications. Wiley & Sons.
- 1167 Nyström, B., Joffe, R., Långström, R., 2007. Microstructure and Strength of Injection Molded  
1168 Natural Fiber Composites. J. Reinf. Plast. Compos. 26, 579–599.  
1169 doi:10.1177/0731684407075536
- 1170 Oksman, K., Mathew, A.A.P., Långström, R., Nyström, B., Joseph, K., Langstrom, R., Nystrom,  
1171 R., Joseph, K., 2009. The influence of fibre icrostructure on fibre breakage and mechanical  
1172 properties of natural fibre reinforced polypropylene. Compos. Sci. Technol., Experimental  
1173 Techniques and Design in Composite Materials (ETDCM8) with Regular Papers 69, 1847–  
1174 1853. doi:10.1016/j.compscitech.2009.03.020
- 1175 Padovani, J., Legland, D., Pernes, M., Gallos, A., Thomachot-Schneider, C., Shah, D.U.,  
1176 Bourmaud, A., Beaugrand, J., 2019. Beating of hemp bast fibres: an examination of a  
1177 hydro-mechanical treatment on chemical, structural, and nanomechanical property  
1178 evolutions. Cellulose 26, 5665–5683. doi:10.1007/s10570-019-02456-3
- 1179 Pantaloni, D., Shah, D., Baley, C., Bourmaud, A., 2020. Monitoring of mechanical performances  
1180 of flax non-woven biocomposites during a home compost degradation. Polym. Degrad.  
1181 Stab. 177, 109166. doi:https://doi.org/10.1016/j.polymdegradstab.2020.109166
- 1182 Paris, O., Zollfrank, C., Zickler, G.A., 2005. Decomposition and carbonisation of wood  
1183 biopolymers—a microstructural study of softwood pyrolysis. Carbon N. Y. 43, 53–66.  
1184 doi:10.1016/j.carbon.2004.08.034
- 1185 Peltola, H., Madsen, B., Joffe, R., Nättinen, K., 2011. Experimental Study of Fiber Length and  
1186 Orientation in Injection Molded Natural Fiber/Starch Acetate Composites. Adv. Mater. Sci.  
1187 Eng. 2011, 1001–1007. doi:10.1155/2011/891940
- 1188 Pickering, K., Rowell, R.M., 2008. Properties and Performance of Natural-Fibre Composites,  
1189 Properties and Performance of Natural-Fibre Composites. Elsevier.  
1190 doi:10.1533/9781845694593.1.3
- 1191 Pickering, K.L., Efendy, M.G.A., Le, T.M., 2016. A review of recent developments in natural fibre

1192 composites and their mechanical performance. *Compos. Part A Appl. Sci. Manuf.* 83, 98–  
1193 112. doi:<https://doi.org/10.1016/j.compositesa.2015.08.038>

1194 Placet, V., 2009. Characterization of the thermo-mechanical behaviour of Hemp fibres intended  
1195 for the manufacturing of high performance composites. *Compos. Part A Appl. Sci. Manuf.* -  
1196 Spec. Issue 15th French Natl. Conf. Compos. - JNC15 40, 1111–1118.

1197 Placet, V., Cissé, O., Lamine Boubakar, M., 2014. Nonlinear tensile behaviour of elementary  
1198 hemp fibres. Part I: Investigation of the possible origins using repeated progressive  
1199 loading with in situ microscopic observations. *Compos. Part A Appl. Sci. Manuf.* 56, 319–  
1200 327. doi:[10.1016/j.compositesa.2012.11.019](https://doi.org/10.1016/j.compositesa.2012.11.019)

1201 Puglia, D., Terenzi, A., Barbosa, S.E., Kenny, J.M., 2008. Polypropylene-natural fibre  
1202 composites. Analysis of fibre structure modification during compounding and its influence  
1203 on the final properties. *Compos. Interfaces* 15, 111–129.  
1204 doi:[10.1163/156855408783810849](https://doi.org/10.1163/156855408783810849)

1205 Pushkin, S.A., Kozlova, L. V., Makarov, A.A., Grachev, A.N., Gorshkova, T.A., 2015. Cell wall  
1206 components in torrefied softwood and hardwood samples. *J. Anal. Appl. Pyrolysis* 116,  
1207 102–113. doi:[10.1016/j.jaap.2015.09.020](https://doi.org/10.1016/j.jaap.2015.09.020)

1208 Ramakrishnan, K.R., Moigne, N. Le, Almeida, O. De, Regazzi, A., Corn, S., 2019. Optimized  
1209 manufacturing of thermoplastic biocomposites by fast induction-heated compression  
1210 moulding: Influence of processing parameters on microstructure development and  
1211 mechanical behaviour. *Compos. Part A Appl. Sci. Manuf.* 124, 105493.  
1212 doi:<https://doi.org/10.1016/j.compositesa.2019.105493>

1213 Réquillé, S., Goudenhoft, C., Bourmaud, A., Le Duigou, A., Baley, C., 2018. Exploring the link  
1214 between flexural behaviour of hemp and flax stems and fibre stiffness. *Ind. Crops Prod.*  
1215 113. doi:[10.1016/j.indcrop.2018.01.035](https://doi.org/10.1016/j.indcrop.2018.01.035)

1216 Rihouey, C., Paynel, F., Gorshkova, T., Morvan, C., 2017. Flax fibers: assessing the non-  
1217 cellulosic polysaccharides and an approach to supramolecular design of the cell wall.  
1218 *Cellulose* 24, 1985–2001. doi:DOI: [10.1007/s10570-017-1246-5](https://doi.org/10.1007/s10570-017-1246-5)

1219 Sallih, N., Lescher, P., Bhattacharyya, D., 2014. Factorial study of material and process  
1220 parameters on the mechanical properties of extruded kenaf fibre/polypropylene composite

1221 sheets. *Compos. Part A Appl. Sci. Manuf.* 61, 91–107.

1222 doi:<https://doi.org/10.1016/j.compositesa.2014.02.014>

1223 Shah, D., Nag, N., Clifford, M., 2016. Why do we observe significant differences between  
1224 measured and 'back-calculated' properties of natural fibres? *Cellulose* 23, 1481–1490.  
1225 doi:10.1007/s10570-016-0926-x

1226 Shah, D.U., 2013. Developing plant fibre composites for structural applications by optimising  
1227 composite parameters: a critical review. *J. Mater. Sci.* 48, 6083–6107.  
1228 doi:10.1007/s10853-013-7458-7

1229 Shah, D.U., Clifford, M.J., 2015. Compaction, permeability and flow simulation for liquid  
1230 composite moulding of natural fibre composites, in: Springer-Verlag, M. (Ed.),  
1231 Manufacturing of Natural Fibre Reinforced Polymer Composites. Springer, New-York,  
1232 USA.

1233 Shon, K., White, J.L., 1999. A comparative study of fiber breakage in compounding glass fiber-  
1234 reinforced thermoplastics in a buss kneader, modular Co-rotating and counter-rotating twin  
1235 screw extruders. *Polym. Eng. Sci.* 39, 1757–1768. doi:10.1002/pen.11570

1236 Siniscalco, D., Arnould, O., Bourmaud, A., Le Duigou, A., Baley, C., 2018. Monitoring  
1237 temperature effects on flax cell-wall mechanical properties within a composite material  
1238 using AFM. *Polym. Test.* 69. doi:10.1016/j.polymertesting.2018.05.009

1239 Soccalingame, L., Bourmaud, A., Perrin, D., Bénézet, J.-C., Bergeret, A., 2015. Reprocessing of  
1240 wood flour reinforced polypropylene composites: Impact of particle size and coupling  
1241 agent on composite and particle properties. *Polym. Degrad. Stab.* 113, 72–85.  
1242 doi:10.1016/j.polymdegradstab.2015.01.020

1243 Stanzl-Tschegg, S., Beikircher, W., Loidl, D., 2009. Comparison of mechanical properties of  
1244 thermally modified wood at growth ring and cell wall level by means of instrumented  
1245 indentation tests. *Holzforschung* 63.

1246 Subasinghe, A.D.L., Das, R., Bhattacharyya, D., 2015. Fiber dispersion during  
1247 compounding/injection molding of PP/kenaf composites: Flammability and mechanical  
1248 properties. *Mater. Des.* 86, 500–507. doi:<https://doi.org/10.1016/j.matdes.2015.07.126>

1249 Tanguy, M., Bourmaud, A., Baley, C., 2016. Plant cell walls to reinforce composite materials:

- 1250 Relationship between nanoindentation and tensile modulus. *Mater. Lett.* 167, 161–164.  
1251 doi:10.1016/j.matlet.2015.12.167
- 1252 Tanguy, M., Bourmaud, A., Beaugrand, J., Gaudry, T., Baley, C., 2018. Polypropylene  
1253 reinforcement with flax or jute fibre; Influence of microstructure and constituents properties  
1254 on the performance of composite. *Compos. Part B Eng.* 139, 64–74.  
1255 doi:10.1016/j.compositesb.2017.11.061
- 1256 Teuber, L., Militz, H., Krause, A., 2016. Dynamic particle analysis for the evaluation of particle  
1257 degradation during compounding of wood plastic composites. *Compos. Part A Appl. Sci.*  
1258 *Manuf.* 84, 464–471. doi:https://doi.org/10.1016/j.compositesa.2016.02.028
- 1259 Thygesen, A., Madsen, B., Bjerre, A.B.A.B., Lilholt, H., 2011. Cellulosic Fibers: Effect of  
1260 Processing on Fiber Bundle Strength. *J. Nat. Fibers* 8, 161–175.  
1261 doi:10.1080/15440478.2011.602236
- 1262 Van Dam, J.E.G., Gorshkova, T.A., 2003. Encyclopedia of Applied Plant Sciences, in:  
1263 Encyclopedia of Applied Plant Sciences. Elsevier, pp. 87–96. doi:10.1016/B0-12-227050-  
1264 9/00046-6
- 1265 Velde, K. Van de, Baetens, E., 2001. Thermal and Mechanical Properties of Flax Fibres as  
1266 Potential Composite Reinforcement. *Macromol. Mater. Eng.* 286, 342–349.
- 1267 Volfson, S., Fayzullin, I., Musin, I., Fayzullin, A., Grachev, A., Pushkin, S., 2015. The  
1268 physicomechanical and rheological characteristics of wood–polymer composites based on  
1269 thermally and mechanically modified ller. *Plast. Massy* 5–6, 39–43.
- 1270 Wang, W., Sain, M., Cooper, P.A., 2006. Study of moisture absorption in natural fiber plastic  
1271 composites. *Compos. Sci. Technol.* 66, 379–386.  
1272 doi:https://doi.org/10.1016/j.compscitech.2005.07.027
- 1273 Wasteneys, G.O., Galway, M.E., 2003. Remodeling the Cytoskeleton for Growth and Form: An  
1274 Overview with Some New Views. *Annu. Rev. Plant Biol.* 54, 691–722.  
1275 doi:10.1146/annurev.arplant.54.031902.134818
- 1276 Yin, Y., Berglund, L., Salmén, L., 2011. Effect of Steam Treatment on the Properties of Wood  
1277 Cell Walls. *Biomacromolecules* 12, 194–202. doi:10.1021/bm101144m
- 1278 Zickler, G., Schoberl, T., Paris O, 2006. Mechanical properties of pyrolysed wood: a

1279            nanoindentation study. *Philos. Mag.* 86, 1373–1386.

1280    Zollfrank, C., Fromm, J., 2009. Ultrastructural development of the softwood cell wall during

1281            pyrolysis. *Holzforschung* 63. doi:10.1515/HF.2009.031

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1286 **Figure Caption**

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1288 **Figure 1.** Range of applied pressures and processing times conventionally used for  
1289 various bio-based composites processing techniques.

1290

1291 **Figure 2.** Geometric and tensile mechanical properties of various plant fibres. (a) length-  
1292 diameter ranges of natural fibres is presented, with lines of different slopes representing  
1293 different fibre aspect ratio ( $l/d$ ). (b) strength-stiffness ranges of plant fibres is presented,  
1294 with generic grouping based on fibre origins. Plots illustrated with data from (Bourmaud  
1295 et al., 2018; Leuwin, 2007; Shah, 2013).

1296

1297 **Figure 3.** Schematic drawing of an elementary flax fibre; PCW = primary cell wall; SCW  
1298 = secondary cell wall with three layers: S1, S2 and S3; TZ = Transition zone between  
1299 S1-S2 and S2-S3 (a). (b) gives details on the transition zones and of the number of  
1300 structural layers for each cell wall layer (Baley et al., 2018; Bledzki and Gassan, 1999).

1301

1302 **Figure 4.** A hemp bundle imaged undergoing the decohesion damage mechanism (the  
1303 'calamar' shape). Imaged under UV excitation.

1304

1305 **Figure 5.** Plant fibre-breakage mechanisms during a process cycle. In a) at the beginning  
1306 of the process cycle, one can observe both bundle decohesion and fragmentation due  
1307 to transverse break (see arrows decohesion and broken). In b) evidence of several types  
1308 of damages highlighted by stars. c) evidences surface flaws and d) is a view of an end  
1309 of an over processing which lead to an enrichment of fine elements.

1310

1311 **Figure 6.** Evolution in the length, diameter, aspect ratio, indentation modulus and  
1312 hardness of the fibres as well as the fine particles content with the number of recycling  
1313 cycles. Example of a PLLA-PBS-flax fibre injected composite (Bourmaud et al., 2016).  
1314 Axis shows the relative evolution of fibre properties (in percent) compared to raw fibre  
1315 ones.

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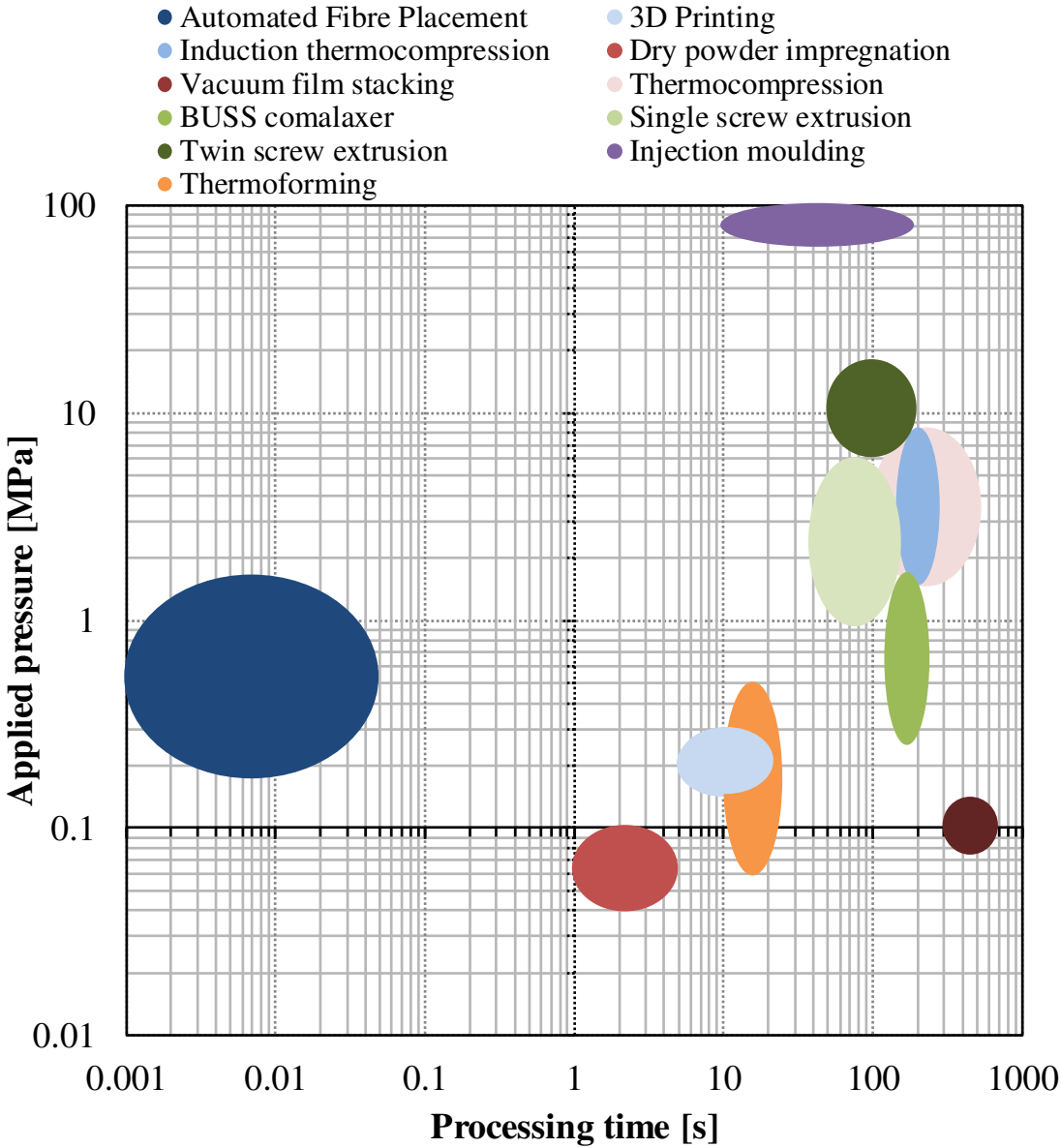
1317 **Figure 7.** Illustration of differences in cell wall composition with the examples of wood  
1318 and flax and impact on mechanical behaviour after seven injection moulding cycles.  
1319 Inspired from (Bourmaud et al., 2016; Mikshina et al., 2013; Rihouey et al., 2017;  
1320 Soccalingame et al., 2015; Yin et al., 2011)

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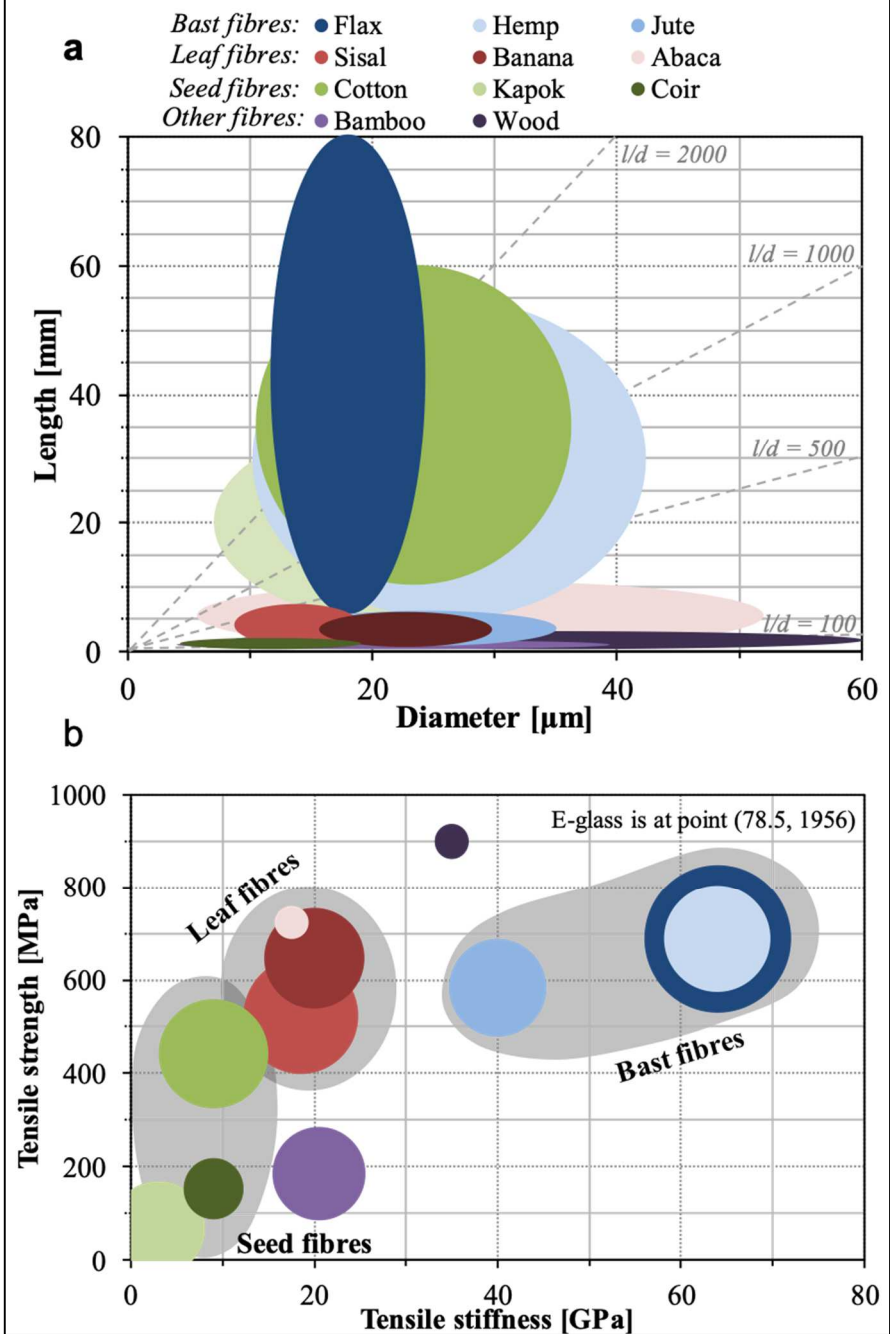


1322 **Figure 8.** The diffusion mechanisms are illustrated: (a) micro-cracks present in resin; (b)  
1323 water molecules reaching in the fibre-matrix interface, and (c) filling the hollow part of  
1324 the flax fibre lumen (Chilali et al 2017). Diffusion phenomenon occurs also through the  
1325 direction of fibres; (d) water molecules ingress by capillarity through the micro-cracks  
1326 present at the fibre-matrix interface and through lumen; (e) micro-cracks present in resin  
1327 and at the fibre matrix interface; (f) fibre swelling and matrix radial cracking (Chilali et al.,  
1328 2017).  
1329

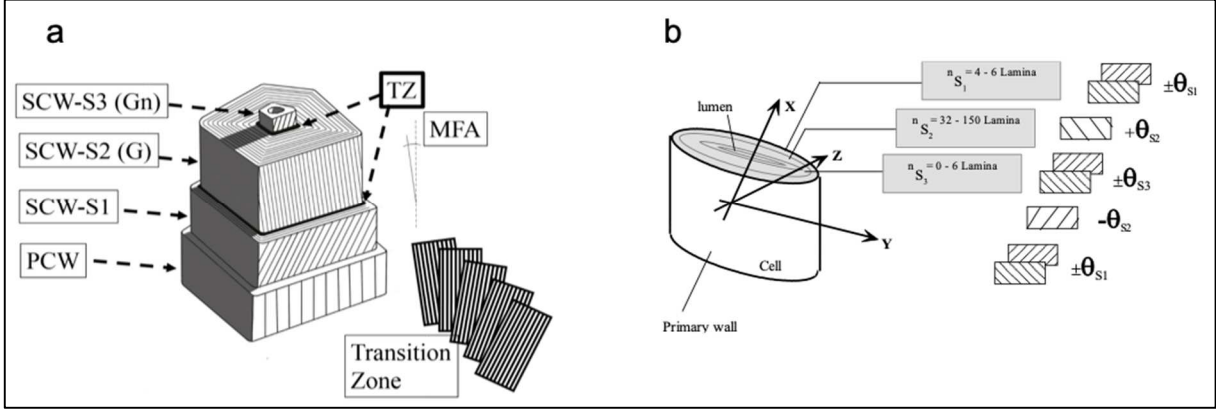
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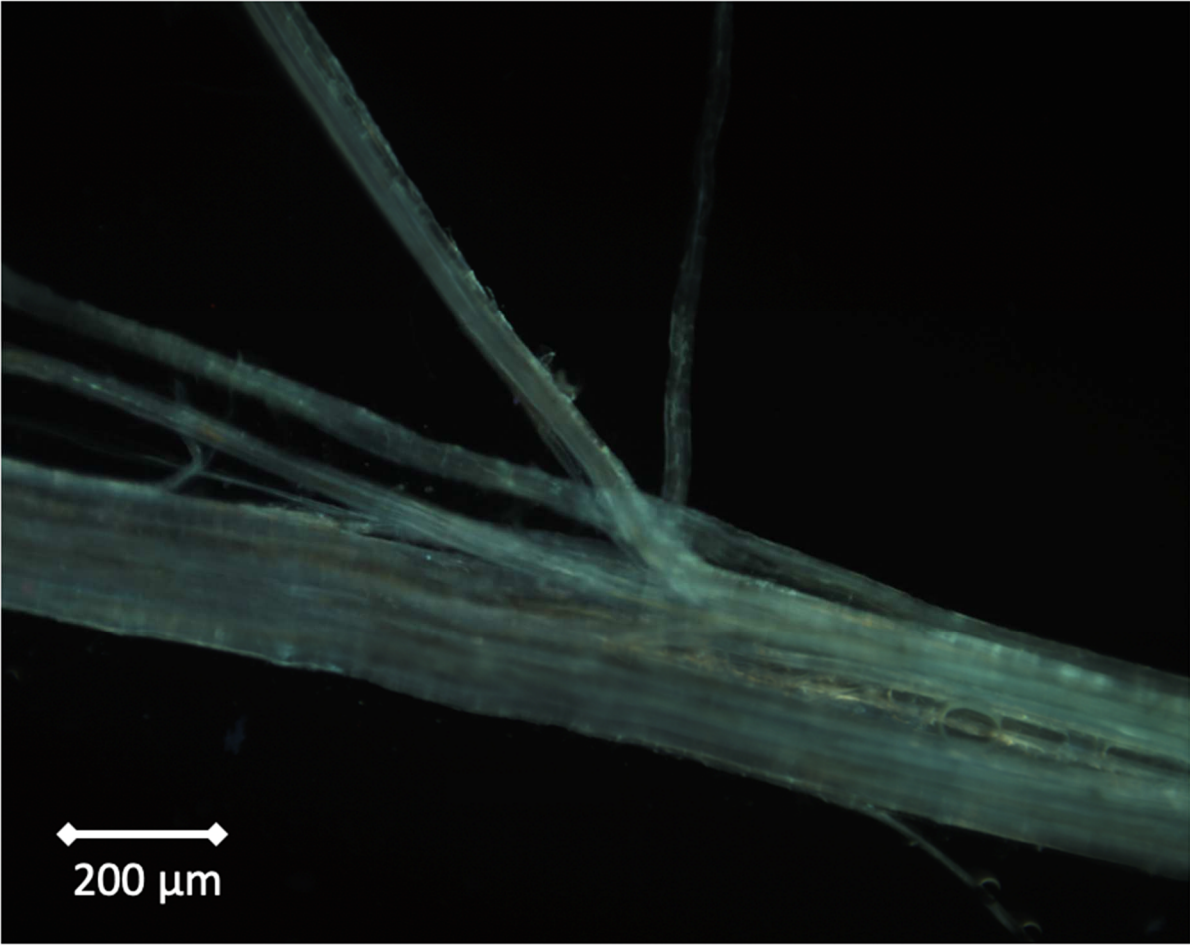
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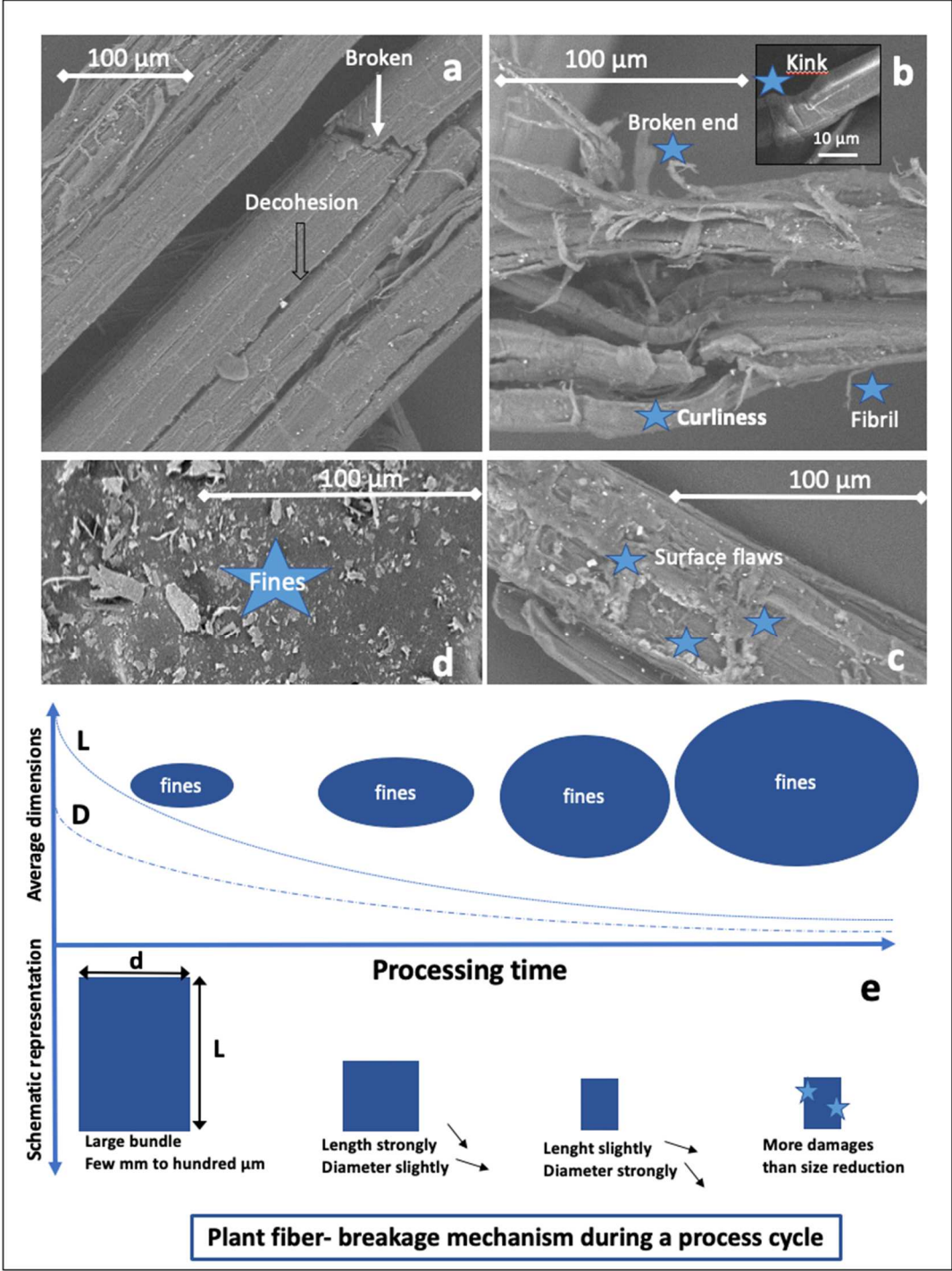


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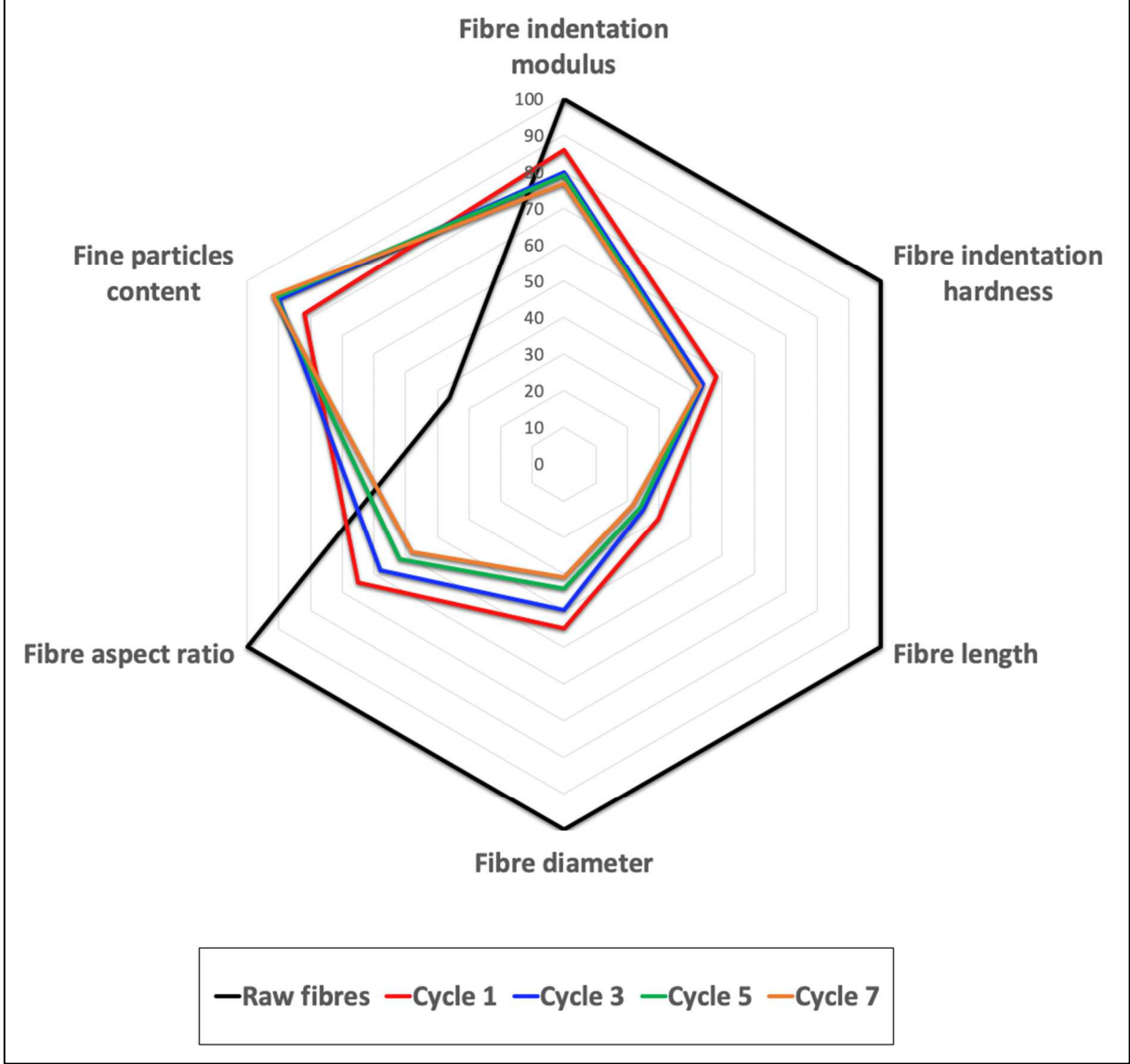


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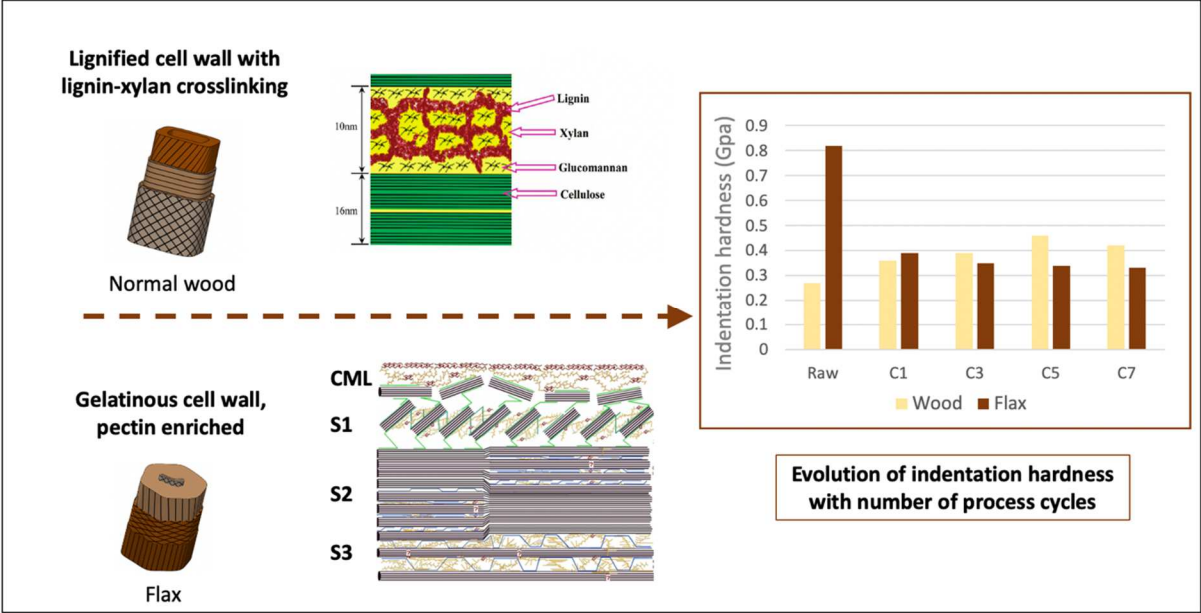
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