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1 Physico-mechanical performances of flax fiber biobased composites: Retting and process effects

2
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11 Abstract

12
13 This research aimed to evaluate the effect of retting (3 levels were concerned) and processing parameters
14 (mainly temperature) on physico-chemical properties of flax-epoxy materials. 9 biobased composites were
15 produced with 3 different processing programs: Setup 1, 2, and 3. An advanced organoleptic study has
16 been carried out on both technical flax fibers and manufactured composites to study in more detail the
17 effects of the processing and retting on the visual aspect. Organoleptic analysis shows that flax, as well as
18 biobased composites, lose saturation and luminance by increasing retting time. Increasing the processing
19 temperature alters the material color. According to SEM analysis, we highlight that the least retted fibers
20 are presented in bundles that are well bonded and coated with each other to form a technical fiber.
21 Depending on retting, technical fibers appear cleaner and more individualized but their mechanical
22 properties are affected. An interesting approach has been applied for the determination of the volumic
23 content of our biobased composites, using both TGA and pycnometer methods. On average, V_f decreases
24 from 63.1% for early retting (-) to 51.5% for late retting (+). This effect could naturally result from the
25 observed individualization of the fibers. Moreover, the porosity rates V_p increase overall with fiber
26 content. On average it varies from 5 to 11% in function of retting. Setup 3, with a processing temperature
27 of 160°C, a processing time of 130 minutes and a processing pressure of 50 bars, is the most desirable
28 because it allows the highest V_f for the lowest V_p . Regarding the mechanical behavior of biobased
29 composites, we have observed a non-elastic behavior of our stress-strain curves, due to the intrinsic
30 behavior of flax fibers. Stress vs strain curves reveal 3 different areas for elastic and plastic transitions. It
31 also appears that setup 3 provides the best modulus of elasticity compared to the other setups. We notice
32 also that E1 Young's modulus gradually increases with retting. By performing a normalization of E1
33 modulus according to the fiber volume, the effect of retting is even more pronounced. A 40% increase in
34 modulus can be observed between retting (-) and (+). At the end, the long retting level of technical flax
35 fibers, as well as the third setup gives the best compromise for our bio based composite performances.

36 Keywords

37
38 flax morphology, retting effect, flax biobased materials, mechanical performances (elasticity and rigidity),
39 porosity rate

40 1. Introduction

41
42
43 In a context of emerging bioeconomy and sustainable development, biocomposites materials represent a
44 niche in the industrial sector with strong dynamic growth. Materials science no longer counts the number
45 of studies devoted to it. These materials have many advantages thanks to the intrinsic properties of natural
46 fibers. The density of the latter being lower than that of glass or carbon (Le Gall et al., 2018; Amiri et al.,
47
48

49 2017), they are potential candidates for applications requiring structural lightenings such as the
50 automobile (Akampumuza et al., 2017), aeronautics (Balakrishnan et al., 2016) and sport (Grande et al.,
51 2018; Pailler et al., 2004).

52
53 Moreover, these natural reinforcements can be produced locally, depending on the climatic conditions
54 (Bourmaud et al., 2018): flax (Haag et al., 2017; Khennache et al., 2019; Pallesen, 1996), hemp
55 (Amaducci et al., 2015; Mazian et al., 2018; Marrot et al., 2013) for temperate climates, sisal, alfa
56 (Hanana et al., 2015), date palm (Dhakal et al., 2018) and ramie (Rehman et al., 2019) for climates with
57 higher temperatures, for example. Their intrinsic properties (chemical and physical) vary according to
58 many parameters: crystallinity, cellulose content, number of walls in the cell, cellulose micro-fibrillar
59 angles (Bourmaud et al., 2013, Bourmaud et al., 2018; Morvan et al., 2003; Cai et al., 2015 ...). These
60 variables depend on their role in the plant. The best Young's moduli (characterizing their mechanical
61 properties) are achieved with ramie fibers, with moduli between 60-128 GPa and fiber strength of 400-
62 1480 MPa according to Giridharan, 2019 and Angelini et al., 2000, approaching glass fibers values.
63 Among all these natural resources, flax is the most cultivated fiber plant in northern Europe (Martin et al.,
64 2013). These fibers are not continuous like glass or carbon fibers. They have an average length between 2
65 and 5 cm (Morvan et al., 2003), tied together in a bundle structure made of 13 to 27 unitary fibers
66 depending on the flax maturity and the position of the fibers in the plant (Morvan et al., 2003). They are
67 bound together by cortical tissue made of pectin (Martin et al., 2013; Morvan et al., 2003). **Young's**
68 **moduli** values for flax fibers are reported between 18 and 57 GPa according to Khennache et al., 2019.
69 This great variability of results can easily be explained by protocols difference and materials used.
70 Particular care must be taken by knowing precisely hygrometric conditions, length and cross-section of the
71 technical fiber, variety of flax used, treatment applied, and its retting. According to several studies (Martin
72 et al., 2013; Ruan et al., 2015), retting tends to improve Young's modulus, ultimate stress and reduce
73 elongation at break for both field and water retting. This improvement has been associated with an
74 increase in the percentage of cellulose, which is mainly responsible for plant rigidity. This improvement
75 has been also observed in polypropylene-short fibers biobased composites, made by injection (Martin et
76 al., 2013). For long fibers, most of the work is done with a thermosetting matrix-like epoxy, which is
77 actually the matrix with the best mechanical properties. Fibers are either woven (twill, satin, plain ...) or
78 unidirectional. Unidirectional applications logically give longitudinal modulus between matrix and fiber
79 ones, according to the law of mixtures. For a 50% volumic fraction, Oksman, 2001 Kersani et al., 2015
80 and Coroller et al., 2013 reported Young's moduli from 27.2 to 39 GPa and maximum stresses from 296 to
81 408 MPa.

82
83 Despite extensive testing, a lot of development and optimization work will still be necessary for a larger
84 industrialization scale. A major problem is the retting control, which highly depends on weather
85 conditions. In the case of flax, the retting applied for biobased composite applications is the same as those
86 used in the textile industry. However, there is no indication that this is the optimal retting process. We
87 need optimal retted flax to improve the fiber-matrix interface without degradation of the fiber itself. Being
88 of different nature compared to synthetic fiber, the organic fiber must have special processing and care to
89 avoid structural defects in the associated composite. Porosity in the biobased composite is one of the
90 defects that can result from poor processing. Porosities are defined as internal defects in a biocomposite
91 structure and could have several origins (processing, fiber-matrix interface, residual moisture). **To**
92 **determine the porosity rates remains very complex according to the nature of involved porosity at different**
93 **scale (macro, meso, micro ...). For the porosity determination, several authors report qualitative (Ledru et**
94 **al. 2009, Zhou et al. 1997, Lin et al. 2009) and quantitative X-Ray microtomography (Weber et al., 2010,**
95 **Nikishkov et al., 2013), pycnometer (Consortium BioLAM, 2018) and mercury porosimeter (Ramakrishna**

96 et al., 1988, Tran et al., 2015) technics. These two latter technics are the most suitable and efficient
97 technics for porous biobased materials. To our knowledge, four main porosities are already existing:
98 porosities coming from fiber, matrix, interface, and impregnation.
99

- 100 - i) The first type of porosity corresponds to the lumen's fiber. This porosity varies in size
101 depending on the fiber's type. It can range from a few percent for flax fibers to 90% for kapok
102 fibers, logically giving a variable rate of porosity in biocomposite using them.
103
- 104 - ii) Matrix porosities are due to two subtypes of porosities (Bodaghi et al., 2016; Grunenfelder and
105 Nutt, 2010). Residual air and water present in the materials create gas inclusions, leading to
106 porosities.
107
- 108 - iii) Porosities coming from the fiber-matrix interface are due to a poor interface between the fiber
109 and the matrix. This may be due to a too low surface energy of fibers, compared to the matrix (Al-
110 Khanbashi et al., 2005; Tran et al., 2015) or a presence of polluting compounds on fibers (Acera
111 Fernández et al., 2016; Al-Khanbashi et al., 2005). They can also occur during the whole lifetime
112 of composites, due to external mechanical stresses that favor fiber-matrix decohesion in areas with
113 low impregnation.
114
- 115 - iv) Porosities coming from impregnation defects (structural porosities) are indirectly linked to
116 fibers. These porosities appear if the matrix is not present enough to fill the free spaces of the
117 biocomposite (Madsen et al., 2007). Structural porosity for a high fiber content biocomposite will
118 be a major constituent. The curing cycle can induce structural defects. The organic nature of fibers
119 will tend to increase this rate compared to inorganic fibers such as glass, as organic fibers contain
120 a higher percentage of water (between 7 and 12%, Müssig et al., 2010).
121

122 For improving flax composite material knowledge and industrialization, this study focuses on Physico-
123 chemical and mechanical studies of flax fiber reinforcements and their epoxy composites manufactured by
124 thermocompression. Retting and processing parameters have been studied to examine their impacts on
125 flax fibers and bio-based composite materials in terms of morphological aspect, mechanical performance,
126 and porosity rate. To determine the different rates (fibre, matrix and water) in our biobased composites, an
127 interesting approach has been applied. This method relies on the use of TGA analysis to determine the
128 weight contents of the flax fibers, the matrix, the water and a pycnometer to determine the porosity rate.
129

130 2. Materials and Methods

131 2.1. Raw materials

132
133
134 Flax cultivation – Bolshoi variety – has been established in Romilly-la-Puthenay, Normandie, based on a
135 well-established agricultural process. Flax was seeded on April 10th, 2017, and harvested on July 13th,
136 2017 as indicated in **Table 1**. The latter date was chosen according to the sum of the cumulative degrees
137 received by the plants, 1014°C, which gives the maturity level of fibers. Winding dates were based on
138 visual estimation of the retting level (**Figure 1**), according to climatic conditions. **Figure 2** shows the
139 different levels of retting on the flax tapes. Consequently, the first winding date **W1** was set for August 7th,
140 2017. Because windrows were not too thick, it was possible to have homogeneous retting without any
141 turn-over. The two other winding dates **W2** and **W3** were set on August 28th (1 turn-over) and September

142 22th (2 turn-overs). The flax was then scutched to separate flax fibers from the stems. No hackling steps
143 were carried out, nor any thermal, chemical, or physical preparations.

144

145 (Insertion of Table 1 here)

146

147 (Insertion of Figure 1 here)

148

149 (Insertion of Figure 2 here)

150

151

152 The matrix used is an epoxy XB 3515/Aradur 5021. XB 3515 is a high-temperature epoxy resin and
153 Aradur 5021 is a polyamine curing agent. It was used as delivered and according to the manufacturer's
154 recommendation for the curing process.

155

156 2.2. Preparation of biobased composites

157

158 Once the flax has been scutched, it receives a pre-impregnation step by Vitech Composite society. The
159 average fiber mass fraction is given as 50 % \pm 3. The matter is then kept in our laboratory in a -18°C
160 room.

161

162 Three different protocols based on thermocompression molding were tested, without any post-curing.
163 Elaboration programs are explained in detail in **Figures 3a** to **3c**. The first protocol (**Figure 3a**) is the
164 actual program used by our industrial partner and has been studied to be optimized in terms of
165 temperature, time, and pressure (**Figure 3b**).

166

167 (Insertion of Figure 3a at 3c here)

168

169 For the elaboration step, prepregs stored in the refrigerator, are cut into 30 cm squares (**Figure 4a**),
170 stacked in a unidirectional pattern of 3-plys, and placed between two 3mm thick metal plates. Teflon films
171 are used to facilitate the demolding step (**Figure 4b**). **Table 2** summarizes the given names to composites,
172 processing variables, and first measurement of thickness and mass per unit area. Retting (-) corresponds to
173 under-retted flax, retting (0) corresponds to nominally retted flax for textile applications and retting (+)
174 corresponds to over-retted flax.

175

176 (Insertion of Table 2 here)

177

178 (Insertion of Figure 4a and 4b here)

179

180

181 2.3. Methods used.

182

183 All the following graphics have been made using Matlab software and Python Programming Language
184 with the Matplotlib, Numpy, and Pandas modules.

185

186 2.3.1. Spectrophotometry analysis

187

188 Spectrophotometry is traditionally used to determine the absolute color of materials. A Konica Minolta
189 CM 2300d spectrophotometer analysis was carried out to quantify the color of raw materials (flax) and
190 biobased composites materials. The coordinates systems are expressed in the CIE 1976 Colorspace
191 **(Figure 5)**:

- 192
- 193 - i) L* coordinate expresses the lightness of the color, ranging from 0 (black) to 100 (white).
 - 194
 - 195 - ii) a* coordinate expresses the green-red component. Negative values result in green colors and
196 positive ones for red colors.
 - 197
 - 198 - iii) Finally, the b* coordinate expresses the blue-yellow component. Negative values result in blue
199 colors and positive ones for yellow colors.
- 200

201 **(Insertion of Figure 5 here)**

202

203 Moreover, for the components a* and b*, the larger the value, the more saturated the color will be.
204 Whiteness Index W* is the distance between a specified color and a perfect white, expressed in the
205 CIELab Colorspace (Pérez et al., 2016). It was calculated using the following equation **(Eq.1)**

206

207
$$W^* = \sqrt{(L^* - 100)^2 + a^{*2} + b^{*2}} \text{ (Eq. 1)}$$

208

209 Where W* is the Whiteness Index, L* is the component L*, a* is the component a*, and b* the
210 component b*. Each result will be an average of 10 measurements and expressed in the CIE Lab 1976
211 color space.

212

213 2.3.2. Scanning Electronic Microscopy (SEM)

214

215 Scanning Electronic Microscopy (SEM) analysis was carried out to observe flax fiber and biobased
216 composite morphology. The tests were conducted under 15kV with magnification ranging from x37 to
217 x200. All the composite samples were polished with a #1000 sanding paper. No coating was applied to
218 either material. Three specimens were analyzed for each material.

219

220 2.3.3. DSC analysis

221

222 Differential scanning calorimetry (DSC) was used to observe phase transitions in materials by heat
223 exchange. A DSC Polyma DSC 214 was used to determine the monomer conversion rate of the different
224 biobased composites. The program consists of two heating ramps ranging from 25°C to 250°C at 10°C.
225 min⁻¹, with an argon flow of 20ml.min⁻¹. The second heating is used to check the total conversion of
226 monomers. The resin used for the manufacture of prepreps was compared to these values. The matrix
227 conversion rate was calculated using the following equation **(Eq.2)**

228

229
$$\alpha = \left(\frac{\frac{dH_c}{W_m}}{dH_r} \right) * 100 \text{ (Eq. 2)}$$

230

231 Where α is the monomer conversion rate, dH_c is the exothermic peak of the composite, W_m is the weight
232 matrix content of the composite, and dH_r the exothermic peak of the resin, derived from Konuray et al.,
233 2017. Each result is an average of 3 measurements made with 10-15 mg of material.

234

235 2.3.3. TGA analysis

236

237 TGA is usually used to observe the thermal stability of the material. As part of this study, it was used to
238 determine the fiber content of biobased composites. The method is based on the studies of Yee and
239 Stephens, 1996, and Mohsin et al., 2019. The method consists of a set of isotherm (i) 1st isotherm of
240 165°C for 30 minutes (to remove the water contained by the fibers) and (ii) 2nd isotherm of 325°C for 60
241 min. This duration (60 min) is the more suitable among 4 different tested durations (20, 40, 60 and 90
242 min), as shown in Figure 6.

243

244 (Insertion of Figure 6 here)

245

246 For TGA analysis, an argon flow of 20ml.min⁻¹ was used. Three specimens were tested for each condition.
247 The theoretical weight fiber content of the composite (W_f) was determined using the following equations
248 (Eq.3) and (Eq.4)

249

$$250 \quad W_f = \frac{\Delta_{composite} - \Delta_{matrix}}{\Delta_{fiber} - \Delta_{matrix}} \quad (\text{Eq. 3})$$

251

$$252 \quad W_m = 100 - W_f - W_w \quad (\text{Eq.4})$$

253

254 Where $\Delta_{composite}$ is the composite loss, Δ_{matrix} is the matrix loss, Δ_{fiber} is the fiber loss, W_f is the weight fiber
255 content of the composite, W_m is the weight matrix content of the composite, and W_w the weight water
256 content of the composite assumed to be the water loss of the composite, observed with TGA data. $\Delta_{composite}$
257 and Δ_{matrix} was determined with the neat

258

259 Then, to determine the volumic content of the different components, equation (Eq. 5), derived from
260 Ahmed and Vijayarangan., 2008 and Sanjay and Yogesha., 2018 was used:

261

$$262 \quad V_f = \frac{\frac{W_f}{\rho_f}}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m} + \frac{W_w}{\rho_w}} \quad (\text{Eq.5})$$

263

264 Where V_f is the volumic fiber content of the composite, W_f is the weight fiber content of the composite,
265 W_m is the weight matrix content of the composite, W_w is the weight water content of the composite, ρ_f is
266 the density of the fiber, ρ_m is the density of the matrix and ρ_w the density of the water.

267

268 2.3.4. Pycnometer analysis

269

270 The pycnometer is usually used to determine the fiber levels by comparing the density of raw materials
271 and composite but assuming a material with 0% void, which is not the case in our study. Then the porosity
272 rate could be calculated, indirectly. Pycnometer analysis was carried out to calculate the density of the
273 biobased composites. Three specimens were tested for each condition. Once the theoretical and

274 experimental density has been calculated, the porosity rate was calculated using the equation (Eq. 6)
275 proposed by Yee and Stephens., 1996.

276

$$277 \text{ Porosity rate} = \left(\frac{\text{Theoretical density} - \text{Experimental density}}{\text{Theoretical density}} \right) \text{ (Eq.6)}$$

278

279 2.3.5. Tensile test for flax fibers

280

281 Mechanical tests were carried out by using an MTS Criterion 43 tensile machine. Tested lengths range
282 from 14 to 100 mm, with 2 mm increments (thirty-three samples by retting mode). The displacement rate
283 was set at 1 mm.min⁻¹. This part was conducted in the frame of Khennache Ph.D study and the first results
284 were published in Khennache et al., 2019. It is important to note that a new method was used to determine
285 the average cross-section of each technical fiber by weighing and accurate knowledge of sample density.

286

287 2.3.6. Tensile test for biobased composite materials

288

289 Tensile tests were carried out on a Shimadzu traction machine with a 50 kN capacity load and self-
290 tightening jaws. The displacement rate was fixed at 2 mm.min⁻¹ and carried out at 23°C and 65% HR. Dog
291 bone specimens, prepared according to ISO 527, were cut by a laser beam with a cutting speed of 35
292 mm.s⁻¹ (Figure 7a). Flax-epoxy plates were glued at the area pinched by the jaws to avoid early breaks
293 (Figure 7b). For each material, five samples were tested.

294

295 (Insertion of Figure 7a and 7b here)

296

297 **3. Results**

298

299 *3.1. Spectrophotometry and morphological analysis of flax fibers*

300

301 **Figure 8** shows the variation of the L*a*b* components for flax modalities with different levels of retting
302 (under-retted, nominally retted, and over-retted). As we can see, there is a significant decrease of the L*
303 components, (from 57.3 to 54.1), a* (from 4.0 to 2.7), and b* (from 21.8 to 13.0) depending on retting.
304 This result is visually reflected in a transition from yellow to grey respectively for the less retted (-) and
305 the more retted (+) flax. Similar observations and trends have also been reported by Pallesen, 1996 and
306 Martin et al., 2013 for flax fibers, by Mazian et al., 2018 for hemp fibers, and Bleuze et al., 2018 for hemp
307 stems. Quantitatively, the results are like those observed by Martin et al., 2013 and Bleuze et al., 2018.
308 Compared to these studies, the slight color variations may be due to several reasons: the type of fiber, the
309 used variety, and the level of applied retting. It should be noted that Chabbert et al., 2020 observed an
310 increase of the L* component and an increase, rapidly followed by a decrease on the a* and b*
311 components for dew-retted flax.

312

313 (Insertion of Figure 8 here)

314

315 Moreover, **Figure 8** illustrates that color transition is not a single phase. Indeed, the color transition from
316 retting (-) to retting (0) seems different from the color transition from retting (0) to retting (+). This first
317 transition only reduces saturation without significantly altering clarity (P-value > 0.05). This could be
318 associated with possible degradation of the soluble components present in flax fibers. In fact, Van Soest
319 results – not presented here – show that soluble components decrease according to the retting levels. The
320 obtained values are 10.4% (± 0.5), 6.1% (± 0.3) and 4.5% (± 1.1) which corresponds respectively to the

321 levels (-), (0) and (+). Statistical analysis shows that the difference between these results is significant
322 (ANOVA results showed that the P-value is equal to 1.58×10^{-4}). The transition from retting (0) to retting
323 (+) is marked by a decrease of clarity and a slight loss of b* component. This transition could be attributed
324 to the colonization of the fiber by a microbial biofilm (Mazian et al., 2018), thus promoting the
325 individualization of elementary fibers.
326

327 **Figure 9** shows the SEM pictures obtained for fiber modalities at different levels of retting. It is important
328 to note that the least retted fibers (-) are presented in bundles that are well bonded and coated with each
329 other to form a technical fiber. Cohesion is potentially ensured by soluble compounds (pectins, fats, and
330 wax) according to Morvan et al., 2003 and Meijer et al., 1995. Depending on retting, this coating tends to
331 disappear and leave the fiber's surface more visible according to Martin et al., 2013. These results are also
332 confirmed for enzymatic retting of flax fibers (Réquillé et al., 2018; Ruan et al., 2020), hemp fibers (Li et
333 al., 2009; Liu et al., 2015), and date palm fibers (Chaari et al., 2020). Elementary fibers are perfectly
334 visible for retting (+) and therefore better individualized. It should be noted that the fibers with the longest
335 retting (+) do not appear to be visually degraded.
336

337 (Insertion of Figure 9 here)

338 3.2. Tensile analysis of flax fibers

339 For tensile analysis, different measurements were carried out on flax fibers and allowed us to deduce two
340 observations:

- 341 - i) When the fiber length tends towards 0 mm, the technical fiber is close to a huge continuous
342 elementary fiber. Its mechanical behaviors tend to that of elementary fiber,
343
- 344 - ii) When the fiber length reaches 100 mm and over, its mechanical behavior is that of long
345 technical fiber, i.e. a sum of elementary fibers linked by pectins.
346
347
348

349 Young's modulus, tensile strength, and failure strain of technical fiber (when the fiber length reaches 0
350 and 100 mm) are given in Table 3. It should be noted that in the case of fiber length assimilated to 0 mm,
351 retting tends to have a double effect: a positive one on fiber stiffness and a negative one on ultimate stress.
352 Retting leads to elementary fiber's dissociation from each other, leading to cleaner fiber surfaces and more
353 spaced fibers as shown by SEM results (Figure 9) and reported elsewhere by Khennache et al., 2019;
354 Martin et al., 2013, Nair et al., 2014 and Bourmaud et al., 2019.

355 In this case, the rigidity of technical fibers being the mean rigidity of all the elementary fibers (length 0
356 mm). At the same time, the fiber section decreases by cleaning effect during the scutching. Therefore, the
357 ratio L/d increases and allows a positive effect on the rigidity. Conversely, the negative effect of retting on
358 the ultimate strength could be explained by the lack of interface and the lack of stress – transfer provided
359 by the middle lamella.
360

361 (Insertion of Table 3 here)

362
363 When the fiber length is assimilated to 100mm, all the mechanical properties decrease when the retting
364 increases. Table 3 shows a 15% decrease in Young's modulus and nearly 50% of the ultimate stress was
365 observed. Internal forces are no longer transmitted by the coat made of pectins, reducing drastically the
366 strength and the rigidity of technical fibers. All these elements and the well-known not only elastic

367 behavior of elementary flax fiber (Poilâne et al., 2014; Keryvin et al., 2015; Richard et al., 2018), result in
368 not linear and not elastic behavior of flax technical fiber.

369

370 3.3. Spectrophotometry analysis of biobased composites

371

372 **Figure 10** shows $L^*a^*b^*$ measurements for biobased composites obtained by setup 1. It can be pointed
373 out that the components (L^* , a^* , b^*) tend to decrease for the biobased materials. It indicates that the
374 resulting color for the materials rather converges towards a dark color (a color that turns brown as shown
375 in **Figures 4** and **5**. It seems that the same trends already observed for flax fibers are also observed for
376 epoxy/flax materials. Compared to the flax fibers, it seems that for biobased composites, L^* and b^*
377 components tend to decrease while the a^* component increases, which is in correlation with the color
378 transition towards a soft brown color. As the retting effect remains clearly visible on flax reinforcement,
379 we highlight that the epoxy resin, which has a transparent aspect once crosslinked, seems to not affect the
380 color transition of biobased materials, essentially at 140°C.

381

382 (Insertion of Figure 10 here)

383

384 More concretely, **Figure 11** shows in 3D the $L^*a^*b^*$ components of flax and flax-epoxy biobased
385 composite obtained with the different setups (1, 2, 3). It shows that for setups 1 and 2 (temperature at
386 140°C), the color of the biobased composite displays the same trend such as for flax. This would indicate
387 a weak effect of processing parameters (time and pressure) applied during implementation for these
388 setups. This could be attributed to the softening and decomposition of soluble products (pectins and
389 waxes) contained in flax fibers. However, a strong color transition is visible for biobased materials made
390 with setup 3 which could be directly associated with step-up temperature (160°C). To check the effect of
391 setup temperature, two additional bio-based composite plates were prepared with less retting (-) flax and
392 with a processing temperature of 80 and 190°C.

393

394 (Insertion of Figure 11 here)

395

396 **Figure 12** shows a^* and Whiteness W^* components as a function of the processing temperature. It should
397 be noted that whatever the temperature, the W^* component increases continuously. However, the a^*
398 component increases steadily until it reaches a threshold from 160°C. Visually, the processing temperature
399 (temperature varies from 80 to 190°C) induces a color variation (a color translation from yellow-orange-
400 red and finally a brown color) of the biobased composite plates. Perhaps this temperature-dependent color
401 variation is due to a chemical reaction induced by the processing step and the biochemical composition
402 and nature of fibers and matrix. Further studies and analysis are still in progress to understand and explain
403 these phenomena.

404

405 (Insertion of Figure 12 here)

406

407 3.4. Volumic determination of biobased composites

408

409 **Table 4** provides experimental weight and volumic fractions of the different components (fibers, matrix,
410 porosity, and water) constituting the biobased composites. The volumic fiber fraction (V_f) ranges from
411 48.2 to 66.7% and the volumic porosity rate (V_p) ranges from 4.9 to 11.3%. These results show better
412 efficiency for setup 3 because of higher V_f and lower V_p compared to Setups 1 and 2. Furthermore, the V_f

413 and the V_p decrease with the retting level which leads to more compact materials. This could be attributed
414 to a possible improvement of the fiber surfaces due to the retting action, as already observed with SEM.

415

416 (Insertion of Table 4 here)

417

418 **Figure 13** shows the V_p as a function of the V_f rate. It shows that despite significant variability, V_p
419 increases overall with V_f . These observations confirm that setup 3 seems to be optimal regarding porosity
420 (higher V_f for the lowest V_p). Our results have porosity rates identical to those observed by Yang, 2017,
421 Berges et al., 2016 and Hallonet et al., 2019 with a higher V_f , ranging from 48.2 to 66.8%. The results
422 were confirmed by image analysis (not presented here), giving approximately the same order.

423

424 (Insertion of Figure 13 here)

425

426 3.5. Curing efficiency

427

428 **Figure 14** shows the percentage of non-converted monomers, calculated according to **Eq.2** described in
429 the "materials and methods" section. We would like to notice that the DSC study was found to be difficult
430 to obtain reproducible results associated mainly with low homogeneity of biobased composites. Standard
431 deviations vary between 6 and 52%.

432

433 (Insertion of Figure 14 here)

434

435 However, it appears that the percentage of unconverted monomers varies mainly with the setup used.
436 Setup 1 seems to convert monomers better than setups 2 and 3. It also seems that the conversion rate is
437 only marginally affected by the retting of the fibers (**Figure 14b**). Indeed, although the best conversion
438 rates are obtained for retting (-) for setup 1 and retting (+) for setups 2 and 3, the results are not
439 statistically relevant (P-value between 0.47 and 0.53). As could be observed, the percentage of
440 unconverted monomers varies greatly depending on the setups used. The lowest percentages 2.9 (± 1.6) of
441 unconverted monomers are obtained with the biobased composites in setup 1 while the highest
442 percentages 9.1 (± 0.9) of unconverted monomers are obtained with the biobased composites in setup 3.
443 This difference could be explained by the processing time, the shorter the curing time, the higher the
444 unconverted monomers. Similar results have been mentioned in the literature (Granado et al., 2018;
445 Teyssandier et al., 2010) and confirm that less processing time leads to a less conversion rate. From these
446 findings, it will be necessary to apply post-curing treatment to allow better resin crosslinking and
447 optimizing the corresponding properties of biobased materials.

448

449 3.6. Mechanical analysis of biobased composites

450

451 **Figure 15a** shows typical stress-strain curves for our biobased composite materials. The observed
452 behavior is typical for flax-based composites loading and has been fully described in the literature (Scida
453 et al., 2013; Poilâne et al., 2014; Richard et al., 2018; Cadu et al., 2019; Bourmaud et al., 2016). The
454 observed failures at the end of the tests were typically longitudinal breaks. Its initiation has been attributed
455 to interfacial fractures between fibers and matrix by Rask et al., 2012. The values deduced from the stress
456 vs strain curves are reported in **Table 5**.

457

458 (Insertion of Table 5 here)

459

460 (Insertion of Figure 15a and 15b here)

461
462 Based on the raw values, elastic property analysis reveals 3 areas (illustrated in **Figure 15b**). Area 1 (0-
463 0.1%) is elastic, Young's modulus, E1, is the initial slope in that area. Area 2 (0.1-0.3%) is a transition
464 area and could be attributed to a rapid rearrangement of the amorphous phase of S2 associated with the
465 arrangement of crystalline cellulose microfibrils resulting in a decrease of rigidity from area 1 to area 3, as
466 already reported by Hughes et al., 2007 and Bensadoun et al., 2017. Area 3 (over 0.3%) presents not only
467 elastic behavior, final secant modulus, E2, and ultimate stress – also called strength – are computed in that
468 area. The non-elastic behavior of polymer reinforced by plant fibers is not fully understood, it was
469 globally explained by microstructural damage potentially accompanied by inelastic or viscoelastic
470 behavior (Hughes et al., 2007) due to the intrinsic non-linearity of the elementary fibers (Bensadoun et al.,
471 2017).

472
473 **Figure 16** shows E1, E2 moduli, and **tensile** strength associated with the different biobased composites
474 manufactured. We observe that E1 gradually increases with retting. It also appears that setup 3 provides
475 the best modulus of elasticity compared to the two other setups. The lowest Young's modulus is 14.3 (\pm
476 0.6) GPa for setup 2 (-) and the best Young's modulus is 19.5 (\pm 0.9) GPa for setup 3 (+). Contrastingly,
477 E2 modulus varies between 11.1 (\pm 0.4) and 14.2 (\pm 0.6) GPa, which is 25% lower than Young's modulus.
478 Setup 3 still seems to allow the best rigidity values, but the effect of setup and retting is not very high for
479 E2 modulus. The effects of process and retting on **tensile** strength are not so simple. The **tensile** strength
480 increases with retting for setup 3, but normal retting is better for setups 1 and 2. The lowest tensile
481 strength, 251 (\pm 16) MPa, is obtained for setup 3 (-) and the best, 381 (\pm 32) MPa, for setup 3 (+).

482
483 (Insertion of Figure 16 here)

484
485 It appears from the previous results that the long retting mode associated with the third setup gives the
486 best compromise for our composite performances. For this setup, the morphological analysis of technical
487 fibers shows optimal elementary fiber individualization. Spectrophotometry analysis of fibers could
488 confirm this quality of fibers dissociation, which is an interesting lead for retting quantification in the
489 field. Indeed, growers look for a scientific method able to quantify the retting in the field before
490 harvesting. However, the porosity rate, which is one of the keys of composite performances, decreases
491 with retting and with setup (according to the setup numbering), giving the lower value also for setup 3 (+).
492 The fiber rate increases with the setup but decreases with the retting; it is due to the facility for the matrix
493 to diffuse between elementary fibers which present the better individualization for long retting.
494 Consequently, the higher specific surface of the fiber-matrix interface is obtained for setup 3 (+). It is
495 another key for composite performances, particularly efficient when the length of fibers is compatible with
496 load transfer, which is the case with elementary fibers as with technical fibers. Note that the third setup is
497 shorter than setup 2 which is shorter than setup 1. It results that the percentage of non-converted
498 monomers increases with setup (see §3.2.4); consequently, one specific post-curing of composites – which
499 has not been applied here – would increase the observed difference of performances, which would result
500 in better performances for setup 3.

501
502 The raw values of strength are typical for such flax composites with a high fraction of fibers. But the raw
503 values of modulus are particularly weak. For unidirectional flax/epoxy composite, Cherif et al., 2013
504 measured 26.3 GPa for $V_f = 44\%$ and Richard et al., 2018 identified 30.7 GPa for $V_f = 47\%$. We recall
505 that no specific preparation of flax except scutching was done before impregnation and that no post-curing
506 of plates has been done.

507
508 The aim of this work is not to obtain the best performances but to compare three degrees of retting and
509 three processes of elaboration of flax composite plates. SEM analysis performed on 2 (-) composite
510 specimens is presented in **Figure 17**. The orientation of the fibers is normal to the observation. We clearly
511 identify epoxy matrix in grey, flax fibers in light grey – with a lumen in the form of thin lines in the fibers
512 themselves, the fibers being flattened, as reported in other works (Le Gall et al., 2018; Madsen et al.,
513 2007; Mahboob et al., 2017) – and various types of porosity in dark grey, including dry areas. We also
514 note some artifacts, foreign matters, or saturated areas that appear in white. Matrix porosities have not
515 been seen, either by their absence or by their small size. The largest dry area, highlighted in **Figure 17b**
516 represents 1/3 of specimen thickness. The numerous interfacial porosities highlighted in **Figure 17d** result
517 in very weak flax-epoxy interfaces. We assume that the weak flax-epoxy interfaces due to the use of raw
518 flax and the high level of percentage of unconverted monomers in the matrix explain the low moduli of
519 the elaborated composite plates. Indeed, studying results for quasi-unidirectional composites with the
520 same order of porosity in literature (Cherif et al., 2016, Scida et al., 2012), we conclude that the global rate
521 of porosity itself can not explain the low modulus of the elaborated composites.

522
523 (Insertion of Figure 17a at 17d here)

524
525 Furthermore, to highlight the efficiency of the retting process, it is necessary to normalize the raw
526 mechanical properties by porosity and fiber contents using the law of mixture. We have chosen to apply
527 the inverse method described by Cherif et al., 2016, which gives the reinforcement efficiency knowing
528 resin and composite properties including porosity rate. For infinite unidirectional composite, the effective
529 Young's modulus of reinforcement and its effective ultimate strength is given by (Eq.7) and (Eq.8),
530 respectively:

$$531$$

$$532 E_{ff} = \frac{E_c * (1 - V_p)^{-2} - E_m * V_m}{V_f} \text{ (Eq.7)}$$

$$533$$

$$534 \sigma_{ff} = \frac{\sigma_c * (1 - V_p)^{-2}}{V_f + V_m * \frac{E_m}{E_c}} \text{ (Eq.8)}$$

535
536 Where E_{ff} is the fiber effective Young's modulus, E_c is the composite Young's modulus, E_m is the matrix
537 Young's modulus, V_f is the volumic fiber content of the composite, V_m is the volumic matrix content of
538 the composite, V_p is the volumic porosity content of the composite, σ_{ff} is the fiber effective ultimate
539 strength and σ_c is the effective ultimate strength of the composite.

540
541 The resulting effective properties are given in **Table 5**. **Figure 18** shows the evolution of the effective
542 modulus and strength of the reinforcement as a function of retting and process. It is clear that retting has a
543 positive impact on the mechanical performance of flax fibers once used as a reinforcement in composite,
544 the longer the retting process the higher the mechanical efficiency of reinforcement. This observation has
545 also been made by Martin et al., 2013. Nevertheless, the values of modulus presented in section 3.2 for the
546 fibers prove that the efficiency of the reinforcement is not optimal for our composites, as we noted in the
547 previous paragraph. Indeed, the effective modulus of the reinforcement computed by an inverse method is
548 much lower than that of elementary flax fiber as well as that of long technical fiber. Oppositely, the
549 effective ultimate stress of the reinforcement is in the same order of magnitude as that of elementary flax
550 fiber, and higher than that of long technical fiber.

552 (Insertion of Figure 18a and 18b here)

553
554 The difficulty on relying on composite properties to reinforcement properties by the law of mixture is well
555 known for plant fiber composites (Shah et al., 2016) and it is why a research effort is necessary to describe
556 plant fiber behavior by phenomenological approach (Poilâne et al., 2014; Richard et al., 2018).
557 Concerning the inverse approach from the law of mixture, note that the strength and the modulus of the
558 composite focus on two opposite phases of reinforcement deformation: the modulus is measured at the
559 beginning of the strain, when not all the fibers are activated, a lot of them is not already stretched
560 (depending to the efficiency of the flax-epoxy interfaces); the strength is measured at the end of the strain
561 when all the elementary fibers are stretched but not at the same step of their behavior (not only elastic) and
562 lot of them have been already broken or dissociated. Nevertheless, an increase up to 37% in effective
563 modulus and 75% in effective strength can be observed by the simple used approach between retting (-)
564 and (+) for setup 3. The elementary fiber individualization is responsible for this property's improvement
565 with retting. The true benefit of setup 3 is more difficult to analyze here. It could be due to the elimination
566 of the initial 20 bar/25°C-plateau – which can locally stress the resin too much at a temperature where it is
567 not very fluid – or to 160°C-maximal temperature – where the flax fiber is submitted to huge
568 modifications which can be positive to increase the efficiency of flax/epoxy interface. Further
569 physicochemical analysis will be required to explore these hypotheses.

570 571 572 **4. Conclusion**

573
574 In this study, physico-mechanical performances of 3-layer flax-epoxy biobased composites manufactured
575 by thermocompression were studied, and more particularly the retting and processing effect. From a
576 morphological point of view, retting tends to individualize the technical fibers bundles into single ones.
577 This individualization phenomenon could be attributed to a possible degradation of middle lamella
578 allowing a cleaner and smoother surface of fibers and affecting their final mechanical properties (15%
579 decrease of Young's modulus, 50% decrease of the ultimate stress). Increasing retting time leads to a lose
580 saturation and luminance, both for flax and biobased materials. However, increasing the processing
581 temperature alters the material color. More particularly, the composite weight fiber (W_f) tends to decrease
582 as a function of retting level for all setups. This effect could naturally result from the observed
583 individualization of the fibers and would therefore lead to a reduction in their compactness, which makes
584 easier the penetration of resin (lead to better resin impregnation). Moreover, the porosity rate, which is one
585 of the keys of composite performances, decreases with the retting and with the used setups (according to
586 the setup numbering), giving the lower value also for setup 3 (+). Consequently, the higher specific
587 surface of the fiber-matrix interface is obtained for setup 3 (+). It is another key for composite
588 performances, particularly efficient when the length of fibers is compatible with load transfer, which is the
589 case with elementary fibers as with technical fibers.

590 Regarding the mechanical behavior and based on the raw values, elastic properties of flax biobased
591 composite reveal three different areas for elastic and plastic transitions, as already reported in the
592 literature. The raw values of tensile strength are typical for such flax composites with a high fraction of
593 fibers, but the raw values of elastic modulus are particularly weak because of the low composite plate
594 cross-linking obtained with manufacturer recommendation for the curing process. However, the resulting
595 effective properties show that retting has a positive impact on the mechanical performance of flax
596 composite, the longer the retting process the higher the mechanical efficiency of reinforcement. The
597 elementary fiber individualization is responsible for this property's improvement with retting.
598 Nevertheless, the values of fiber modulus prove that the efficiency of reinforcement is not optimal for our

599 composites. Indeed, the effective modulus of the reinforcement computed by the inverse method is much
600 lower than that of elementary flax fiber as well as that of long technical fiber. Conversely, the effective
601 ultimate stress of the reinforcement is in the same order of magnitude as that of elementary flax fiber, and
602 higher than that of long technical fiber. The long retting mode associated with the third setup gives the
603 best compromise for our composite performances. Furthermore, physico-chemical analyses are necessary
604 to confirm the nature of chemical reactions happening during the curing and manufacture of flax
605 composites structure.

606

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608

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611

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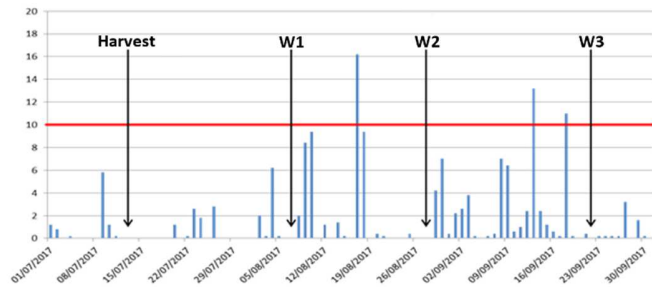


Figure 1: Winding dates based on visual estimation of the retting level and according to climatic conditions

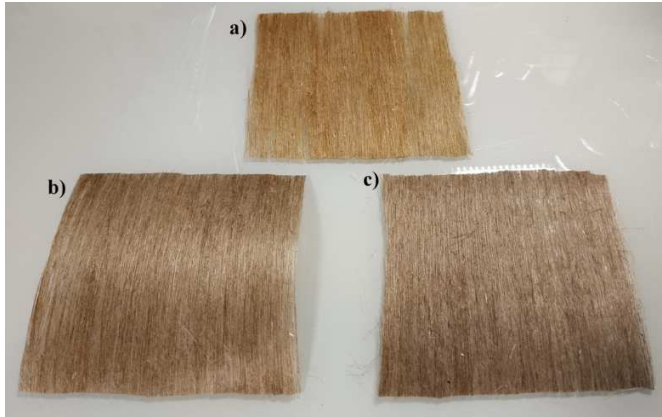


Figure 2: a) Under-retted flax, b) Retted flax, c) Over-retted flax

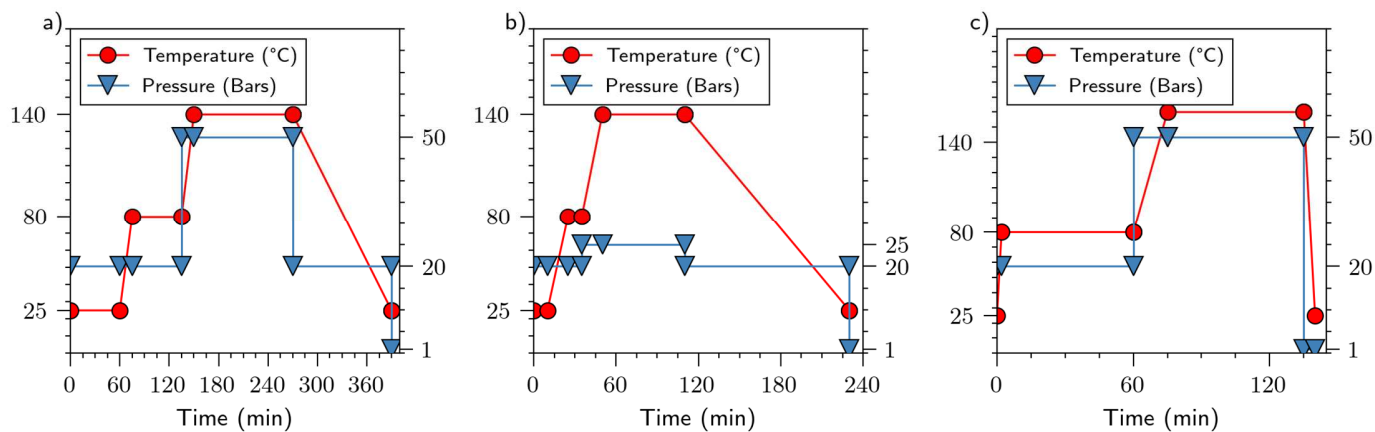


Figure 3: Biobased composites processing program a) Program 1, b) Program 2, c) Program 3

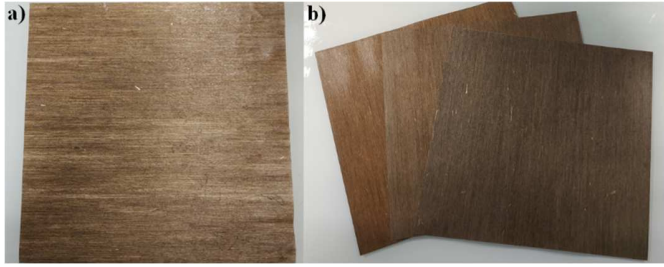


Figure 4: Biobased composites a) Prepreg of flax fibers, b) Flax-epoxy biobased composites

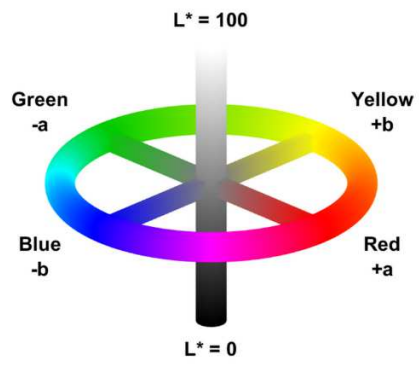


Figure 5: CIE Lab color space (Made with Matlab software)

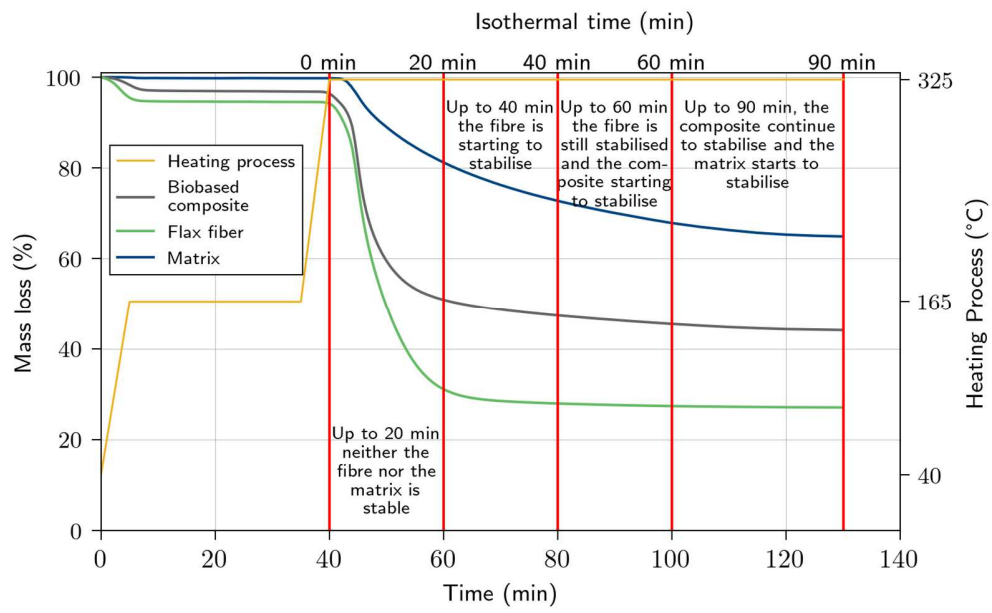


Figure 6 : TGA isothermal curves for flax fiber, matrix and Bio based composites

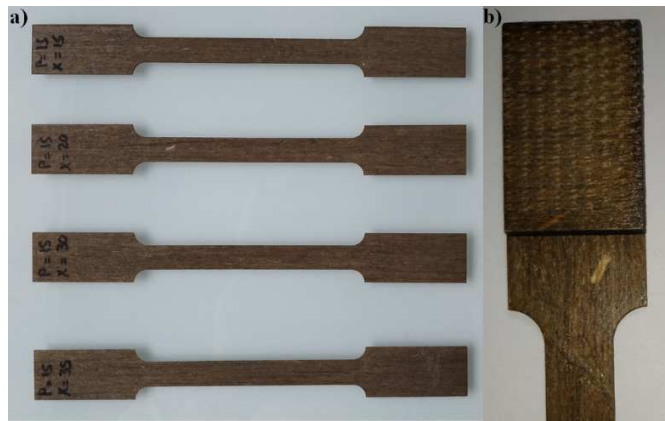


Figure 7: Flax-epoxy tensile test specimens a) general shape b) zoom on the grip section.

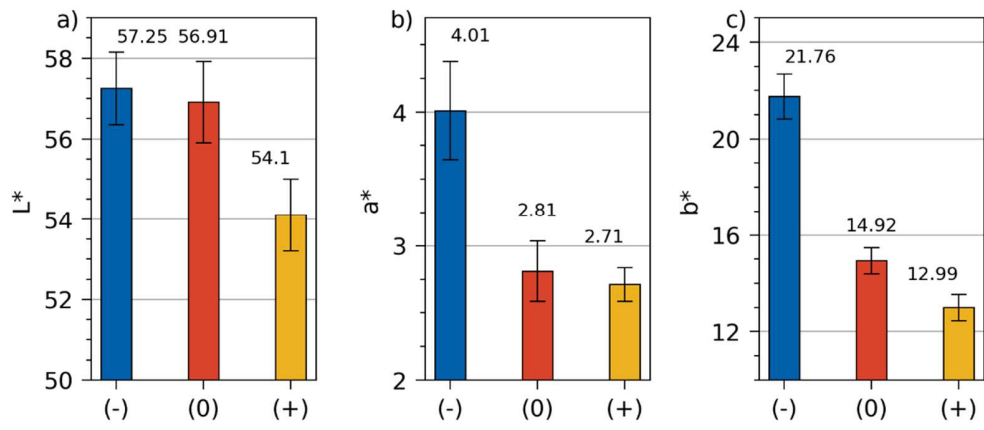


Figure 8: L*a*b* component for flax modalities at different retting

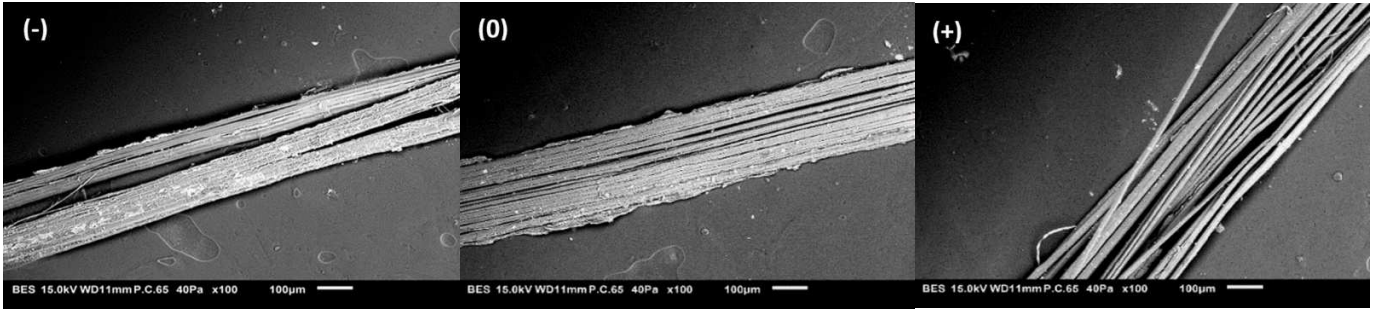


Figure 9: SEM pictures of flax technical fibres a) retting (-), b) retting (0), c) retting (+), (magnification x100)

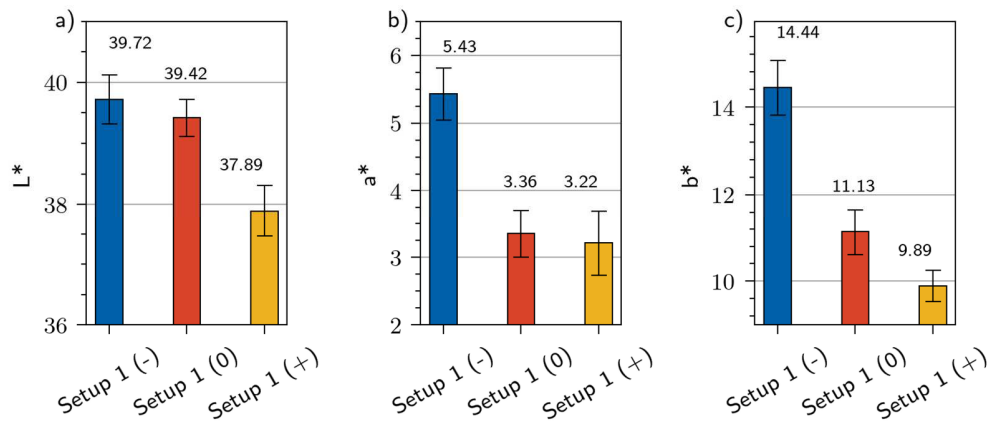


Figure 10: L*a*b* component for flax epoxy biobased composites made with setup 1

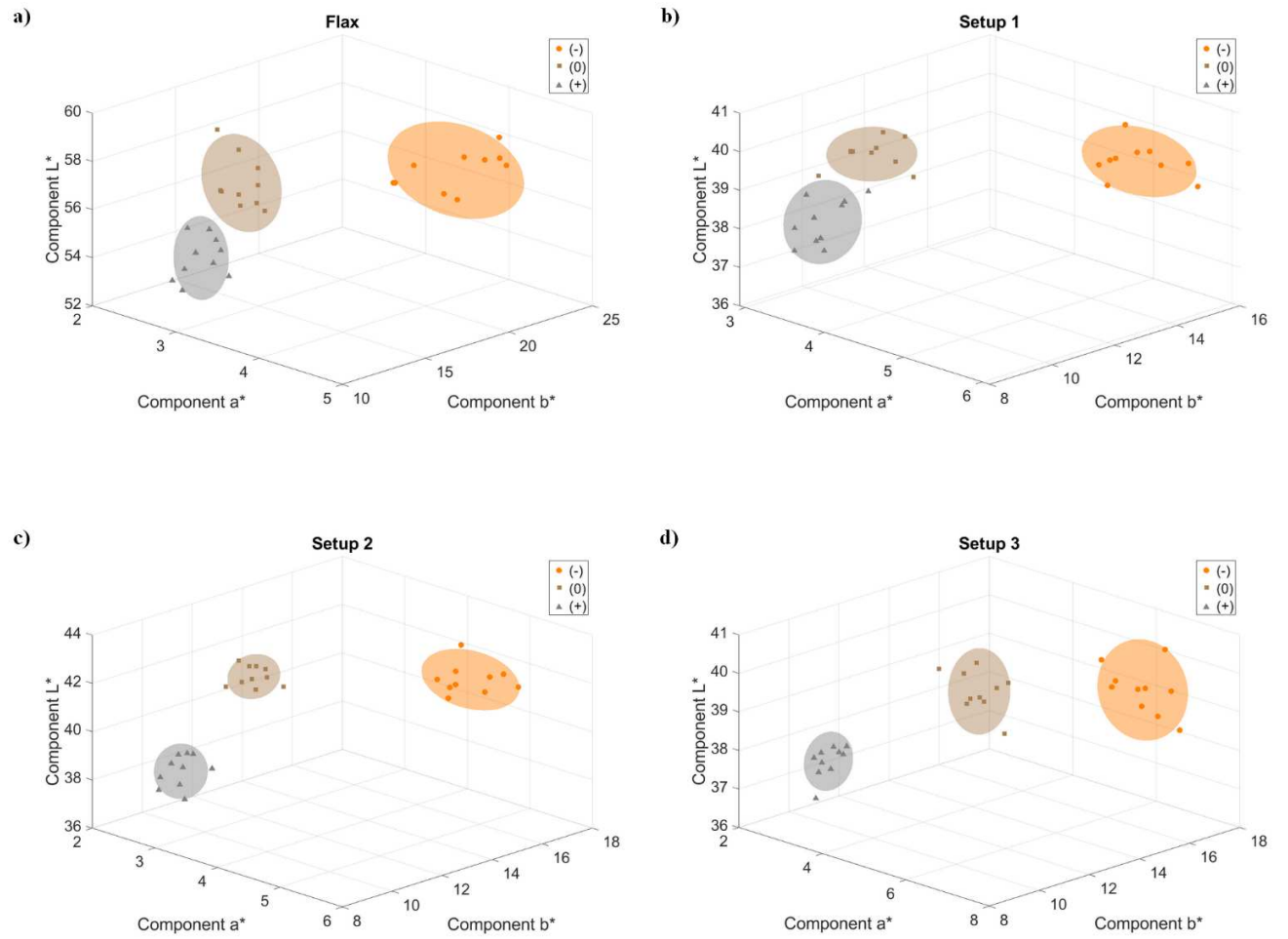


Figure 11: Spatial representation of L*a*b* components for a) flax, b) setup 1, c) setup 2, d) setup 3 (Made with Matlab software)

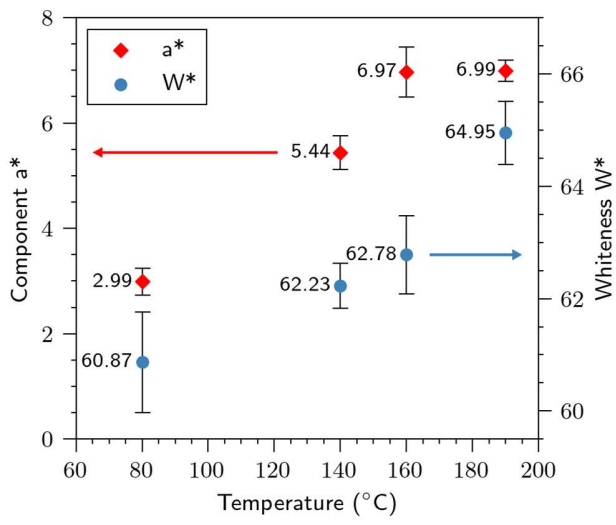


Figure 12: Effect of processing temperature on a* component and Whiteness Index

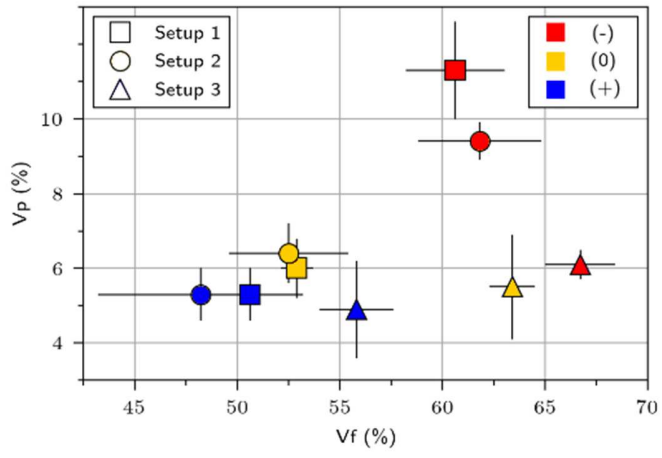


Figure 13: Biobased composite porosities versus experimental V_f

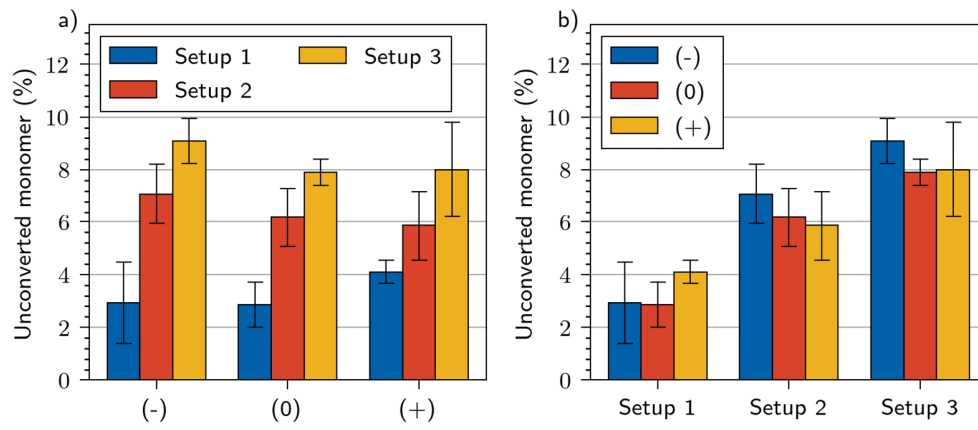


Figure 14: Curing efficiency of biobased composites a) Processing influence b) Retting influence.

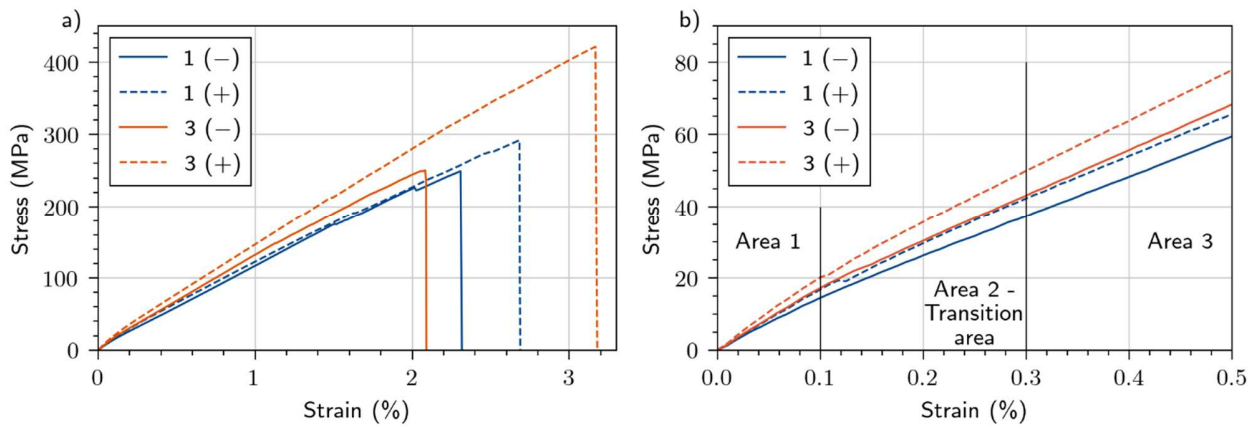


Figure 15: Stress-strain curves of biobased composites a) Global curve, b) Zoom in small deformations area.

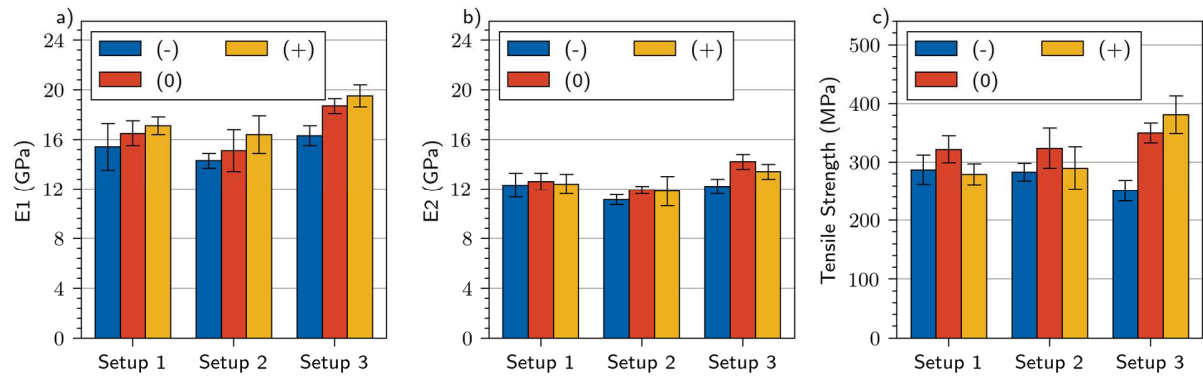


Figure 16: Influence of retting and setup on raw mechanical properties a) E1 modulus, b) E2 modulus, c) Maximal stress,

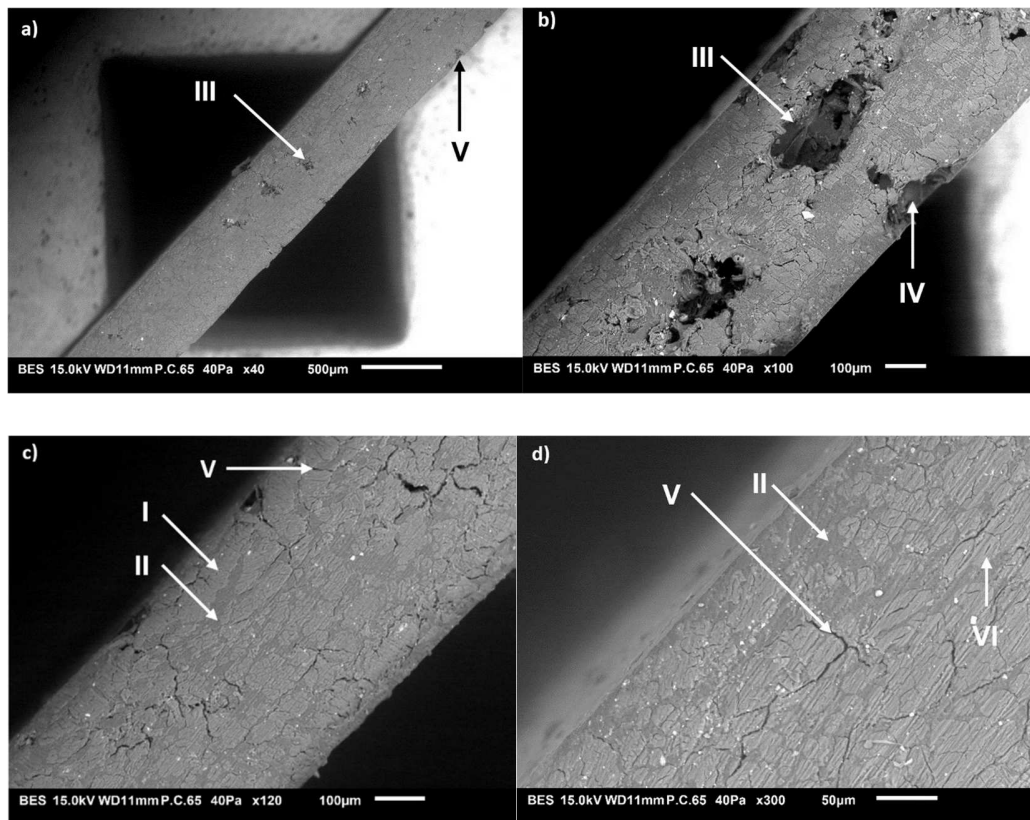


Figure 17: SEM pictures of the composite 2 (-) with magnification X40, X100, X120 and X300 - flax fibres (i), epoxy matrix (ii), structural porosity or dry area (iii), open porosity (iv), interfacial porosity (v), lumen (vi)

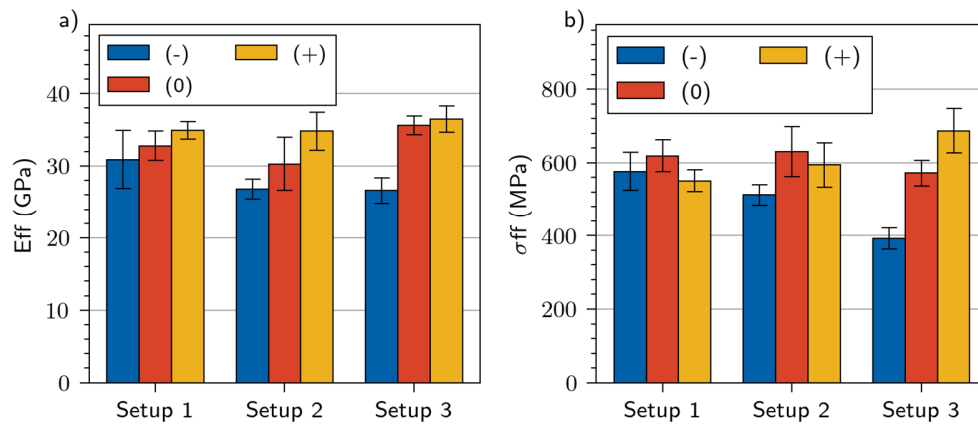


Figure 18: **Influence of retting and setup on** effective mechanical properties of reinforcement a) effective modulus- E_{ff} , b) effective strength- σ_{ff}

Table 1 : Data of cultivation and retting (detailer)

Retting	Seeding	Harvesting	Winding (W)	Total precipitation (mm)
Under retted (-)			W1 = 07/08/2017	17,2
Nominally retted (0)	10/04/2017	13/07/2021	W2 = 28/08/2017	66
Over retted (+)			W3 = 22/09/2017	130

Table 2 : Biobased composite manufactures

Setup	Retting	Times (min)	T max (°C)	P max (Bars)	Thickness (µm)	Area density (g.m ⁻²)
1	(-)	370	140	50	495 ± 21	685 ± 29
1	(0)	370	140	50	485 ± 22	654 ± 30
1	(+)	370	140	50	473 ± 13	634 ± 17
2	(-)	175	140	25	553 ± 15	766 ± 21
2	(0)	175	140	25	524 ± 18	706 ± 25
2	(+)	175	140	25	485 ± 19	647 ± 25
3	(-)	130	160	50	506 ± 24	704 ± 33
3	(0)	130	160	50	458 ± 13	631 ± 18
3	(+)	130	160	50	458 ± 10	620 ± 13

Table 3 : Mechanical properties of technical flax fibers

Modalities	Extrapolations to 0mm length			Extrapolations to 100mm length		
	(-)	(0)	(+)	(-)	(0)	(+)
Young's modulus (GPa)	68.9	77.1	88.2	66.8	58.6	41.3
Tensile Strength (MPa)	631	612	553	477	350	224
Failure strain (%)	1.07	1.03	0.85	0.86	0.76	0.69

Table 4: Weight and volumic composition of biobased composites

Composite	W_f	V_f	V_m	V_p	V_w
1 (-)	72.97 ± 2.22	60.57 ± 2.07	24.13 ± 2.07	11.28 ± 1.23	4.06 ± 0.31
1 (0)	61.47 ± 0.50	52.90 ± 0.45	37.19 ± 0.45	6.00 ± 0.80	3.90 ± 0.15
1 (+)	58.60 ± 2.57	50.56 ± 2.34	40.56 ± 2.34	5.30 ± 0.70	3.59 ± 0.14
2 (-)	79.99 ± 3.09	61.80 ± 2.89	24.15 ± 2.89	9.42 ± 0.48	4.63 ± 0.41
2 (0)	61.26 ± 2.94	52.47 ± 2.68	37.37 ± 2.68	6.45 ± 0.80	3.71 ± 0.72
2 (+)	56.24 ± 5.11	48.24 ± 4.62	42.32 ± 4.62	5.30 ± 0.71	4.13 ± 0.32
3 (-)	75.65 ± 1.57	66.75 ± 1.48	22.26 ± 1.48	6.11 ± 0.32	4.87 ± 0.71
3 (0)	71.75 ± 0.10	63.40 ± 0.09	27.34 ± 0.09	5.54 ± 1.39	3.72 ± 0.48
3 (+)	63.81 ± 1.50	55.83 ± 1.38	35.17 ± 1.38	4.90 ± 1.25	4.11 ± 0.58

Table 5 : Raw and normalized data

Composite	Fiber raw data			Matrix	Fiber effective properties	
	E 1 (GPa)	E 2 (GPa)	σ (MPa)	Em (GPa)	Ef (GPa)	σ_f (MPa)
1 (-)	15.42 \pm 1.91	12.31 \pm 1.02	287.4 \pm 25.3	3.5	30.91 \pm 4.01	576.0 \pm 52.4
1 (0)	16.45 \pm 0.98	12.57 \pm 0.74	322.2 \pm 23.1	3.5	32.84 \pm 2.02	619.1 \pm 42.6
1 (+)	17.08 \pm 0.96	12.37 \pm 0.76	279.1 \pm 17.9	3.5	34.87 \pm 1.24	550.8 \pm 29.0
2 (-)	14.29 \pm 0.58	11.11 \pm 0.42	283.1 \pm 14.5	3.5	26.82 \pm 1.37	511.6 \pm 27.6
2 (0)	15.09 \pm 1.69	11.89 \pm 0.28	323.5 \pm 33.9	3.5	30.34 \pm 3.67	630.1 \pm 68.1
2 (+)	16.38 \pm 1.46	11.83 \pm 1.23	290.2 \pm 36.1	3.5	34.87 \pm 2.58	594.1 \pm 59.7
3 (-)	16.30 \pm 0.83	12.18 \pm 0.65	250.9 \pm 16.2	3.5	26.61 \pm 1.84	392.4 \pm 29.1
3 (0)	18.68 \pm 0.57	14.20 \pm 0.57	350.0 \pm 17.4	3.5	35.59 \pm 1.31	572.0 \pm 34.5
3 (+)	19.48 \pm 0.91	13.42 \pm 0.59	381.6 \pm 32.1	3.5	36.52 \pm 1.82	687.4 \pm 59.5