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1 **About the frontier between filling and reinforcement by fine** 2 **flax particles in plant fibre composites**

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4 ¹Alain Bourmaud, ²Claire Mayer-Laigle, ¹Christophe Baley, ^{3,4}Johnny Beaugrand

5
6 ⁽¹⁾ Univ. Bretagne Sud, UMR CNRS 6027, IRDL, F-56100 Lorient, France

7 ⁽²⁾ IATE, Univ Montpellier, CIRAD, INRA, Montpellier SupAgro, Montpellier, France

8 ⁽³⁾ Biopolymères Interactions Assemblages (BIA), INRA, rue de la Géraudière, F-44316
9 Nantes, France

10 ⁽⁴⁾ Fractionnement des Agro Ressources et Environnement (FARE), INRA, Université de
11 Reims Champagne-Ardenne, 2 esplanade Roland Garros, F-51100 Reims, France

12 Corresponding author: Alain Bourmaud, alain.bourmaud@univ-ubs.fr

13 14 **Abstract**

15 Whatever in pulp or biocomposite sectors, the elements called fines coming from plant fibres
16 have generally a length lesser than 200µm. Their mechanical impact has long been debated
17 in short plant fibre thermoplastic composites. Are they solely a filling agent or on the contrary,
18 have they a potential of reinforcement in such composites depending on their numbers, their
19 length and aspect ratio? This work proposes an original experimental approach to explore
20 the mechanical role of fine flax particles. Based on controlled milling of an initially
21 homogeneous flax fibre batch that provides a population of fines (99% under 200µm,
22 average Lw of 147µm), we devised a set of composites made of an increasing content of flax
23 fines (0, 3.1, 5.6, 12.3, 20.4, 34.6 and 40.2%-vol) mixed with poly(propylene) (PP) and
24 maleic anhydrid grafted PP (PP-PPgMA). Reference composites reinforced with chalk and
25 also with cut flax fibre (Lw of 2000 µm) were also manufactured and studied. Results
26 demonstrate that, despite a low aspect ratio (5 ± 0.2 for 20.4%-vol), fines can act more than
27 as just a simple filler, a slight modulus reinforcement is depicted but only beyond a high
28 threshold of about 20%-vol (+29% compared to raw PP for 20.4%-vol). In addition to PP, we
29 then investigated the mechanical influence of the flax fines in two representative matrix
30 thermoplastic families Poly(amide)-11 (PA11) and poly(butylene-succinate) (PBS). We
31 highlighted an increase of the Young's modulus of PA11 and PBS fines composites (+41%

32 and +115, respectively for 20.4%-vol), whereas strengths were lower compared to the
33 respective neat polymers, exhibiting the possible negative role of fines on composite
34 mechanical properties.

35 **Key-words:** Flax fibre; Fines elements; Thermoplastic polymer; Extrusion; Rheology;
36 Mechanical properties; Fibre length

37

38 1. Introduction

39 The transformation of composites reinforced with plant fibres is developing and is now
40 reaching a level of maturity in numerous industries, to manufacture products such as
41 automotive non-woven parts (Renouard et al., 2017), sporting goods (Mohanty et al., 2018)
42 as well as for original applications due to their specific hygroscopic behaviour (Abida et al.,
43 2019; Duigou and Castro, 2017). However, the knowledge of these materials still needs to be
44 progressed; not all reinforcement mechanisms or the specificities of these fibres are yet
45 mastered. This is particularly true in the case of extruded and injected blends where the
46 behaviour of the fibres, very different from that of the synthetic reinforcements, has a direct
47 impact on the microstructure (Bourmaud et al., 2013) and consequently on the performance
48 of the composites.

49 Plant fibres have a very specific structure (Goudenhooff et al., 2019, 2018). It is possible to
50 assimilate them to a tubular composite structure consisting of a stack of plies, each having a
51 different microstructure (Bourmaud et al., 2018). In the case of flax, this stack consists of a
52 primary wall and a secondary wall consisting of 2 main layers S1 and S2. The major layer S2
53 represents about 80% of the fibre section and consists of cellulose fibrils inserted into a
54 matrix of non-cellulosic polymers. These fibrils are oriented with a micro fibrillar angle (MFA)
55 of about 10° with the axis of the fibre which gives it remarkable mechanical performances. In
56 some cases, an S3 layer is present; its origin depends on the maturity of the wall; it is a
57 portion, often minimal, of the S2 layer that has not reached full maturity. Thus, the breaking
58 and damage mechanisms of a plant fibre (Beaugrand et al., 2017; Hughes, 2012) are very
59 different from those of a synthetic fibre for which the breaks occur mainly in areas of defects
60 created during the extrusion of the fibres. Flax fibres also have surface defects, called kink
61 bands (Baley, 2004), which are preferred breaking zones. This was demonstrated through
62 optical rheology by Le Duc et al. (Le Duc et al., 2011) ; the link between the distance
63 between defects, such as kink bands, and final lengths of flax fibres after injection was
64 confirmed by Gourier et al. (Gourier et al., 2017) on PA11-flax composites.

65 During an extrusion or injection process of a molten polymer, the reinforcing fibres are
66 subjected to numerous thermomechanical stresses; in particular, during the compounding

67 phase in a twin screw extruder, fibres are submitted to mixing, shearing, conveying or a
68 combination of these actions (Albrecht et al., 2018; Gallos et al., 2017). **The intensity of these**
69 **damages and final fibre length may vary according to the screw profile can consequently**
70 **causes a reduction of the fibre length.** Berzin et al. (Berzin et al., 2014) have shown that the
71 decrease in the length of hemp fibre occurred principally in the mixing zones. These mixing
72 zones consist of shearing elements causing the fibre to break. The process conditions used
73 during compounding also have a crucial influence. **During the injection step, most aggressive**
74 **steps are the plasticizing and injection phases where the most shearing occurs, which**
75 **strongly modifies the morphology of the fibres.** The greatest reduction in fibre length occurs
76 at the beginning of plasticization, under the effect of high shear stresses due to solid//molten
77 interactions (Gupta et al., 1989). Although the greatest reduction in fibre length is due to the
78 compounding step, the injection step again significantly impacts the lengths (Ausias et al.,
79 2013). Thus, during a processing cycle, the plant fibres will show significant decreases in
80 length but also in diameter because they are originally assembled into cohesive bundles in
81 the plants (Goudenhooff et al., 2017). As the number of cycles increases, the lengths and
82 diameters decrease, which allows the plant fibre reinforcements to have a relatively stable
83 aspect ratio (L/D) over the cycles (Bourmaud and Baley, 2007), unlike glass fibres.

84 Whilst in most studies on the subject, the evolution of fibre geometry is highlighted, the finest
85 particles, so called fines, are often neglected, arguably due to technical limitations because
86 of the difficulty in measuring them. They were first defined in the pulping sector as particles
87 or fragments being smaller than 150 microns in size (Ferreira et al., 1999); other limits were
88 defined between 150 and 300 microns in length for biocomposite materials (Beaugrand and
89 Berzin, 2013; Teuber et al., 2016). Fine particles resulted from the breakage of the
90 elementary fibres or bundles during processing; they are generated at the same time by the
91 ruptures of the fibres in their length (Thygesen et al., 2014) but also by the destructuring of
92 the plant cell. Le Moigne et al. (Le Moigne et al., 2011) demonstrated that manual optical
93 measurement methods could not identify them and that only automated optical analysis
94 systems could reliably quantify these fines fibre elements. Recently the generation of fines
95 attracted consideration in wood polymer composites (WPC), where Teuber et al. (Teuber et
96 al., 2016) monitored a high quantity of fines according to twin screw processing parameters.
97 For plant fibres, fewer studies on fines and their impact are available. Bourmaud et al.
98 (Bourmaud et al., 2016a) studied the evolution of their content in case of PP-flax blends
99 recycling; it was shown that fines were present in batches of cut fibres even before their
100 introduction into the polymer at fractions of about 30% by number; after a extrusion and
101 injection cycles, their ratio increases tremendously up to 90% by number. Their presence is
102 therefore not anecdotal and they can potentially constitute an important bottle neck for the
103 recycling of biocomposites. Furthermore, when part design and numerical modelling are

104 carried out, a fibre's aspect ratio is considered to estimate composite properties but the
105 presence of fines particles is ignored, resulting in an overestimation of this aspect ratio,
106 which is one of the main relevant indicators that define the fibre's potential of reinforcement.
107 From the compounding community, it is admitted that the fines, arbitrarily considered as
108 particles of lengths longer than 200 μm (Beaugrand and Berzin, 2013; Le Moigne et al.,
109 2011), have a role more as a filler rather than a reinforcement. It is generally stated that both
110 reinforcements and fillers induce an increase of the composite stiffness whereas a
111 reinforcement increases also the material strength.

112 The objective of this work is to study the impact of flax fines particles on mechanical
113 properties of a range of biocomposites. Firstly, batches of flax fines particles were artificially
114 created by a suitable grinding technology and then characterized. Then, the mechanical
115 behaviour of PP-PPgMA matrix composites made with an increasing volume fraction of flax
116 fines (from 0 to 40.2%-vol) was studied and compared with composites reinforced with 2 mm
117 cut flax fibres. The PP-g-MA fines composites were benchmarked with chalk, and also to a
118 ternary mix of fibre + fines. In addition, 20.4%-vol composites were manufactured with PA11
119 and PBS matrices to deeper investigate the fines mechanical impact according to the various
120 rheological grades of polymers. For each of these batches the tensile and impact mechanical
121 performances were investigated.

122

123 2. Experimental section:

124 2.1 Materials

125 The flax fibre (*Linum usitatissimum* L.) used in this study is from the Alizée variety (harvested
126 in 2015) and was cultivated in Normandy (France). Flax seeds were sown in March. As
127 growth is temperature and humidity dependent, the plants were pulled out of the ground at
128 the end of June, when the conventional cumulated degree of temperature was raised. The
129 plants were then laid on the soil to enable dew-retting. After the harvest, the plants were
130 stored, scutched and the fibres carded and cut into 2 mm lengths. The tensile Young's
131 modulus, strength and elongation at break of the elementary fibres are shown in Table 1
132 (Bourmaud et al., 2015), respectively. The average diameter of the elementary fibres was
133 measured to be $15.5 \pm 2.7 \mu\text{m}$, as determined by optical microscopy for 400 fibres after
134 inclusion in epoxy resin and polishing of the section (Bourmaud et al., 2015). In order to
135 produce flax fines, the flax fibres were ground in a vibratory batch ball mill DM1 (SWECO,
136 USA). Basically, the milling device consists of a grinding chamber of 36 litres in abrasion-
137 resistant elastomer which is filled with milling media and product to grind. The chamber is set
138 in motion by a vibrating mechanism composed of high-tensile steel springs. Here, 1 kg of flax

139 fibres was preliminary dried in an oven at 60 °C for 24 hours, and was put into the milling
140 chamber filled with 25 kg of ceramic cylinders (diameter and length: 13.5 mm) and 25 kg of
141 ceramic balls (diameter 13.5 mm). This combination, by reducing the voids between the
142 milling media maximizes the friction and optimizes the grinding. The milling time (23 hours)
143 was determined based on preliminary tests so that the 90th percentile of the particle size
144 distribution (d90) was below 200 microns. To be consistent with previous studies (Berzin et
145 al., 2014; Le Moigne et al., 2011; Teuber et al., 2016) about the presence or aim of fines in
146 plant fibres biocomposites, the length of 200 µm was considered to be the lower limit to
147 speak about fibres; fines being below this limit. To produce enough flax fines, 2 batches of 1
148 kg were produced and they were homogenized in a Turbula® T10 B blender (WAB,
149 Germany) for 10 min.

150 The chalk (CaCO₃) used in this study is a commercial grade (Omyalite®) from OMYA
151 (France). This component is generally added to decrease the cost of formulations or to
152 improve their processability, stiffness or viscosity. Here, it plays a baseline function, giving a
153 suitable reference for comparison with flax fines regarding their respective morphologies.
154 The main objective of the introduction of chalk in the study is to compare mechanical
155 reinforcement of chalk with fine's one.

156 Three different matrices have been used, PP-PPgMA as a reference and due to its broad
157 use in biocomposite industry, the PPgMA has an proved effect on chemical bonding of the
158 polymers and particles in the compound (Felix and Gatenholm, 1991; Graupner et al., 2014).
159 In addition, PA11 and PBS were used; they have demonstrated a very interesting potential,
160 when used with plant fibres, due to their easy process and their good affinity with plant cell
161 walls (Bourmaud et al., 2016b, 2015). The first is a **poly-(propylene)** (PP) PPC10642 from
162 Total Petrochemicals®. The melt flow index of this PP injection grade is 44 g/10 min at
163 230°C (under a load of 2.16 kg). In order to improve the compatibility between the fibres and
164 the PP matrix, we used a maleic anhydride grafted PP (PPgMA), OREVAC 100, from Total
165 Petrochemicals®, which is a PP with 4 wt% of PPgMA. **The poly-(butylene-succinate)** (PBS)
166 used in this study is Bionolle 1020 MD supplied by Showa Denko (Tokyo, Japan) with a Melt
167 Flow Index (MFI) of 20–34 g/10 min (at 140 °C and 2.16 kg) and a density of 1.26 g/cm³.
168 **poly-(amide 11)** (PA11) under the trade name Rilsan PM 11 LMFO is supplied by ARKEMA
169 in pellet form with a Melt Flow Index (MFI) of 25 g/10 min (at 210 °C and 2.16 kg) and a
170 density of 1.02 g/cm³. The average degrees of crystallinity and melt temperature of the PA11
171 matrix are 21.9 ± 1.8% and 188.7 ± 0.9°C, respectively (Bourmaud et al., 2016b).

172

173 2.2 Morphological analysis of fines and fibres before compounding

174 The particle size distribution of the flax fines and chalk powder was determined by laser
175 diffraction using a laser diffraction particle size analyser Hydro 2000S (Malvern Instruments
176 Ltd., United Kingdom) with a liquid ethanol (ethyl alcohol: 96% v/v) carrier to avoid particle
177 swelling. The determination of the size is based on the assumption that particles are spheres
178 and results are expressed in volume. This analysis technique is not adapted for raw flax
179 fibres since they presented an elongated shape. Thus, the size and shape of the raw flax
180 fibre were determined using a prototype (Berzin et al., 2014) MorFi automatic analyser
181 (Techpap, Grenoble, France) fully described in (Di Giuseppe et al., 2016). To do so, a
182 precise mass of approximately 0.1 g was diluted in distilled water, and the fibre's elements
183 were tested in triplicate samples to determine their length mean values. The length is a
184 characteristic fibre element size, one of the three relevant morphometric features identified
185 earlier for a fibre element population morphology description (Legland and Beaugrand,
186 2013). Over 8,000 fibre elements were counted for each sample, and the results were
187 expressed in mean values.

188 2.3 Scanning Electron Microscope analysis

189 Fibres, fines and chalk were metallized with gold before being observed through a JEOL
190 JSM 6460LV (Jeol, Croissy Sur Seine, France) scanning electron microscope (SEM).

191 2.4 Thermogravimetric analysis

192 Experiments were performed using a SetaramTM 92 apparatus. The heating rate was 10°C
193 /min under air atmosphere from 25°C to 900°C. Around 40 mg of each kind of fibre was
194 used. Changes in weight versus temperature were recorded.

195 2.5 Compounding and processing

196 Both the flax fibres and fines were dried under vacuum at 60°C for 12hrs prior to the
197 extrusion step. Composites were prepared using a laboratory-scale twin-screw co-rotating
198 extruder ZSE 27 MAXX Torque (Leistritz, Germany) having a screw diameter of 28.3 mm,
199 and length/diameter ratio of 36. The screw profile is detailed in Figure 1. The twin-screw
200 profile included in addition conveyed elements to a venting zone for the evacuation of water
201 steam and a kneading block after area 1, for the melting of the polymer matrix, and two extra
202 mixing blocks after fibre introduction (area 2).

203 All mixtures, polymer, fines or chalk were introduced before the three shearing zones in
204 position 2 (area 1, Fig 1). The flax fibres were introduced in area 2 (Fig 1) between the first
205 and second shearing zones cutting-edge (in red in Figure 1). A fixed barrel temperature of

206 140 °C, 190 °C and 210 °C for PBS, PP-PPgMA and PA11 composites was set respectively.
207 The total feed rate was 3 kg/h for all blends with a screw speed of 200 rpm. Table 2 collates
208 the different elaborated compounds, according to the type of materials and weight fractions.
209 After the extrusion step, the formulations were immediately put into a cold-water container,
210 and then pelletized into approx. 3 mm length granules. Injection moulding was carried out on
211 a Battenfeld BA 800 machine. The mould temperature was maintained at 30 °C for all the
212 compounds. The compounds were injected into a mould designed to produce ISO-527
213 normalized specimens. The screw temperature was fixed at 140 °C, 190 °C and 210 °C for
214 PBS, PP-PPgMA and a PA11 matrix respectively.

215 2.6 Rheological experiments

216 To check the consistency with standard injected materials and record the recycling effect, the
217 granulated composites were dried at 60°C for a period of 15h prior to testing. The tests were
218 made on initial shredded plates and after each injection cycle (including the last injection
219 using a compression moulding method). A capillary rheometer (Göttfert RG20, Göttfert,
220 Buchen, Germany) was used to measure the shear viscosity of the melt. The barrel
221 temperature was pre-set to 140 °C, 190 °C and 210 °C for PBS, PP-PPgMA and PA11
222 composites respectively. The samples were heated for 300s in the barrel and then extruded
223 through 10, 20 and 30 mm lengths and 1 mm diameter dies. The experiments were
224 performed at increasing shear rates of 10, 50, 100, 500, 1000, 2000, 5000 and 10000 s⁻¹.
225 The pressure needed to extrude the material through the 3 dies at each shear rate was
226 recorded when constant (having less than 3% deviation) reading values were reached. After
227 the experiments, the Bagley (Bagley, 1957) and Rabinowitsch (Rabinowitsch, 1929)
228 correction was applied to correct the apparent shear rate and to calculate the true shear
229 viscosity.

230 2.7 Morphological analysis of fines and fibres after compounding

231 For the measurement of the length of the fibre elements after processing each transformation
232 cycle (extrusion coupled with injection) the fibre elements length distribution was quantified
233 for the PP, PA11 and PBS-flax samples. At first, the PP and PBS matrices were extracted
234 using a Soxhlet extraction methodology as described elsewhere (Berzin et al., 2014). The
235 PA11 is extractable with trifluoroacetic acid (TFA, Sigma-Aldrich, Germany) and so PA11
236 composites were submitted to Soxhlet extraction. Several renewals of the TFA were
237 necessary and the extraction duration took up to 3 days.

238 In this study, the average values L (geodesic length) and D in weight or “conharmonic
239 mean” are provided, and are also termed as average weight L_w, D_w. Thus the aspect ratio
240 L/D is the (L/D)_w.

241 2.8 Tensile characterisations

242 Static tensile tests were performed on a MTS Synergie RT/1000 tensile machine equipped
243 by a 10 kN load cell and a 25 mm nominal length extensometer at a crosshead displacement
244 speed of 1 mm/min. The values presented in this paper are average values of five
245 reproducible tests, according to ISO-527-2. Prior to the tensile experiments, injected samples
246 were conditioned for one week at 23°C and at a constant humidity of 48% RH. Average
247 tensile modulus, strength and strain at break were calculated on at least 5 reproducible
248 samples.

249 2.9 Impact test

250 Impact resistance of each material was characterized using a TINIUS OLSEN Model Impact
251 503 impact tester. Tests were carried out according to ISO 179-1 (non-notched Charpy
252 impact) on 10 specimens measured and averaged. The following formula was used:

$$253 \quad I_e = \frac{E_c}{h \cdot b} \cdot 10^3$$

254

255 With I_e the impact energy, E_c the absorbed energy (J), h and b the sample thickness and
256 width (mm), respectively.

257

258

259 3. Results and discussions

260 3.1 Characterization of fines and fibres elements before compounding

261 3.1.1 SEM analysis

262 Figure 2 presents the observations obtained by SEM on the three types of reinforcements.
263 The cut flax fibres (Figure 2.A) have on overall a satisfactory appearance with a
264 homogeneous and regular surface. It is possible to distinguish kink-bands which are
265 considered as zones of brittleness; it has been demonstrated that during a shaping process
266 in a thermoplastic, the fibres break in a preferential way at their level (Le Duc et al., 2011). A
267 correlation between the distance between defects and the final length of the flax fibres after

268 extrusion and injection has also been shown with a PA11 matrix (Gourier et al., 2017).
269 Finally, on the surface of the fibres, we note the presence of residues of the middle lamellae
270 or cortical walls which may result from moderate scutching or under retting of the plants;
271 these pectic elements can be a drawback for the fibre-matrix interface in the case of severe
272 sub retting (Le Duigou et al., 2012). As far as flax fines are concerned, a complete
273 destructuring of the fibres can be noted; the initial geometry of the fibres is no longer visible,
274 the efficiency of the selected grinding system is confirmed and interestingly, the
275 morphologies of the generated fines are close to those that we observe in PP-PPgMA -flax
276 composites after several cycles of recycling during previous works (Bourmaud et al., 2016a).
277 The morphology of both chalk particles and clusters (Figure 2.C) follows with the objective of
278 similarity to the ground flax fibres, confirming the relevance of the selection of this
279 component as a reference. One can see that not one of the chalk and flax fines clusters are
280 bigger than the other, but the regularity of the surface of the chalk seems higher than flax
281 fines.

282 *3.1.2 Morphological analysis*

283 Figure 3 shows the length distribution of fibres and the particle size distribution for flax fines and
284 chalk before incorporation into composites. Due to the contrasted aspect ratio of those particles,
285 we chose to adapt our morphometric measurement in agreement, therefore the fibres (L greater
286 than 200 μ m with a high L/D) were tested and measured using a Morfi automatic analyser.
287 Whereas more reliable data were expected through laser diffraction analysis for flax fines and
288 chalk (low L/D), one notes that the profile of flax fibre and fines differs greatly. Flax fibre exhibits a
289 narrow and well centred distribution on the targeted length of 2 mm with an average length of
290 1811 μ m (Table 3), highlighting the efficiency of the fibre cutting process; only a small population
291 appears under 0.8 mm (Fig 3), probably representative of a fraction of small particles produced
292 during this cutting step and confirming the presence of fines particles even in a batch of raw cut
293 fibres (Bourmaud et al., 2016a). Conversely, the shape distribution of fines particles is less
294 homogenous and wider, in good accordance with the SEM observation. Furthermore, 99.2% of
295 the flax fines particles obtained after milling have a size below the targeted value of 200 μ m; as
296 evidenced on Figure 3, only a much reduced fraction of fines elements exhibit a size greater than
297 this value.

298 Although its average dimensions are slightly smaller than those of fines particles and its
299 distribution is narrower, we can consider that chalk powder particles represent a good basis for
300 comparison in terms of reinforcement compared to fines. This filler is widely used in the field of
301 thermoplastic composites and it will be interesting to compare the performances of composites
302 reinforced with fines with those of chalk reinforced ones.

303

3.1.3 Thermal behaviour

304 Figure 4 shows the behaviour obtained through thermo gravimetric analysis for flax fibres
305 and fines. For each type of reinforcement, 3 successive losses of mass can be distinguished,
306 the first corresponds to the water loss of the plant walls, the second to the degradation of the
307 components of the most heat-sensitive walls (pectins, hemicelluloses and amorphous
308 cellulose) and the third to the loss of the most heat-resistant components such as condensed
309 lignin or crystalline cellulose chains with high degrees of polymerization (Bourmaud et al.,
310 2010). A lower thermal stability can be noted for fines; the inflection points of their mass loss
311 curves occurring at a lower temperature of 35°C and 36°C for peaks 2 and 3, respectively,
312 relative to the fibres. In addition, the quantity of degraded constituents is 6% higher than
313 peak 2 for fines while it is 9% lower for peak 3; part of the constituents has therefore evolved
314 during the process of milling flax fibre into fines, leading to an earlier thermal degradation of
315 the latter. In addition, fines have a higher fraction of water, visible at the beginning of the
316 curve, being 4.8% and 8.0% for fines and fibres, respectively.

317 These different findings can be related to the evolution of the structure of plant walls as well
318 as to the data in the literature. It has been shown that severe ball milling results in a
319 significant decrease in the crystallinity of plant walls (Khan et al., 2016; Nada et al., 1998)
320 and an increase in their water absorption (Schell and Harwood, 1994; Tarafdar et al., 2001).
321 As shown in Figure 2, ball milling results in a significant destructuring of the morphology of
322 plant cell walls, making available both newly water bonding sites or porosity that favours
323 water retention. In addition, the possible decrease in the crystallinity of cellulose after a
324 milling phase is linked to a depolymerisation of a significant fraction of the most thermo
325 stable cellulose; lignin can also be impacted by this depolymerisation. This evolution of the
326 structure of the constituents generates a larger fraction of thermo labile polymers; the
327 changes in thermal behaviour observed are in phase with these structural modifications.

328 3.2 Mechanical performances of fully flax fines or flax fibre PPgMA-composites

329 Figure 5 compares the mechanical performance of composites made with only fines or fibres.
330 Tensile Young's moduli and strength at break are represented as a function of the volume fraction
331 of reinforcements. A contrasted behaviour is observed between fines or fibres. For fibres, a linear
332 increase in stiffness with fibre content is observed starting from roughly 6%-vol (10% wt) to nearly
333 37%-vol (50% wt%). When fines are used, an increase of the tangent Young's modulus is
334 observed but with a marked offset, in fact the increase starts only with 20.4%-vol and the slope is
335 much less pronounced compared to the one of the fibre. This observation should be directly
336 related to the aspect ratio of the particle components (Table 3) which was determined after
337 PPgMA extraction of the solids phase on injected composites. The initial morphology and length
338 of the introduced particles has a direct impact on the performance of the composites. The fines

339 demonstrate undoubtedly a measurable contribution in terms of material stiffness that one can
340 consider as marginal compared to the fibre contribution. For instance, for a volume rate of
341 approximately 37.4%, they produce an increase in modulus of +57% stiffness compared to PP-
342 PPgMA alone, while the same increase is +254% if fibres are used; the fibres have better
343 mechanical properties and their much higher aspect ratio enables them to align in the direction of
344 flow and to reinforce composites much more effectively (Tanguy et al., 2018). This is roughly a
345 ratio of 1/5 contribution for fines compared to fibres, and this only occurs with a large volume of
346 fines (37.4% in our experimental procedure) when it has already increased stiffness with only
347 5.6%-vol fibres (Fig.5A). This result gives us a first indication of the influence of the presence of
348 fines on the mechanical performance of associated composites.

349 Evolution of strength (Fig 5B) confirms this result; in the case of cut fibres, the tensile strength at
350 break of the injected composites increases with the fibre volume content. Then, it decreases
351 slightly beyond a specific content, corresponding to a critical fraction of reinforcements; above it,
352 the significant volume of fibre bundles leads to the appearance of areas of weakness. The latter
353 thus have preferential areas of rupture; this limit is about 32%-vol. When fines are added to the
354 material, contrasted behaviour is experienced. The strength at break of the PP-PPgMA increases
355 slightly as long as a minimal quantity of 3.1%-vol is added, but does not change thereafter
356 regardless of the volume rate of fines added. The increase observed on the stiffness (Fig 5A)
357 does not increase the strength values, which remain unchanged regardless of the volume rate of
358 fines added. For a fines volume rate of 34%, the stress increase is only +24% compared to that of
359 virgin PP-PPgMA, while it is +254% for a fibre volume rate of 32%, so an efficiency ratio of
360 approximately 1/10, leads us to consider that the strength increase produced by the fines is
361 negligible compared to fibre contribution.

362 Mechanically speaking, fines reinforced composites therefore have much lower properties in
363 comparison to fibre composites. The lengths and aspect ratios of the introduced reinforcements
364 play a major role and morphological differences of the raw reinforcements are reduced but are
365 still present after an extrusion cycle and injection moulding (Table 3). In addition, the structure of
366 the cell walls is considerably altered by the grinding process (Figure 2), as they cannot regain
367 their original mechanical properties. Thermo gravimetric analyses have shown major changes in
368 the properties and stability of flax fibres after severe grinding. The matrix and structural polymers
369 of flax cell walls such as pectins, hemicelluloses and cellulose have been modified and arguably
370 deconstructed, which in turn no longer allows them to play their mechanical or cohesive function,
371 which is essential for fibres to display a high mechanical performance. Finally, the surface of the
372 fibres has been modified, the destructuring of the walls makes some of their components
373 accessible to the PP-PPgMA matrix; the coupling agent formulated to optimise the adhesion
374 between poly(propylene) and the OH groups available on the fibre surface cannot fully fulfil its
375 function, which is detrimental to the mechanical performance of the composites produced.

376

377 3.3 Ternary blends: evolution of composite performances according to the polymer matrix

378 *3.3.1 Evolution of fibre length after processing*

379 Table 3 shows the length of flax fines and fibres measured with the MorFi automatic analyzer
380 after dissolution of the polymer matrix.

381 After the compounding and injection cycle with a poly(propylene) matrix, the morphology of the
382 fines changes little; the aspect ratio and consequently the potential for particle reinforcement
383 remain low. Flax fibres, despite a significant decrease in their length, retain an aspect ratio of 31
384 ± 4 due to the combined decrease in their diameters. We observe that this $18 \pm 6 \mu\text{m}$ diameter is
385 very close to that of the elementary flax fibres ($15.85 \pm 3.9 \mu\text{m}$); the plant bundles initially present
386 in the plant and still partially assembled after the scutching and cutting of the fibres, have
387 undergone a complementary division during the transformation process, favourable to the
388 reinforcement of the composites. The length of the fibres in the composite is close to $600 \mu\text{m}$,
389 which is consistent with the values usually found in the literature (Beaugrand and Berzin, 2013;
390 Bourmaud et al., 2016a). Logically, for the PP-f-F-30 mixture, the morphological values of the
391 reinforcements are positioned in an intermediate way between the fines and the fibres.

392 Depending on the nature of the matrix, the morphologies of the fibres differ after injection. PA11
393 has a high affinity for flax fibres (Le Duigou et al., 2016) and a much lower viscosity (Bourmaud
394 et al., 2016b) than PP or PBS (Bourmaud et al., 2016a), which results in a significant break in
395 fibre lengths of $434 \pm 35 \mu\text{m}$ compared to 592 ± 183 and 497 ± 19 for PP and PBS respectively.
396 This is probably due to a higher shear during the processing related to the fluidity of the polymer.
397 Conversely, the fibre bundles appear less divided, which may appear contradictory. Its good
398 adhesion to the fibres probably enables it to maintain a strong cohesion of the bundles during the
399 process. PBS favours division, the average diameter of $14 \pm 1 \mu\text{m}$ is similar to that of elemental
400 flax fibres, whilst also reducing lengths significantly compared to the PP matrix. Of the three
401 polymers, it is the most viscous, which seems to have a significant impact on the individualization
402 of the reinforcements. Finally, we can assume that despite the meticulous extraction protocols,
403 polymer extraction can sometimes be incomplete. In this way, the TFA used for PA11 extraction
404 may have at least partially digested some flax particles, because this acid is often used for
405 lignocellulose hydrolysis prior to biochemical investigation.

406

407 *3.3.2 Rheological analysis*

408 The influence of the presence of fines on the rheological properties of the biocomposites is
409 studied by capillary rheology. Figure 6 shows the curves obtained on different PP-PPgMA matrix
410 formulations. Generally speaking, one notes that the presence of particles significantly increases

411 the viscosity of the polymer, moderately for fines and much more so for flax fibres. Note that the
412 viscosity of the formulation containing only fines (30%wt) is very similar to that made with chalk
413 powder, which is a filling agent. Thus, the addition of fines in significant quantities only slightly
414 impede the viscosity of the composite, and these fines are not a drawback to the injection of thin
415 walls as can be the case with fibres. Regardless of the apparent viscosity curve considered, a
416 significant dependence on the shear rate can be observed (Steller, 2005); it is more pronounced
417 when fibres are added acting as a reinforcement. In addition, for low viscosities, the fibres are
418 entangled and poorly oriented in the direction of flow, which produces high viscosities compared
419 to the virgin polymer or reinforced by particles with smaller shape factors such as fines or chalk.
420 With an increasing shear rate, the viscosity of the composite decreases more significantly than
421 that of the virgin polymer, the reinforcements flow more easily. Flow properties can depend on
422 many factors such as the stiffness of the reinforcements, their adhesion to the matrix, the volume
423 ratio or their geometric characteristics. In our case, most of parameters are similar between the
424 mixtures and the main influential one, here it is morphology, and in particular the aspect ratio of
425 the particles. The work of Le Duc et al. (Le Duc et al., 2011) has shown that the viscosity of
426 composites reinforced by plant walls is influenced by the size of the reinforcements; when the
427 latter are less than 200 microns long, fibre-fibre interactions are reduced and the nature of the
428 flow is between a concentrated and semi-liquid mode; this is confirmed by our measurements, at
429 high shear rates. The viscosity of the composite reinforced by fines is very close to that of the
430 polymer, highlighting the low impact of the particles on its flow.

431

432 *3.3.3 Effect of the polymer matrix type on biocomposite mechanical* 433 *properties*

434 In addition to PP-PPgMA, in order to enlarge the range of polymer types, we have tested PBS
435 and PA11 polymers and assessed the influence of the polymer. Based on the PP results (Fig 5),
436 new tests with the upper rate above the threshold identified were performed; a loading rate of
437 30%-wt was chosen to be able to depict a putative specific polymer contribution. Figure 7 shows
438 the tensile mechanical properties of injection-moulded composites. With regard to Young's
439 modulus, a similar trend is observed according to the matrix used. Fibre materials are the most
440 efficient for reinforcement. As already shown in Figure 5, composites reinforced with fines
441 (30%wt) have a much lower stiffness, assumed to be due to the fines low aspect ratio, resulting in
442 a much lower reinforcement potential for fines than for fibres. Moreover, structural damages
443 during fines milling have probably induced a decrease of their mechanical performances. Fines-
444 fibre mixtures offer intermediate stiffness. However, it should be noted that a significant number
445 of fines are generated during the process (Bourmaud et al., 2016a) and that even fibre blends
446 contain a fraction of fines, especially after two processing cycles (extrusion-injection) as is the
447 case here. Given the shear rates involved, it is illusory to want to produce fractions composed

448 only of flax fibres by extrusion and injection. Note that fines have a higher reinforcement potential
449 than chalk in terms of stiffness. Regardless of the matrix considered, the Young's modulus of
450 fines composites is higher than that of mixtures containing chalk, this increase ranges from +17%
451 for PP-PPgMA to +35% for PBS. Generally the stiffness of compounds containing PBS is greatly
452 improved with the addition of fines or fibres. As far as fibres are concerned, a mass addition of
453 30% produces an increase in the modulus of the composite by +325% whereas it is only +163%
454 with PA11 and +111% with PP-PPgMA; note that fibre elements extracted from PBS-F-30
455 composite exhibit the highest aspect ratio with a value of 38 (Table 3), especially by comparison
456 with PA11, due to high viscosity of PA11 with the selected process conditions (Gourier et al.,
457 2017).

458 The strength values (Figure 7) illustrate results depending on the nature of the matrix, a
459 reinforcing effect is noted only for the PP-PPgMA matrix and only when fibres are used. The use
460 of fines, chalk or fines-fibres never allows to increase the matrix strength whatever the
461 considered polymer. Regarding the specific case of fines particles, probably due to the presence
462 of reinforcement clusters generating areas of fragility, they do not improve the tensile strength
463 when used alone or even mixed with flax fibres. Except for PP-F and PP-f-F compounds, the
464 presence of reinforcement causes a systematic decrease in strength at max, which is less
465 pronounced when fibres are introduced but remains significant; however, the stress levels of
466 these matrices are high and if we take the case of PA11, the addition of 30% fines makes it
467 possible to obtain a significantly higher strength than that obtained with PP-PPgMA -fibres. The
468 level of tensile strength obtained, close to 40 MPa, is therefore quite satisfactory for a short fibre
469 biocomposite. With the PA11 matrix, the strength reduction between the virgin matrix and
470 compounds containing fines and fibres is -19% and -10%, respectively, while it is -39% and -12%
471 with a PBS matrix. Despite the slight decrease observed when the reinforcements were
472 introduced with PA11 and PBS, high levels of strength at break are maintained; with PP matrix
473 the gap between polymer and composite strength is lower but the values reached do not enable
474 to target semi-structural applications with fines or fines-fibres blends. As with the modulus, the
475 aspect ratio (Table 2) of the reinforcements is also a major criterion for the mechanical
476 performance of the materials.

477 Thus, mixtures containing fines have strength levels slightly lower than those containing chalk but
478 their stiffness is significantly higher. The fines thus play a real role of mechanical reinforcement in
479 such a tailored experiment where an uncommon rate of fines is use. Nevertheless, this latter
480 remains very far from the potential of the fibres and their presence in a composite is finally quite
481 strongly penalizing for its mechanical performances.

482 Finally, Figure 8 shows the impact energy of the various composites manufactured. The impact
483 energies of the raw polymers or those reinforced with chalk were not illustrated, as these
484 composites do not break during the tests. As with tensile strength at break results, the results are

485 not only strongly influenced by the nature of the particles but also by the matrices used. For the
486 PP-PPgMA matrix, which has a low-quality interface with flax fibre, the nature of the
487 reinforcement does not matter and the difference between fines and fibres is not significant.
488 Conversely, for PA11 and PBS, the use of fibres rather than fines makes sense for impact
489 resistance. This is particularly pronounced for PA11 compounds which have a very good
490 interface with flax fibres. In this case, the presence of fines in the composite is very detrimental.

491

492 **4. Conclusion**

493 The objective of this work was to deeper understand the behaviour of flax fines particles within a
494 thermoplastic polymer matrix and to estimate their reinforcement capacity. Even if the
495 reinforcement capacity of the fines has been demonstrated in terms of stiffness, it remains
496 modest compared to short flax fibres. The stiffness achieved with a 2 mm fibre volume fraction of
497 5.6% is only achieved with 37.4% of fines, i.e. a ratio of about 6.7. Their presence is therefore
498 very detrimental in terms of reinforcement, especially since we have been able to show that in
499 some composites they can reach rates of 90% in number. This low reinforcement capacity was
500 confirmed with a panel of polymers, the mechanical performance of fines-strengthened polymers
501 being much lower than those containing fibres, regardless of the matrix considered. This trend is
502 also much more pronounced for tensile stress than for Young's modulus. This is confirmed when
503 comparisons are made with chalk which has a morphology similar to that of fibres; chalk-
504 reinforced polymers generally have higher tensile stresses than those reinforced with fines, but
505 the stiffness of thin composites is better, probably due to their intrinsic performance and
506 reinforcement structure.

507 Interestingly, fines particles induce a decrease in the viscosity of the mixtures which does not
508 constitute a negative point but which will nevertheless impact the microstructure of the part and
509 consequently its mechanical performance. Finally, with regard to impact performance, fines
510 cause a decrease in absorbed energy, which is particularly visible for PA11 matrix composites.
511 This can be explained by the high temperatures used during the processing of this polymer, due
512 to the low thermal resistance of the fines compared to that of the fibres.

513 This work has shown that fines particles have a significant impact on the mechanical
514 performance of biocomposites. They are generated by the processing cycles but also during the
515 preparation of the fibres. Thus, their quantity must be reduced as much as possible so as not to
516 damage the performance of composites. It is therefore important to limit process times and the
517 number of transformation cycles, but also to adapt the extraction and cutting methods of the
518 fibres to limit the quantity of fines within the parts as much as possible.

519

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528

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663

664

665 **Table caption**

666 **Table 1.** Mechanical properties of elementary flax fibers (Bourmaud et al., 2015).

667 **Table 2.** Formulations of the different composites. 'F' represents fibres and 'f' represents
668 fines.

669 **Table 3.** Morphometric characteristics of the reinforcement after injection.

670

671 **Figure captions**

672 **Figure 1.** Screw profiles and fibres/fines/chalk introduction area on the twin-screw extrusion
673 system.

674 **Figure 2.** SEM images of flax fibres (A), flax fines (B) and chalk (C).

675 **Figure 3.** Distribution of fibre and particle size before incorporation into the composites.

676 **Figure 4.** Thermal degradation of flax fibres and fines

677 **Figure 5.** Young's modulus (A) and strength at break (B) of flax fines and fibres PP/PPgMA
678 composites for a range of reinforcement volume fractions.

679 **Figure 6.** Influence of the reinforcement on the rheological properties of the composite.
680 Example of PP composites.

681 **Figure 7.** Tensile Young's modulus (A) and strength at max (B) of the different composites

682 **Figure 8.** Impact energy of the different composites. No breakage with this test occurred for
683 pure polymers, therefore results are not shown.

684

685

Figure 1. Screw profiles and fibres/fines/chalk introduction areas on the twin-screw extrusion system.

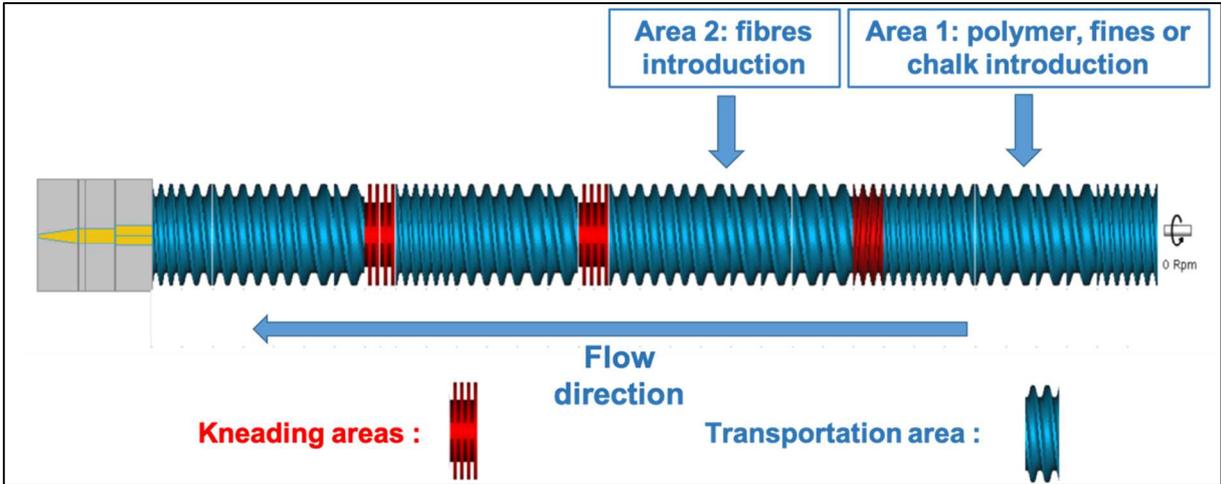


Figure 2. SEM images of flax fibres (A), flax fines (B) and chalk (C)

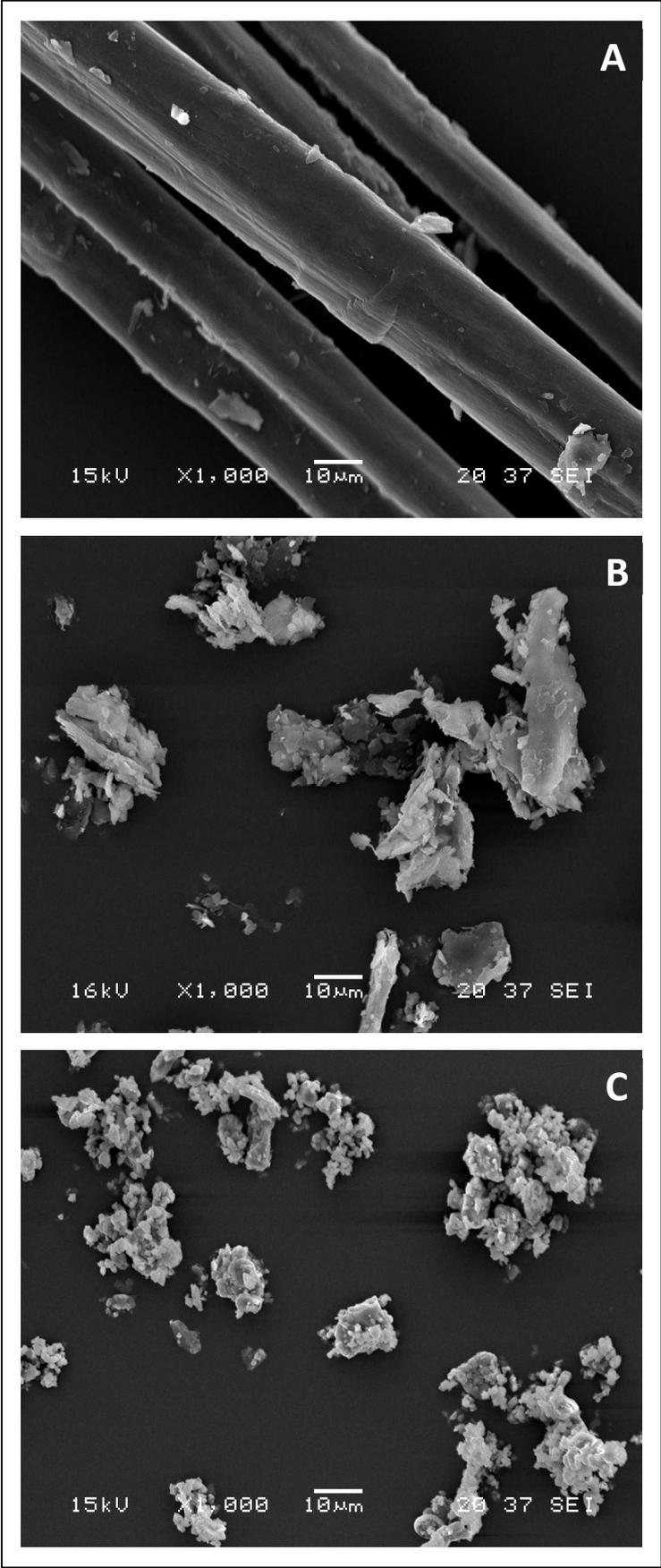


Figure 3. Distribution of fibre and particle size before incorporation into the composites.

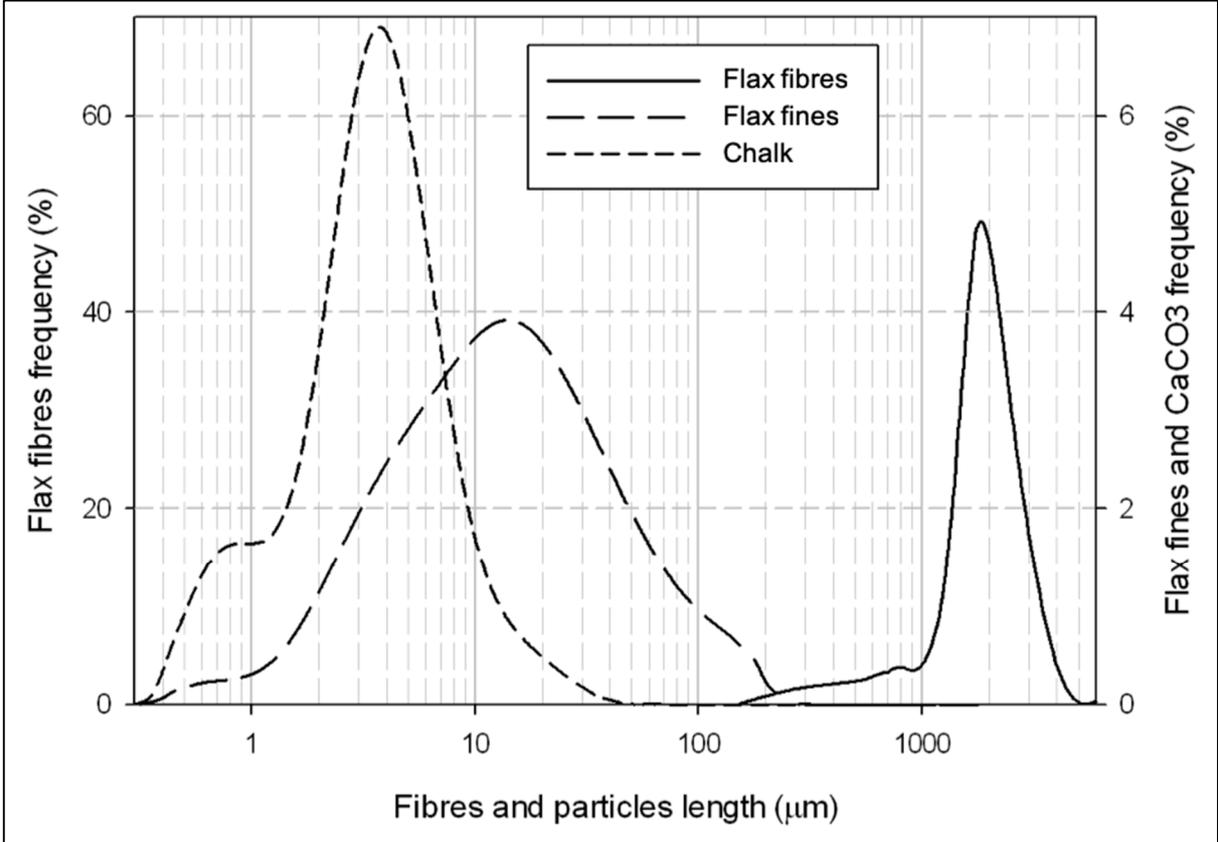


Figure 4. Thermal degradation of flax fibre and fines

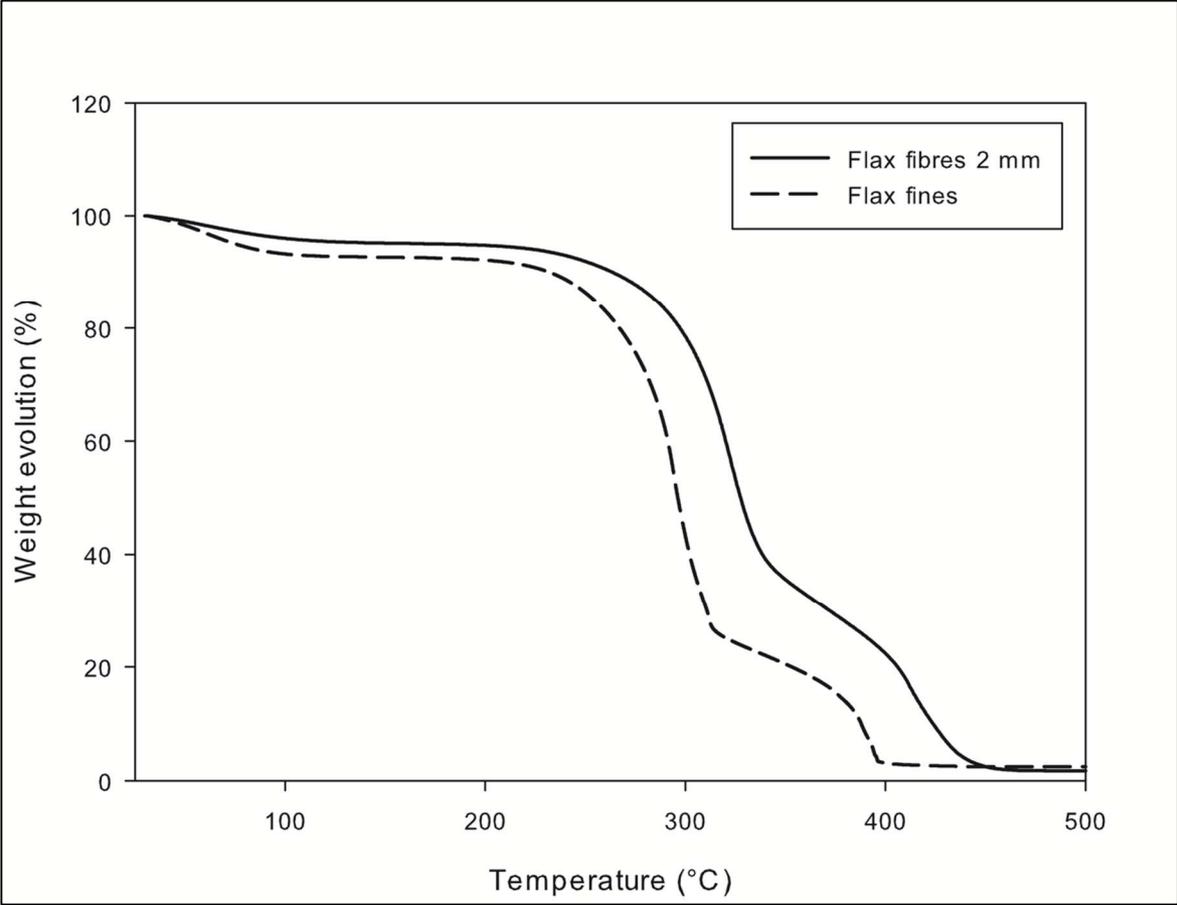


Figure 5. Young's modulus (A) and strength at break (B) of flax fines and fibres PP/PPgMA composites for a range of reinforcement volume fractions.

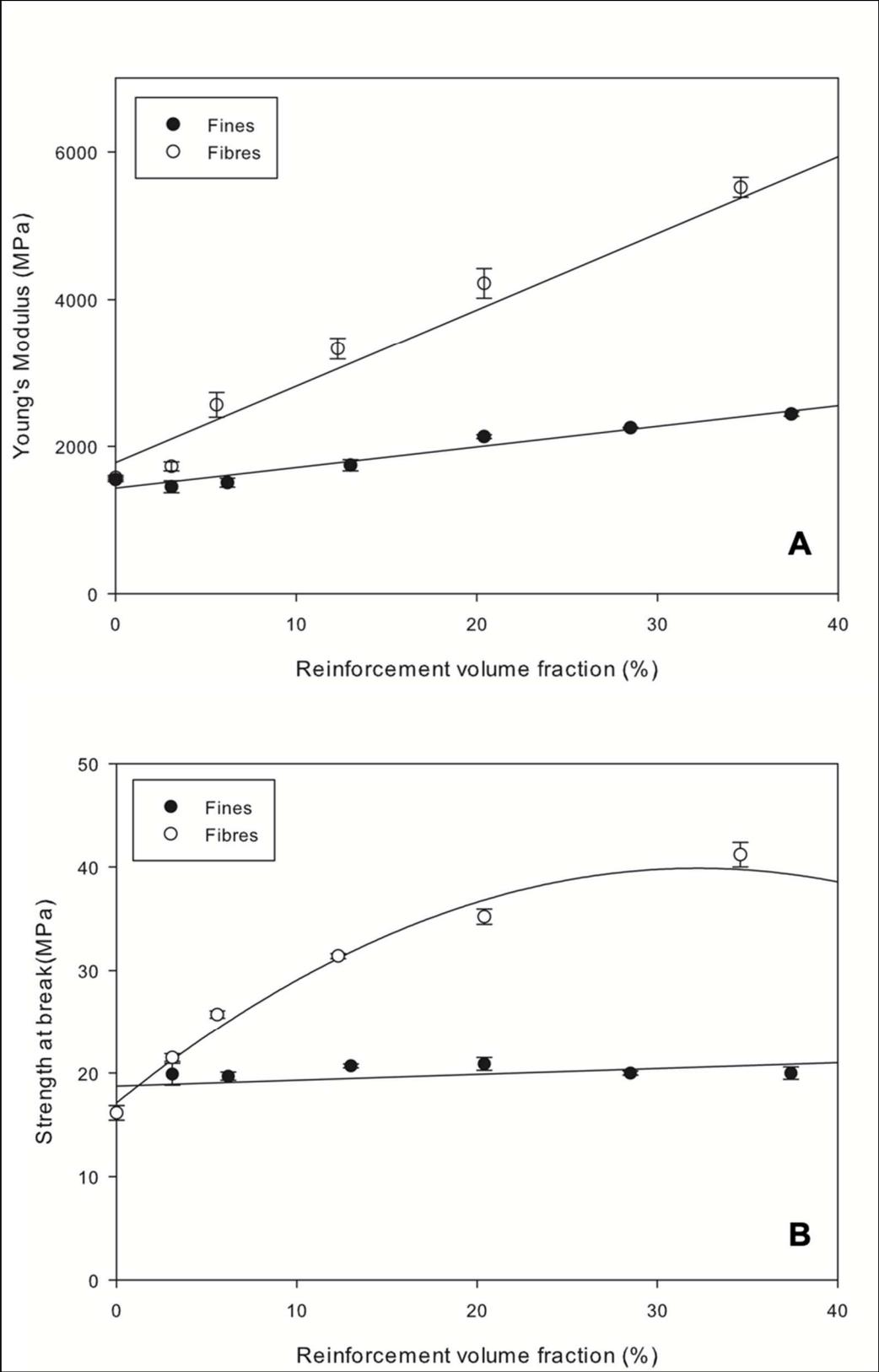


Figure 6. Influence of the reinforcement on the rheological properties of the composite. Example of PP composites.

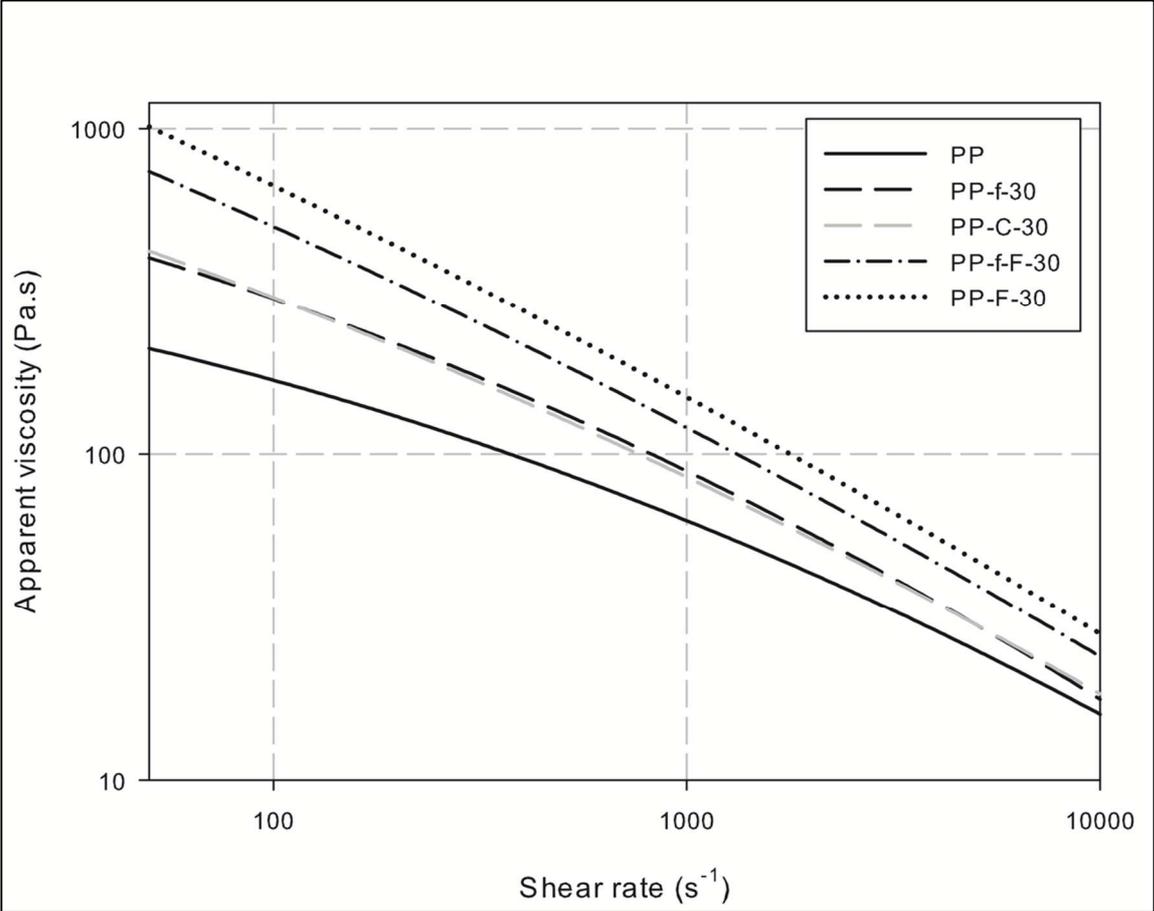


Figure 7. Tensile Young's modulus (A) and strength at max (B) of the different composites

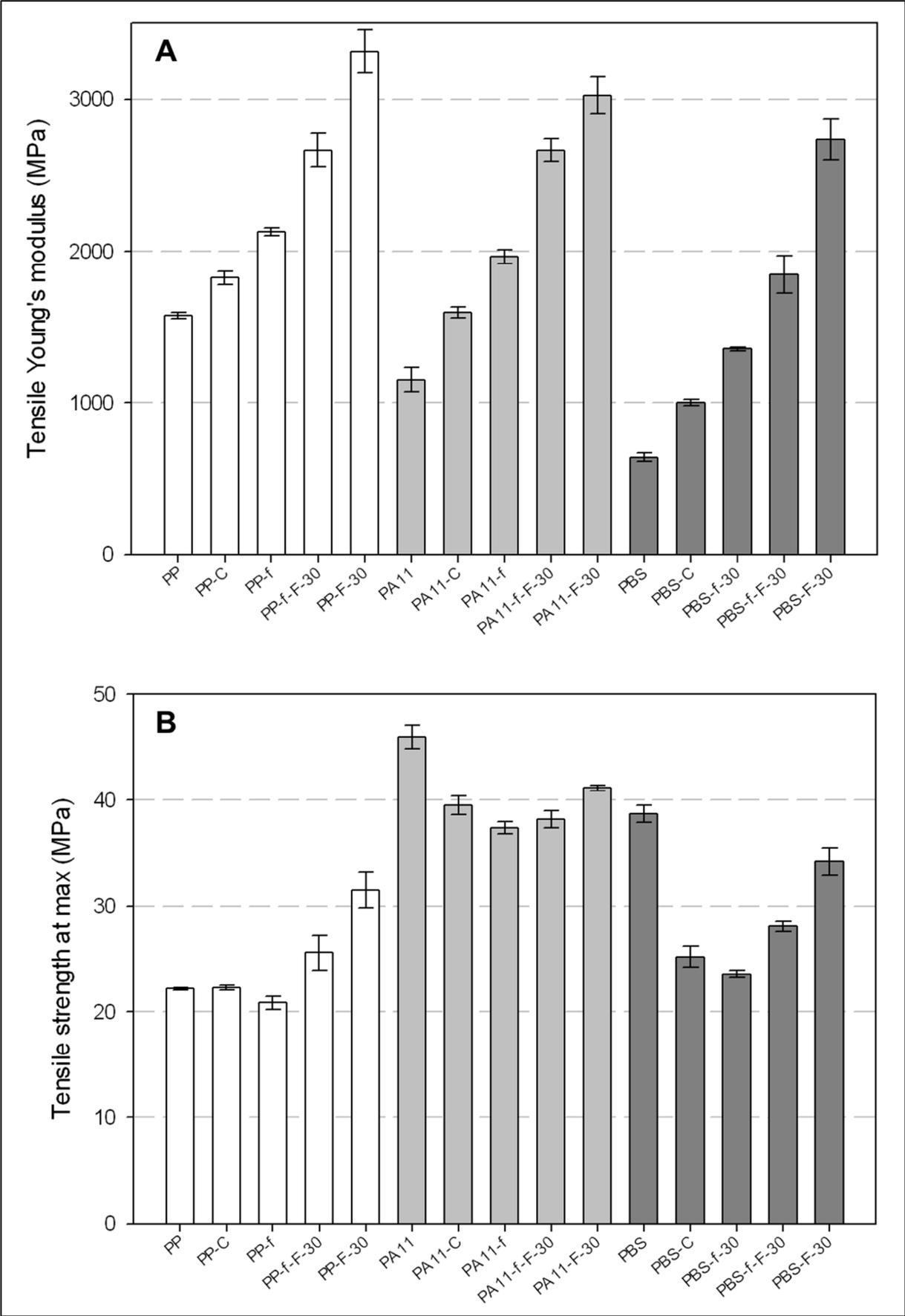


Figure 8. Impact energy of the different composites. No breakage with this test occurred for pure polymers, therefore results are not shown.

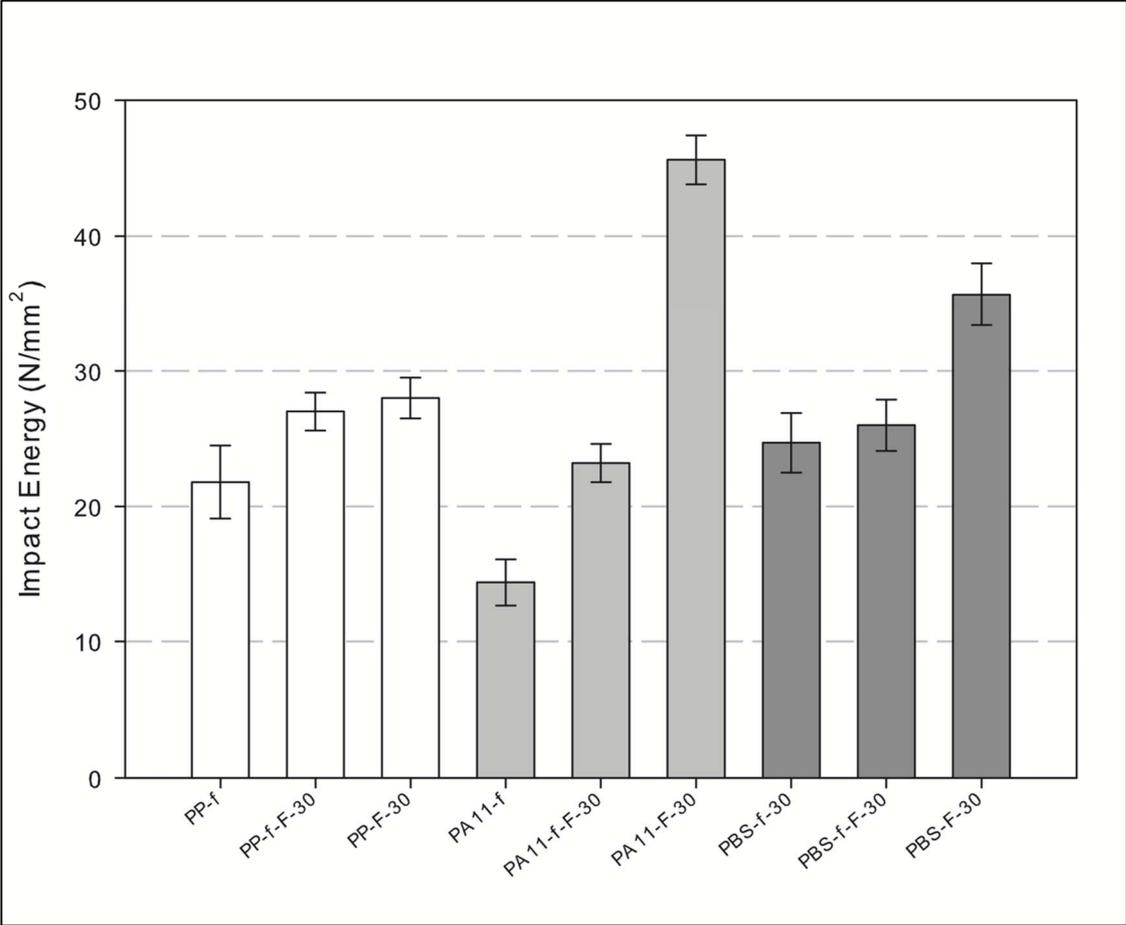


Table 1. Mechanical properties of elementary flax fibers (Bourmaud et al., 2015).

Materials	Number of fibers	Diameter (μm)	Young's modulus (GPa)	Strength at break (MPa)	Elongation at break (%)
Marilyn flax fibers	90	15.5 ± 2.7	53.8 ± 14.3	1215 ± 500	2.24 ± 0.59

Table 2. Formulations of the different composites, 'F' represents fibres and 'f' represents fines.

Sample	PP/PP-g-MA mass fraction (%)	PBS mass fraction (%)	PA11 mass fraction (%)	Fibres mass (and volume) fraction (%)	Fines mass (and volume) fraction (%)	Chalk mass (and volume) fraction (%)
PP-PPgMA	100	0	0	0	0	0
PBS	0	100	0	0	0	0
PA11	0	0	100	0	0	0
PP-f-5	95	0	0	0	5 (3.1)	0
PP-f-10	90	0	0	0	10 (6.2)	0
PP-f-20	80	0	0	0	20 (13.0)	0
PP-f-30	70	0	0	0	30 (20.4)	0
PP-f-40	60	0	0	0	40 (28.5)	0
PP-f-50	50	0	0	0	50 (37.4)	0
PP-F-5	95	0	0	5 (3.1)	0	0
PP-F-9	90	0	0	9 (5.6)	0	0
PP-F-19	80	0	0	19 (12.3)	0	0
PP-F-30	70	0	0	30 (20.4)	0	0
PP-F-47	60	0	0	47 (34.6)	0	0
PP-F-53	50	0	0	53 (40.2)	0	0
PP-f-F-30	70	0	0	15 (9.5)	15 (9.5)	0
PP-C-30	70	0	0	0	0	30 (12.7)
PBS-f-30	0	70	0	0	30 (20.4)	0
PBS-f-F-30	0	70	0	15 (9.5)	15 (9.5)	0
PBS-F-30	0	70	0	30 (20.4)	0	0
PBS-C-30	0	70	0	0	0	30 (12.7)
PA11-f-30	0	0	70	0	30 (20.4)	0
PA11-f-F-30	0	0	70	15 (9.5)	15 (9.5)	0
PA11-F-30	0	0	70	30 (20.4)	0	0
PA11-C-30	0	0	70	0	0	30 (12.7)

Table 3. Morphometric characteristics of the reinforcement after injection.

Sample	Lw (μm)	Dw (μm)	L/D (-)
PP-f-30	225 \pm 6	42 \pm 2	5 \pm 0.2
PP-f-F-30	430 \pm 100	39 \pm 8	11 \pm 2.0
PP-F-30	592 \pm 183	18 \pm 6	31 \pm 4.0
PA11-F-30	434 \pm 35	36 \pm 9	12 \pm 3.0
PBS-F-30	497 \pm 19	14 \pm 1	38 \pm 0.5