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Upcycling Sunflower Stems as Natural Fibers for Biocomposite Applications

Jean-Denis Mathias,^{a,*} Arnaud Alzina,^b Michel Grédiac,^{c,d} Philippe Michaud,^{c,d} Philippe Roux,^e Hélène De Baynast,^{c,d} Cédric Delattre,^{c,d} Nicolas Dumoulin,^a Thierry Faure,^a Pyrène Larrey-Lassalle,^c Narimane Mati-Baouche,^{c,d} Fabienne Pennec,^b Shengnan Sun,^{c,d} Nicolas Tessier-Doyen,^b Evelyne Toussaint,^{c,d} and Wei Wei^a

One of the big global, environmental, and socioeconomic challenges of today is to make a transition from fossil fuels to biomass as a sustainable supply of renewable raw materials for industry. Growing public awareness of the negative environmental effects of petrochemical-based products adds to the need for alternative production chains, especially in materials science. One option lies in the value-added upcycling of agricultural by-products, which are increasingly being used for biocomposite materials in transport and building sector applications. Here, sunflower by-product (obtained by grinding the stems) is considered as a source of natural fibers for engineered biocomposite material. Recent results are shown for the main mechanical properties of sunflower-based biocomposites and the socioeconomic impact of their use. This paper demonstrates that sunflower stem makes a good candidate feedstock for material applications. This is due not only to its physical and chemical properties, but also to its socioeconomic and environmental rationales.

Keywords: Agricultural by-product; Biocomposite; Natural fiber; Sunflower stem; Waste management

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INTRODUCTION

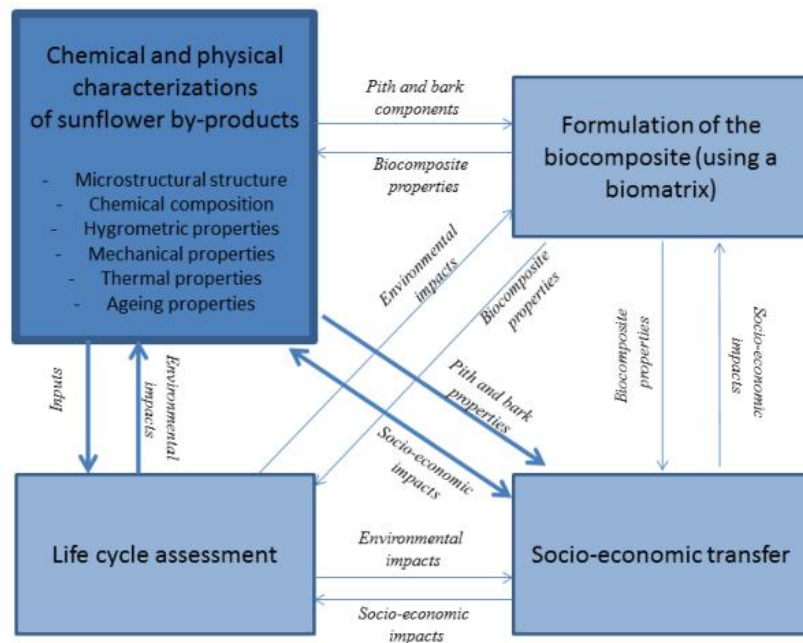
Over the last few decades, increasing environmental concerns have prompted a surge in research by the composite science community to develop natural-fiber biocomposites. These materials can be completely degraded in soil, or, by composting, do not emit volatile organic compounds, and are softer on the environment than petrochemical resource-based products (Mohanty *et al.* 2000; Lithner *et al.* 2011). Agricultural by-products have several advantages over classical natural fibers: they do not need dedicated agricultural fields, they are already readily available, and they offer valuable environmental compatibility over standard-feedstock fibers (Reddy and Yang 2005). These factors are increasingly central now that biocomposites have found widespread use in all areas of life. The reason for this increasing use of biocomposites is performance at lower cost and reduced density when compared to classic synthetic materials (Reddy and Yang 2005). Nonetheless, some agricultural by-products are already exploited by second-generation biorefineries (Pfaltzgraff and Clark 2014).

52 Therefore, the main objective for the bio-based material sector now is to find new sources
53 of fibers to avoid competition with the growth of crops for human food or biofuels
54 (Kopetz 2013). In this context, the present work focuses on a promising agricultural by-
55 product, sunflower stems. Sunflower by-products are of interest because they are not
56 currently exploited, their composition enables low-impact extractability from the field,
57 and oilseed biorefineries can achieve greater economic viability by selling their by-
58 products.

59 Sunflower-based oil ranks fourth in world oil crop production, with nearly 25
60 million hectares (FAOSTAT 2013). Seed and oil have been the main compounds
61 exploited by industry. In most cases, seed and oil are both extracted from the head, and
62 the stems are left in the fields. No significant industrial use of the stems that are shredded
63 after seed harvesting has currently been proposed, although sunflower stems are exploited
64 for combustion applications, animal feed, and/or fuel production (Chen and Lu 2006).
65 These solutions consume only a small fraction of the sunflower by-product production.
66 We propose to explore a new way of extracting value from sunflower stems by evaluating
67 their potential as a natural fiber feedstock for biocomposite applications. Considering five
68 tons of sunflower stalks per hectare, the potential production of this by-product reaches
69 125 million tons. In comparison with other natural fibers (not including wood), this
70 potential production tonnage is higher than that of bamboo farming (30 million tons,
71 mostly in Asia and South America), which, alongside cotton, is one of the most heavily
72 produced sources of commercial fiber in the world (Faruk *et al.* 2012). The potential
73 value of sunflower by-products as a biofiber is enhanced by the fact that sunflower is
74 grown worldwide (FAOSTAT 2013). This could create opportunities to build a new
75 worldwide agricultural economy and is a key advantage over other agricultural by-
76 products, like bamboo, that are not available across the world. Furthermore, sunflower
77 by-products are available in large amounts at zero or negligible price in an economic
78 context, where the natural-fiber biocomposites market grew by 15% between 2005 and
79 2010 (Lucintel 2011). Indeed, the entire composite market is growing. For example, the
80 polymer composites market has increased from 33 billion Euros in 2002 to 41.5 billion
81 Euros in 2005 (Friedrich and Almajid 2013). This surge in the natural fibers market is
82 primarily driven by the automotive and building sectors (John and Thomas 2008). In the
83 automotive sector, EU and US legislations impose specific directives on the end-of-life of
84 vehicles. For instance, the non-recycled fraction of materials will be cut by 5% in 2015 in
85 Europe (European Commission. Directive 2000/53/EC 2000). In addition, natural fibers
86 are expected to provide a 30% weight reduction and a 20% cost reduction compared to
87 classic composites (Bledzki *et al.* 2006). Furthermore, the low density of natural fibers
88 equates to significant energy savings (primarily fuel) and their economic value may be
89 extended to all fields of transportation (railway, marine, aerospace) (Bledzki *et al.* 2006;
90 Friedrich and Almajid 2013). Natural fibers are also exploited in building applications,
91 not only for their low density but also for their thermal insulating properties. Their
92 development was recently stimulated in the USA and in Europe by legislation imposing
93 enhanced energy efficiency of existing buildings by 2020 (European Commission.
94 Directive 2010/31/EU 2010), which yielded a significant market in green retrofit
95 solutions.

96 This work presents the main results obtained from a project (Demether 2011)
97 whose objective was to produce biocomposites for building insulation by factoring not
98 only chemical and physical properties but also the environmental and socio-economic
99 impacts tied to processing and use (Fig. 1). In view of the results obtained, it is argued

100 that sunflower stems can be useful for other biocomposite-using applications such as
 101 automobiles. First, general results are presented corresponding to sunflower by-product
 102 properties, highlighting both unpublished and published data by giving associated
 103 references. Note that examples of biocomposite engineering using sunflower by-products
 104 can be found elsewhere (Mati-Baouche *et al.* 2014, 2015; Sun *et al.* 2015). In this
 105 context, the objective here was twofold: i) to report the main results of the project about
 106 the properties of the sunflower stems; ii) to report the general project conclusions on the
 107 use of sunflower by-products to give the interested reader a clear picture of what can be
 108 expected from this innovative type of biocomposite.



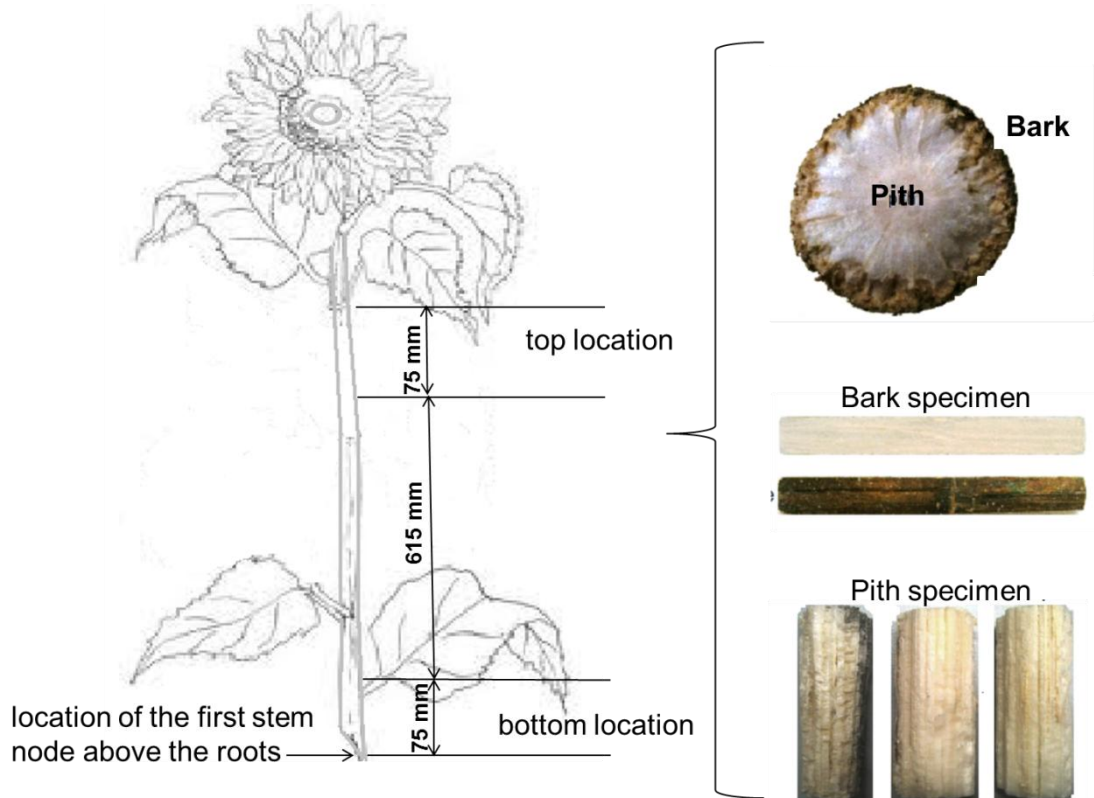
109
 110 **Fig. 1.** General flowchart of the design of insulating biocomposite. The article focuses on the
 111 main physical and chemical properties of sunflower stems obtained under this project framework.
 112

113 114 EXPERIMENTAL

115 116 Sample Description

117 This study characterized the material properties of the stems of LG5474
 118 sunflower species harvested in September 2010 in Perrier, France. Two particular on-
 119 stem locations were defined as the bottom and the top of the stalk (Fig. 2). The bottom
 120 location was defined as the level of the first node above the roots. Note that no specific
 121 (mechanical or chemical) treatment was performed, as it has been shown that specific
 122 treatments may alter certain properties (Li *et al.* 2007), as will also be shown by results
 123 presented in the discussion that follows. However, as explained earlier, this paper focuses
 124 on the properties of fibers, and any investigation into the influence of mechanical or
 125 chemical treatments would require a dedicated companion paper. Evidence that these

126 fibers are useable without any particular treatment can be found elsewhere (Mati-
 127 Baouche *et al.* 2014; Sun *et al.* 2015).
 128



129
 130 **Fig. 2.** Sampling zones and specimens tested
 131

132 **Microstructural Analysis**

133 Sections of bark were first separated from the stem, saturated with water,
 134 immersed, and kept in three PEG (polyethylene glycol electrolyte) solutions at various
 135 concentrations (30%, 60% and 100%) for 24 h each. A 20 μm -thick sample was cut using
 136 a fully automated Leica (Wetzlar, Germany) RM2255 rotary microtome. It was then
 137 colored with the so-called double-staining method using safranin (for the presence of
 138 lignin) and astra blue (for the presence of cellulose). After coloration, the samples were
 139 dried with Joseph paper. They were mounted on a cover-slip with the fast-drying Eukitt
 140 (Freiburg, Germany) mounting medium. Finally, micrographs of these cross-sections
 141 were obtained using a Zeiss (Oberkochen, Germany) optical microscope. These images
 142 were processed with the ImageJ software (National Institutes of Health, USA) to estimate
 143 the porosity of the barks extracted from both the bottom and top locations. Macroscopic
 144 voids in the pith make it difficult to separate pith and bark. Therefore, the analysis should
 145 be carried out on complete stem sections. The analysis was performed using the Skyscan
 146 (Anvers, Belgique) CT-Analyzer with two sections of stem extracted from the bottom
 147 and top locations. The working length was 30 mm.
 148

149 **Cellulose and Lignin Assays**

150 A biochemical analysis was performed on bark of different stem specimens at
 151 different locations (bottom, centre, and top). For the pith, cellulose and lignin assays were
 152 applied without distinction of in-stem location. The Henneberg protocol (Henneberg and

153 Stohmann 1860, 1864) was used to quantify the percentage of cellulose (C). Lignin
154 content (L) was evaluated by the procedure of Jarrige (Jarrige 1961).
155

156 **Hygrometric Analysis**

157 Absorption and desorption tests were performed at various relative humidities
158 (RH) (8%, 33%, and 75%) to deduce both the absorption and desorption coefficients. A
159 desiccant (phosphorus pentoxide) was placed in the oven beforehand. The specimens
160 were then placed in a conditioning chamber (one for each desired value of RH). These
161 chambers were polymer jars in which saturated aqueous salt solutions imposed a certain
162 RH. The RH depends on the nature of the salt. Absorption and desorption coefficients
163 were deduced from the mass-time curves using suitable relationships that depend on
164 specimen geometry. The different solutions corresponding to different RH levels were
165 prepared according to standard ISO 483 procedure (2005). These tests lasted at least three
166 days to ensure that equilibrium was obtained within the specimens. Six bark specimens
167 and five pith specimens were tested for each experimental condition. See Sun *et al.*
168 (2013, 2014) for further details.
169

170 **Mechanical Analysis**

171 Results for bark specimens were obtained using a Deben (Suffolk, UK) micro-
172 machine equipped with a 2-kN load cell. The cross-head speed was 2 mm/min with a
173 clamping length of 30 mm. Results for pith specimens were obtained by compression
174 tests using an Instron (Norwood, USA) 5543 testing machine equipped with a 500-N load
175 cell. The cross-head speed was 5 mm/min. Ten specimens were tested for each
176 experimental condition.
177

178 **Thermal Analysis**

179 The thermal diffusivities of the bark and pith specimens were measured with the
180 laser flash method. The specific heat capacity was measured with a C80 Setaram
181 (Caluire, France) calorimeter. Finally, the thermal conductivity of the bark and pith
182 specimens was deduced by multiplying apparent density (equal to the mass divided by
183 the volume of cylindrical specimens) by thermal diffusivity and heat capacity. Another
184 transient technique (Hot Disk from ThermoConcept, France) was used to check the
185 thermal conductivity values on pith specimens and yielded similar results. Six samples
186 were tested for each experimental condition.
187

188 **Ageing Analysis**

189 Three weather conditions were tested: humidity, temperature, and UV radiation.
190 The humidity and temperature values used for the ageing analysis were 75% and 80 °C,
191 respectively. Specimens were tested for the ageing conditions of 75% humidity, 80 °C,
192 and the combination of both. The ageing condition of 75% humidity was achieved
193 according to the procedure given in the ISO 483 (2005) standard. Conditioning at 80 °C
194 was performed using a Salvislab Thermocenter oven (Rotkreuz, Switzerland). The
195 combined conditions were obtained using a Vötsch (Hanau, Germany) VCL 4003
196 climatic oven. The UV exposure (1000 h) was performed in the accelerated conditions
197 given by the Atlas MTT (Mount Prospect, USA) SEPAP 12 – 24 chamber, which
198 corresponds to the ageing condition described in the usual standards on this subject (NF-
199 T51-195-5 2008; BS EN 16472 2014).
200

201 Spectroscopic Analysis

202 Fourier-Transform Infrared (FT-IR) measurements were carried out using a
203 Thermo Scientific (Waltham, Massachusetts) Nicolet 6700 FT-IR instrument. The IR
204 spectra (128 scans) were recorded at room temperature on a MTEC (Ames, USA) 200
205 photoacoustic detector (referenced against carbon black powder; detector chamber was
206 purged with dry helium gas) with a wave-number range of 700 to 4000 cm^{-1} . The spectra
207 were analyzed with Thermo Scientific (Waltham, Massachusetts) Omnic software. Six
208 bark specimens and four pith specimens from the bottom and top locations were tested.

210 Environmental Assessment

211 For the comparison of environmental impacts between maize and sunflower,
212 EcoInvent data for crop production (Nemecek and Kagi 2007) was used. The endpoint
213 impacts (Goedkoop *et al.* 2009) associated with the production of maize grain and
214 sunflower seeds in one hectare (Nemecek and Kagi 2007) were compared, *i.e.*,
215 9279 kg/ha for maize and 3151 kg/ha for sunflower. The farming system considered here
216 was integrated production (IP). Included processes were soil cultivation, sowing, weed
217 control, fertilization, pest and pathogen control, harvesting, and drying the grains.
218 Machine infrastructure and a shed for housing the machine were included. Inputs of
219 fertilizers, pesticides, and seed, as well as their transport to the regional processing centre
220 (10 km), were considered.

223 RESULTS AND DISCUSSION

225 Obtained results are detailed and analyzed in the following sections. However, for
226 the sake of clarity, the main results are reported schematically in Fig. 3. The pith and bark
227 properties are compared with those of other natural fibers in Table 1.

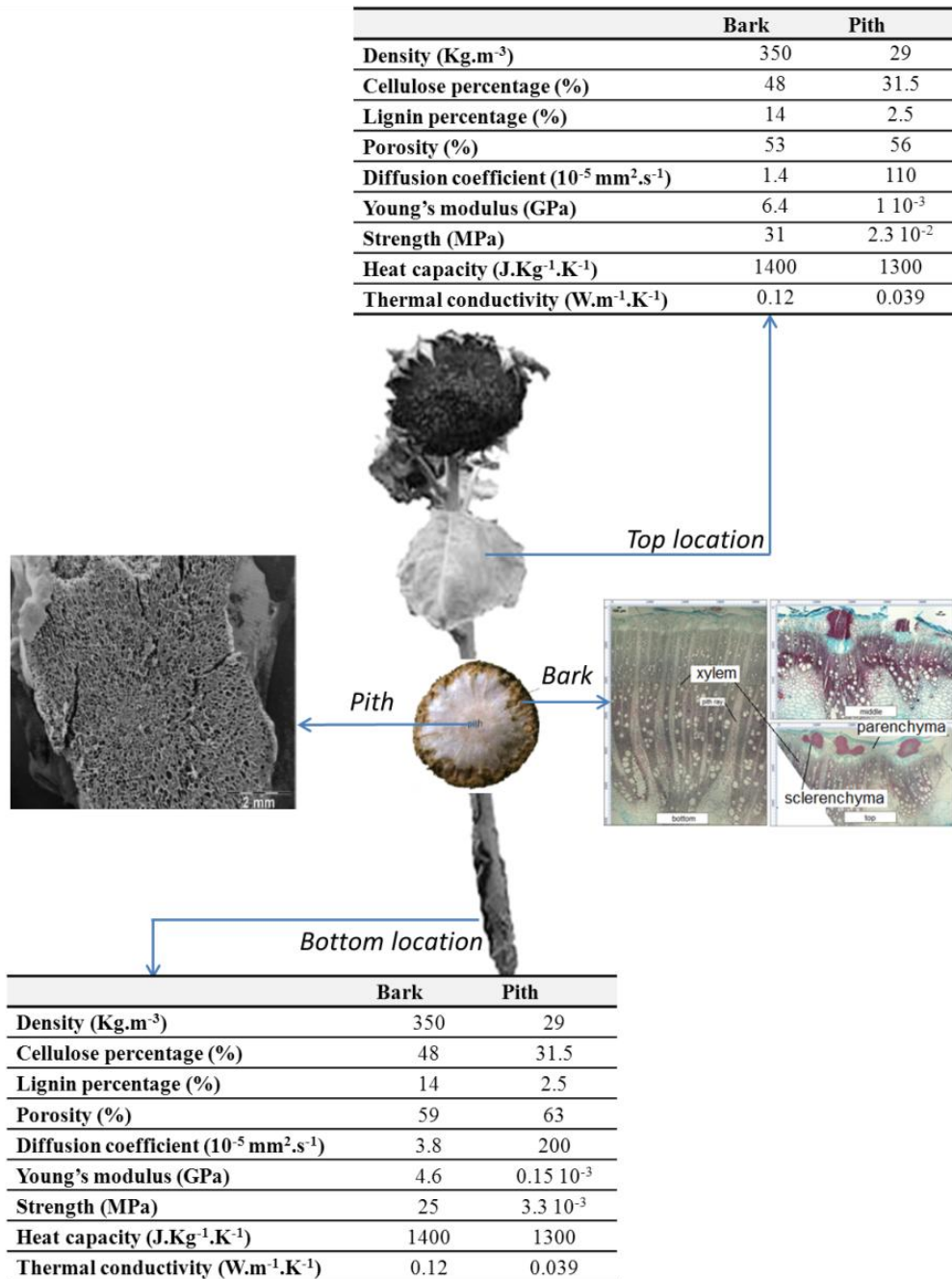
229 **Table 1.** Main Properties of Bark, Pith, and Other Natural Fibers

	Bark	Pith	Other natural fibers	References
Young modulus (GPa)	[4.6-6.4]	$[0.15-1] \cdot 10^{-3}$	Pineapple : 1.4 Oil palm: 3.2 Jute: 10 Flax: 80	(Faruk <i>et al.</i> 2012) (Faruk <i>et al.</i> 2012) (Ahmad <i>et al.</i> 2015) (Ahmad <i>et al.</i> 2015)
Specific modulus ($\text{GPa} \cdot \text{m}^3 \cdot \text{Kg}^{-1}$)	[0.013-0.018]	$[0.005-0.034] \cdot 10^{-3}$	Coir : [0.0033-0.005] Jute: [0.00685-0.0206] Flax: [0.0184-0.053]	(Ahmad <i>et al.</i> 2015)
Strength (MPa)	[25-31]	$[3.3-23] \cdot 10^{-3}$	Coir : 175 Jute : [393-800] Flax: [800-1 500]	(Ahmad <i>et al.</i> 2015)
Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	0.12	0.039	Flax: [0.035-0.075] Hemp: [0.040-0.094] Glass wool: [0.04-0.05] Stone wool: [0.035-0.05]	(Kymäläinen and Sjöberg 2008)

231 Pith and Bark Microstructures

232 The stem volume constitutes 90% of the sunflower. It is made of two main parts:
233 bark and pith. Intuitively, the bark can be expected to be used for applications requiring
234 mechanical strength, and the pith for thermal insulation purposes, because of its large
235

236 volume fraction of intragranular pores. Preliminary microscopy observations showed that
 237 the pith and bark both change in appearance along the stem (Fig. 3). The number of
 238 sclerenchyma fibers in the bark increases going up the stem, while porosity decreases
 239 from 59% at the bottom to 53% at the top. The pith shows more macroscopic voids at the
 240 bottom of the stem (63%) than at the top (56%).
 241



242
 243
 244 **Fig. 3.** Main physical and chemical properties of sunflower stems
 245

246 **Biochemical Composition**

247 Biochemical analysis revealed that the chemical composition did not vary along
 248 the stem, with a mean composition of 48% cellulose and 14% lignin for the bark, and

249 31.5% cellulose and 2.5% lignin for the pith. Note that the chemical composition of
250 sunflower stem bark (14% of lignin) is very close to that of jute (13% of lignin)
251 (Summerscales *et al.* 2010). The chemical composition may directly influence the
252 material properties of these two parts of the stem. However, it does not completely
253 explain the variations in material properties observed along the stem. Therefore, the
254 influence of microstructure along the stem on material properties was examined. Because
255 it is well known that RH significantly influences the material properties of natural fibers,
256 hygroscopic tests were performed beforehand.

257

258 **Hygroscopic Behavior**

259 The tests results clearly revealed that the diffusion coefficients for moisture of
260 both the bark and pith specimens were higher at the bottom ($3.8 \times 10^{-5} \text{mm}^2 \cdot \text{s}^{-1}$ for the bark
261 and $200 \times 10^{-5} \text{mm}^2 \cdot \text{s}^{-1}$ for the pith) than at the top of the stem ($1.4 \times 10^{-5} \text{mm}^2 \cdot \text{s}^{-1}$ for the
262 bark and $110 \times 10^{-5} \text{mm}^2 \cdot \text{s}^{-1}$ for the pith). This is primarily because of the difference in
263 porosity along the stem. The moisture diffusion mechanism depends directly on cell
264 cavities, as described and explained for other materials such as wood (Times 2002a,b).
265 Two mechanisms govern the moisture diffusion process in sunflower stems: bound water
266 diffusion through the cell walls, and vapour diffusion through the cell cavities. Moisture
267 diffusion through cell cavities is more significant than moisture diffusion through the cell
268 walls. Therefore, the porosity of both the bark and pith specimens is expected to change
269 the value of the macroscopic diffusion coefficient obtained from the hygroscopic tests. In
270 the situation considere in this work, the increase in amount of porosity or decrease in
271 amount of cell wall content of the specimens is expected to increase the value of the
272 moisture diffusion coefficient. Subsequently, the effect of various RH levels was
273 evaluationed relative to both the mechanical and thermal properties.

274

275 **Mechanical Properties**

276 Mechanical tests were carried out to evaluate Young's modulus and the strength
277 of both the bark and the pith. As expected, bark specimens expressed higher Young's
278 modulus values (4.6 GPa at the bottom and 6.4 GPa at the top) than pith specimens
279 (0.15 MPa at the bottom and 1 MPa at the top). It is worth noting that high RH tended to
280 decrease the Young's modulus (a near 10% differential between 0% RH and 75% RH).
281 However, this effect was less significant than the influence of the sample location along
282 the stem. The difference in Young's modulus between bark and pith was in accordance
283 with their chemical composition. Bark has a higher lignin percentage and a lower mean
284 intergranular pore volume fraction than pith. Furthermore, the Young's modulus of both
285 bark and pith increased along the stem, obtaining higher values at the top, which was
286 attributed mainly to the lack of cavities. There was also an increase in the mechanical
287 strength of bark (from 25 to 31 MPa) and pith (from 3.3 to 23 kPa).

288

289 The Young's modulus of sunflower stem bark (4.6 to 6.4 GPa) is on a par with
290 other by-product fibers, including oil palm (3.2 GPa) or pineapple fibresones (1.4 GPa)
291 (Faruk *et al.* 2012). With respect to other natural fibers extracted from stems, such as
292 flax, hemp or jute, the Young's modulus of sunflower stem bark is slightly lower (lying
293 between 10 GPa for jute and 80 GPa for flax fiber) (Ahmad *et al.* 2015). The trade-off
294 between the Young's modulus and the density is also a key-issue in many applications,
295 for instance, in the automotive industry. In the case of sunflower stem bark, the specific
296 modulus (ratio of the Young's modulus by the density) is between 13 and 18 $\text{GPa} \cdot \text{m}^3 \cdot \text{Kg}^{-1}$,
1, which is very close to the value of the Young's modulus of jute (Ahmad *et al.* 2015).

297 This value enables designers to consider the sunflower stem bark for producing
298 components of vehicles to reduce weight and therefore fuel costs as well.
299

300 Thermal Properties

301 The thermal conductivity also were investigated for both the bark and the pith
302 (Pennec *et al.* 2013). As expected, pith showed a lower mean thermal conductivity (0.039
303 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) than bark (0.12 $\text{W}\cdot\text{mm}^{-1}\cdot\text{K}^{-1}$). In contrast to the Young's modulus, the thermal
304 conductivity of both the bark and the pith did not evolve along the stem. The variation of
305 the pore volume fraction is thought to be too small to have a significant influence on
306 thermal conductivity. Moreover, both bark and pith demonstrated significant heat
307 capacity values (mean values of 1400 and 1300 $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ for bark and pith, respectively)
308 approaching levels found in hemp fiber (nearly 1500 $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$). Additionally,
309 preliminary experiments carried out while varying the RH of the samples from 0 to 100
310 wt% revealed that the thermal conductivity of pith and bark can double because of the
311 absorbed water.

312 In terms of thermal insulation applications, the pith showed interesting thermal
313 properties. Its thermal conductivity (0.039 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) was even better than the thermal
314 conductivity of glass wool (0.046 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and its heat capacity was on a par with
315 hemp. The thermal conductivity of the pith was competitive with other natural fibers. For
316 example, flax's ranges between 0.035 to 0.075 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, depending on the harvest
317 location and the variety (Kymäläinen and Sjöberg 2008). Hemp's is between 0.040 and
318 0.094 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (Kymäläinen and Sjöberg 2008). Therefore, sunflower pith may be
319 considered as raw materials for thermal insulation applications.
320

321 Ageing Results

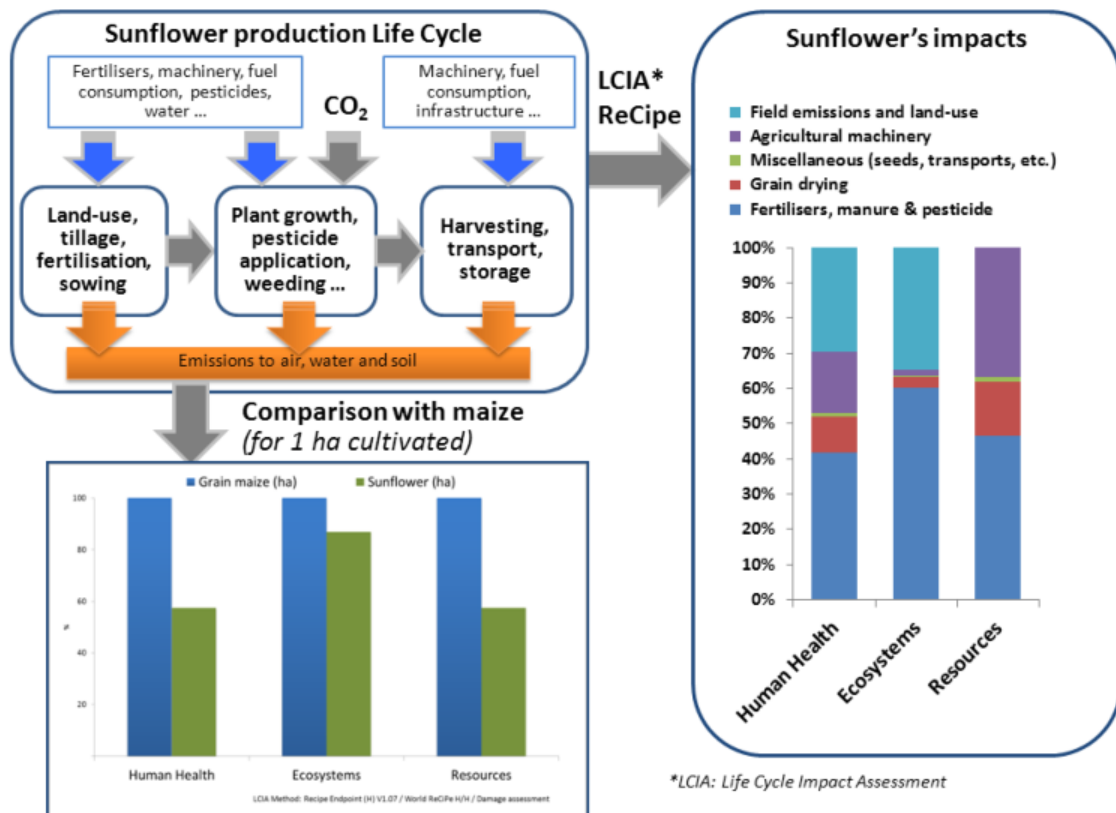
322 The biodegradable character of sunflower plants makes them environmentally
323 safe for waste disposal but makes sunflower-based fiber sensitive to weather conditions.
324 The ageing properties were studied by testing the influence of different weather
325 conditions such as humidity, temperature, and UV radiation on the variation in Young's
326 modulus. The Young's modulus of both the bark and the pith were unaffected if only one
327 weather condition was increased (temperature or moisture exposure alone). Increasing
328 both the temperature and moisture exposures (80 °C and 75% RH) did not affect the
329 Young's modulus of the bark, but it diminished the Young's modulus of the pith by about
330 30% after one week (and 50% after two weeks). After UV treatment for 1000 h
331 (equivalent to a 3-year exposure), the oxidation of organic matter was detected by FTIR
332 measurements. Absorption bands at 1703 and 3500 to 2200 cm^{-1} were detected and
333 attributed to the C=O and OH stretching vibrations of carboxylic groups, respectively.
334 These carboxylic acids were most likely from the breaking of polymeric chains.
335

336 Environmental Impact

337 Finally, the environmental impact of exploiting sunflower stems in the rural
338 economy was investigated. Life cycle assessment is a requirement to evaluate the
339 environmental impacts of natural fibers (Joshi *et al.* 2004). The reasonable quantities of
340 water, fertilizers, and pesticides that are needed per hectare seem promising compared to
341 maize, rape, and wheat crops. Using available EcoInvent data for crop production
342 (Nemecek and Kagi 2007), it is possible to assess the impact of sunflower plants over
343 their entire life cycle. Figure 4 presents these results using the ReCipe impact assessment
344 method (Goedkoop *et al.* 2009) for three impact categories, which are human health,

345 ecosystems, and resources. The various effects of sunflower plants over their life cycle
 346 were compared against those of maize, which is the most widely grown grain crop. The
 347 question of a partial allocation of the agricultural phase to stems depends on their status.
 348 As long as sunflower stems are considered agricultural waste, then no impact of the
 349 agricultural phase should be allocated to their production. However, a huge surge in the
 350 use of sunflower stems for biocomposite applications would lead to competition for their
 351 exploitation, which would prompt a change in the status of sunflower stems and a move
 352 them up from “waste” to a valuable “co-product.” In this case, either (i) the part of the
 353 environmental impacts of sunflower production should be allocated to the production of
 354 the stems, based for instance on a financial allocation; or (ii) the system boundaries
 355 should be extended and substitutions should be studied to share agricultural impacts.

356 Sunflower cultivation has less environmental impact, in terms of water need,
 357 fertilizer, and pesticide, than a standard crop production such as maize. Moreover, using
 358 existing by-products constitutes an environmental benefit in comparison with other natural
 359 fibers, which require a dedicated agricultural field that increases the environmental
 360 impacts.



361
 362 **Fig. 4.** Environmental analysis of sunflower production
 363

364
 365 **CONCLUSIONS**

366
 367 In Europe and in the USA, legislative and public opinion pressures affecting the
 368 use of bio-based materials are rising (Technology Road Map for Plant/Crop Based
 369 Renewable Resources 2020 in the USA or the Biomass Action Plan in Europe). The

370 sunflower stems, not yet valued, constitute a promising raw material for a variety of
371 applications. This is mainly due to their mechanical and thermal properties as well as to
372 their environmental impact. Detailed studies will be required in order to characterize the
373 influence of different treatments or industrial processes on the properties of the sunflower
374 bark and pith, depending on the industrial application. Sunflower also offers a number of
375 socioeconomic assets in a growing natural fiber market of large stocks, low price, and
376 worldwide crop ability. It is also necessary to study in details (like other natural
377 resources), such as how to organise the local agricultural sector for collecting and storing
378 the sunflower stems as well as processes for their conversion into bio-based materials.
379 Further research is therefore needed for moving away from a promising raw material to
380 an effective solution in terms of both physical properties and socio-economic
381 valorization.

382

383

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391

392

393 REFERENCES CITED

394

- 395 Ahmad, F., Choi, H. S., and Park, M. K. (2015). "A review: Natural fiber composites
396 selection in view of mechanical, light weight, and economic properties," *Macromol.*
397 *Mater. Eng.* 300(1), 10-24. DOI: 10.1002/mame.201400089
- 398 Bledzki, A. K., Faruk, O., and Sperber, V. E. (2006). "Cars from bio-fibres," *Macromol.*
399 *Mater. Eng.* 291(5), 449-457. DOI: 10.1002/mame.200600113
- 400 BS EN 16472 (2014). "Plastics — Method for accelerated photoageing using medium
401 pressure mercury vapour lamps," British Standards Institute, London, UK.
- 402 Chen, J. H., and Lu, X. F. (2006). "Progress in bio-fuel combustion in circulating
403 fluidized bed boiler," *Transactions of the Chinese Society of Agricultural*
404 *Engineering* 22(10), 267-270.
- 405 European Commission. Directive 2000/53/EC of the European Parliament and the
406 Council on end-of-life vehicles. *Official Journal of the European Communities.*
- 407 European Commission. Directive 2010/31/EU of the European Parliament and of the
408 Council of 19 May 2010 on the energy performance of buildings. *Official Journal of*
409 *the European Communities.*
- 410 Demether (2011). "Development of biomaterials from agricultural byproducts for the
411 thermal insulation of existing buildings," French National Project Granted by the
412 French National Research Agency (anr-10-ecot- 004 grant).
413 <http://demether.cemagref.fr>.
- 414 FAOSTAT database. (2013). Food and Agriculture Organization of the United Nations.
415 <http://faostat3.fao.org/>.

- 416 Faruk, O., Bledzki, A. K., Fink, H. P., and Sain, M. (2012). "Biocomposites reinforced
417 with natural fibers: 2000-2010," *Prog. Polym. Sci.* 37(11), 1552-1596.
418 DOI:10.1016/j.progpolymsci.2012.04.003
- 419 Friedrich, K., and Almajid, A. A. (2013). "Manufacturing aspects of advanced polymer
420 composites for automotive applications," *Appl. Compos. Mater.* 20(2), 107-128.
421 DOI:10.1007/s10443-012-9258-7
- 422 Goedkoop, M., Heijungs, R., Huijbregts, M., De Schryver, A., Struijs, J., and Van Zelm,
423 R. (2009). "Recipe 2008 - A life cycle impact assessment method which comprises
424 harmonised category indicators at the midpoint and the endpoint level," First Edition
425 Report I: Characterisation. <http://www.pre-sustainability.com/>.
- 426 Henneberg, W. and Stohmann, F. (1860). *Beiträge zur Begründung Einer Rationellen*
427 *Fütterung der Wiederkäuer, Heft 1*, Schwetschke and Sohn (ed.), Braunschweig,
428 Deutschland.
- 429 Henneberg, W., and Stohmann, F. (1864). *Beiträge zur Begründung Einer Rationellen*
430 *Fütterung der Wiederkäuer, Heft 2*, Schwetschke and Sohn (ed.), Braunschweig,
431 Deutschland.
- 432 ISO 483 (2005). "Plastics — Small enclosures for conditioning and testing using aqueous
433 solutions to maintain the humidity at a constant value," International Organization for
434 Standardization, Geneva, Switzerland.
- 435 Jarrige, R. (1961). "Analyse des constituants des plantes fourragères. Fractionnement des
436 constituants de la membrane par les hydrolyses acides," *Annales de Biologie Animale.*
437 *Biochimie. Biophysique* 1(2), 163-212.
- 438 John, M. J., and Thomas, S. (2008). "Biofibres and biocomposites," *Carbohydr. Polym.*
439 71(3), 343-364. DOI:10.1016/j.carbpol.2007.05.040
- 440 Joshi, S. V., Drzal, L. T., Mohanty, A. K., and Arora, S. (2004). "As natural fiber
441 composites environmentally superior to glass fiber reinforced composites," *Compos.*
442 *Part A-Appl. S.* 35(3), 371-376. DOI:10.1016/j.compositesa.2003.09.016
- 443 Kymäläinen, H.-R., and Sjöberg, A.-M. (2008). "Flax and hemp fibres as raw materials
444 for thermal insulations," *Build. Environ.* 43(7), 1261-1269.
445 DOI:10.1016/j.buildenv.2007.03.006
- 446 Kopetz, H. (2013). "Renewable resources: Build a biomass energy market," *Nature*
447 494(7435), 29-31. DOI:10.1038/494029a
- 448 Li, X., Tabil, L. G., and Panigrahi, S. (2007). "Chemical treatments of natural fiber for
449 use in natural fiber-reinforced composites: A review," *J. Polym. Environ.* 15(1), 25-
450 33. DOI: 10.1007/s10924-006-0042-3
- 451 Lithner, D., Larssoni, A., and Dave, G. (2011). "Environmental and health hazard
452 ranking and assessment of plastic polymers based on chemical composition," *Sci.*
453 *Total Environ.* 409(18), 3309-3324. DOI:10.1016/j.scitotenv.2011.04.038
- 454 Lucintel (2011). "Report: Opportunities in natural fiber composites,"
455 <http://www.lucintel.com/LucintelBrief/PotentialofNaturalfibercomposites-Final.pdf>.
- 456 Mati-Baouche, N., De Baynast, H., Lebert, A., Sun, S., Lopez-Mingo, C. J. S., Leclaire,
457 P., and Michaud, P. (2014). "Mechanical, thermal and acoustical characterizations of
458 an insulating bio-based composite made from sunflower stalks particles and
459 chitosan," *Ind. Crop. Prod.* 58, 244-250. DOI:10.1016/j.indcrop.2014.04.022
- 460 Mati-Baouche, N., De-Baynast, H., Sun, S., Lebert, A., Petit, E., and Michaud, P. (2015).
461 "Polysaccharidic binders for the conception of an insulating agro-composite,"
462 *Composites Part A.* 78, 152-159.

- 463 Mohanty, A. K., Misra, M., and Hinrichsen, G. (2000). "Biofibres, biodegradable
464 polymers and biocomposites: An overview," *Macromole. Mater. Eng.* 276-277(1), 1-
465 24. DOI: 10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W
- 466 Nemecek, T., and Kagi, T. (2007). "Life cycle inventories of agricultural production
467 systems," Final Report Ecoinvent v2.0 no. 15a, www.ecoinvent.ch, 2007.
- 468 NF-T51-195-5 (2008). "Plastics — Method of exposure to laboratory light sources —
469 Part 5: Medium pressure mercury vapour lamps," AFNOR, France.
- 470 Pennec, F., Alzina, A., Tessier-Doyen, N., Naït-ali, B., Mati-Baouche, N., De Baynast,
471 H., and Smith, D. S. (2013). "A combined finite-discrete element method for
472 calculating the effective thermal conductivity of bio-aggregates based materials," *Int.*
473 *J. Heat Mass Tran.* 60, 274-283. DOI:10.1016/j.ijheatmasstransfer.2013.01.002
- 474 Pfaltzgraff, L. A., and Clark, J. H. (2014). "Green chemistry, biorefineries and second
475 generation strategies for re-use of waste: An overview," in: *Advances in*
476 *Biorefineries*, Waldron, K. (ed.), Woodhead Publishing, UK, pp. 3-33.
- 477 Reddy, N., and Yang, Y. (2005). "Biofibers from agricultural byproducts for industrial
478 applications," *Trends Biotechnol.* 23(1), 22-27. DOI:10.1016/j.tibtech.2004.11.002
- 479 Summerscales, J., Dissanayake, N. P. J, Virk, A. S., and Hall, W. (2010). "A review of
480 bast fibres and their composites. Part 1 – Fibres as reinforcements," *Compos. Part A-*
481 *Appl. S.* 41(10), 1329-1335. DOI:10.1016/j.compositesa.2010.06.001
- 482 Sun, S., Mathias, J. D., Toussaint, E., and Grédiac, M. (2013). "Hygromechanical
483 characterization of sunflower stems," *Ind.Crop. Prod.* 46, 50-59.
484 DOI:10.1016/j.indcrop.2013.01.009
- 485 Sun, S., Mathias, J. D, Toussaint, E., and Grédiac, M. (2014). "Characterizing the
486 variance of mechanical properties of sunflower bark for biocomposite applications,"
487 *Bioresources* 9(1), 922-937. DOI: 10.15376/biores.9.1.922-937
- 488 Sun, S., Grédiac, M., Toussaint, E., Mathias, J. D., and Mati-Baouche, N. (2015).
489 "Applying a full-field measurement technique to characterize the mechanical
490 response of a sunflower-based biocomposite," *Exp. Mech.* 55(5), 917-934. DOI:
491 10.1007/s11340-015-9988-1
- 492 Times, B. (2002a). "Studies on hygroscopic moisture transport in Norway spruce. Part 1:
493 Sorption measurements of spruce exposed to cyclic step changes in relative
494 humidity," *Holz Roh Werkst.* 60(4), 271-276. DOI : 10.1007/s00107-002-0303-3
- 495 Times. B. (2002b). "Studies on hygroscopic moisture transport in Norway spruce. Part 2:
496 Modelling of transient moisture transport and hysteresis in wood," *Holz Roh Werkst.*
497 60(6), 405-410. DOI : 10.1007/s00107-002-0334-9
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