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1 PERFORMANCE OF PARTICLEBOARDS BASED ON ANNUAL PLANT 2 BYPRODUCTS BOUND WITH BIO-ADHESIVES

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4

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12

13 Abstract

14 Because the timber market is more and more competitive, the particleboard manufacturers are looking
15 for new sources of plant raw material. In the same time, the use of healthier, safer and more
16 environmentally friendly materials becomes a priority in the building sector. In this context, using bio-
17 based adhesives to bond the particles instead of the synthetic ones is an interesting alternative. In the
18 same time agricultural byproducts as annual plant stems can be a sustainable alternative raw material.
19 These resources are abundant, renewable and safe raw material. Moreover, their porous structure gives
20 them interesting properties for building materials such as lightness and thermal insulation capacity. Two
21 agricultural byproducts abundant in France have been studied: flax shives and sunflower bark.

22 Particleboards were made at laboratory scale by thermocompression of the plant raw particles to a target
23 density of 500 kg.m⁻³. The plant particles were bonded by different methods:

24- * without addition of any adhesive. In that case water was sprayed on the plant particles before the
25 forming process and was evaporated during the thermocompression. It leads to extraction of soluble and
26 lignocellulosic compounds from the agroresources that can act as adhesives.

27- * with addition of a biobased adhesive based on casein, the protein from bovine milk, or based on a
28 commercial caseinate, added at different ratios to the plant particles.

29- The effect of the type of agroresources, the particle size, the formulation of the biosourced adhesive, and
30 its application are evaluated testing the physico-chemical properties of the particleboards: mechanical
31 properties (bending test and internal bond), thermal properties, and behavior towards water and fire.

32 Using a biobased adhesive improves the mechanical properties of the particleboards significantly

33 compared to the version without added adhesive. Panels made with flax shives generally showed better

34 properties than with sunflower bark, so flax shives seem more suitable for particleboard manufacturing.
35 But after optimization of the formulation and the process, both raw materials could be used with casein-
36 based adhesive yielding efficient and fully biobased particleboards for applications such as furniture or
37 door panels.

38

39 **Keywords:**

40 Totally biobased particleboards, agricultural byproducts, biobased adhesive, internal bond, plant particle
41 adhesion.

42

43

44 **1 INTRODUCTION**

45

46 The exponentially growing consumption of raw materials in the building sector has a strong impact on the
47 objectives of sustainable development, both environmental and socio-economic. More than in any other industry,
48 the use of biomass feedstocks can provide a set of relevant responses to these needs. Renewable by nature,
49 available in large quantities, sustainably stocking carbon, and generally requiring little production energy and local
50 development vectors, agricultural raw materials are adapted to the manufacture of biosourced materials for the
51 building sector as demonstrated by Vo et al. [1]. In addition, the problem of end-of-life management of building
52 materials containing synthetic adhesives as binders due to the resistance of thermosetting resins to
53 environmental degradation make the development of biobased materials coming from renewable resources a
54 priority area of research as Laycock et al. [2] explain about the biodegradable polymers.

55 Agricultural productions generate many co-products that are potential sources of renewable raw materials to
56 produce environmentally friendly materials. Optimal use of resources tends towards the valorization of the whole
57 plant: seeds for food; long fibers for the textile industry or technical composite materials; straw, bark, pith, oilcake
58 and other co-products as new sources of supply for the manufacture of materials that do not compete with food
59 production. Numerous biobased compounds or coproducts can also be used as biosourced and biodegradable
60 adhesives such as various polysaccharides, proteins, tannin, or plant resins.

61 In this context the development of particleboards based on agricultural by-products, such as annual plant stems,
62 is an attractive alternative to wood. Many studies use agricultural residues as raw material for particleboards such
63 as straw of various botanical origins. For example Klimek et al. [3] used miscanthus stalks, Zhang et al. [4] rice
64 straw and coir fibers, Nguyen et al. [5] bamboo fibers, Mati-Baouche et al. [6] sunflower stalks, El Hajj et al. [7]
65 and Privas et al. [8] flax shives, Viel et al. [9] hemp shives and corn cob, and Fiorelli et al. [10] green coconut and
66 sugarcane bagasse fibers to produce particleboards. All these attempts are justified in their choice of
67 agrosources by their renewability and availability in the location where the studies took place. These studies

68 vary in terms of the adhesive used and parameters of the thermocompression process. All conclude to the
69 possibility of using agricultural residues in particleboards, but improvements are still necessary, especially
70 concerning resistance to water and the elasticity modulus of these boards.

71 To use materials based on agricultural byproduct in a virtuous cycle, these materials must be compostable to be
72 put back on the ground after utilization, and safe for human health. Classical synthetic binder as UF resin should
73 be avoided to reduce the formaldehyde emission. In that case two possibilities can be considered: the plant
74 particles can be self-bound without addition of other binder than water; or they can be bound with the addition of a
75 biobased adhesive. For binderless particleboards the process consists on taken advantages of chemical
76 composition of the agroressources. The lignocellulosic compounds contained in plant particles undergo chemical
77 changes during thermocompression with water according to the mechanisms described by Zhang et al. [11]. As
78 also explained by Nasir et al. [12], during hot pressing, several reactions such as dehydration, hydrolysis and
79 oxidation reactions are observed, especially on hemicelluloses, which are poor thermally stable compound. The
80 residual compounds can produce good adhesive between plant particles interfaces. Nevertheless, the properties
81 of particleboards thus bound are limited especially for boards with low density. That is why a lot of researchers
82 turn towards the formulation of biobased adhesives. In a previous work binderless particleboards made of various
83 blends of sunflower bark and flax shives have been studied and compared with same plant particles bonded with
84 a classical UF resin [13]. These biosourced boards present poor mechanical properties especially due to a lack of
85 internal cohesion. That is why in this study we have tried to improve the adhesion in the particleboards by addition
86 of a biosourced adhesive.

87 In the search for alternatives to petroleum-based wood adhesives, efforts have been dedicated to develop
88 adhesives by using phenolic substitutes based on wood extracts as tannin or lignin as described by Ang et al. [14]
89 and Ji et al. [15], or lignin extracted from other agroressources as studied by Ghaffar et al. [16]. Ferreira et al. [17]
90 proposed to use byproducts of wood pulping process as natural binder for particleboards and Privas et al. [8]
91 worked with liginosulfonate. Other biobased compounds as polysaccharides can be used, for example starch or
92 sodium alginate, Ji et al. [12] and Mati-Baouche et al. [6] studied chitosan as bio-adhesive in particleboards and
93 Norström et al. [18] studied various plant gum. In many other studies proteins were used as biobased adhesives,
94 for example soy proteins by Mo et al. [19], wheat gluten by Khosravi et al. [20] or bone glue by Nguyen et al. [5].
95 Casein, the protein from bovine milk obtained by precipitating from the milk after acid treatment, is available in
96 large quantities. El Hajj et al. [7] have used casein as adhesive with flax shives. In this study the casein-based
97 adhesive was used in high proportions in the composite material (50% to 70%). The results are interesting in
98 terms of mechanical, thermal and acoustical properties but the resistance to humidity was still too low. For
99 different materials, it has been demonstrated that casein or caseinate can provide other interesting properties,
100 such as flame retardancy as shown by Alongi et al. [21] for cotton fabrics or antimicrobial effects as shown by
101 Arrieta et al. [22] who mixed carvacrol or lysozyme with casein in edible films for food packaging. These

102 properties can also be interesting in building materials to which specifications in terms of resistance to fire and
103 durability against microorganisms are required.

104 The study presented here reports on the formulation of an adhesive based on casein in aqueous solution and on
105 the preparation of particleboards with this adhesive and using agricultural by-products; additionally, the casein
106 based adhesive system was optimized according to the achieved mechanical properties of the particleboards.
107 The optimized casein adhesive is then used to bind flax shives and sunflower bark of two different particle sizes in
108 order to obtain particleboards of 500 kg.m⁻³ density. To evaluate the effects of the adhesive addition, these
109 particleboards are compared with boards from the same plant particles but without any adhesive. All the
110 particleboards are characterized by their mechanical, thermal and hygroscopical properties, which allow
111 understanding the structure-property relationships of the plant particles with the adhesive and to conclude on the
112 capacity of these materials to be used in construction according to EN 15197 [23].

113

114 **2 MATERIALS AND METHODS**

115

116 **2.1 Raw materials**

117 *Agroressources*

118 The flax shives used in this study are by-products of the production of flax fiber and came from the Northwest of
119 France. Flax shives represent the woody part of plant stalks. They are used as animal litter and for particleboard
120 manufacturing (only with synthetic resin as binder). This agricultural byproduct is very abundant in the North of
121 France. In 2018, 115 000 tons of scutched flax have been produced from 98 000 hectares of grown flax. 50% of
122 the scutched flax are flax shives and 50% are flax fibers. After harvesting the flax balls are stored in warehouses
123 before to be scutched all the year round.

124 The sunflower bark is the external part of sunflower stalks. It can be obtained after separation of the sunflower
125 pith which forms the internal part of the stalks. The sunflower bark used in this study came from the center-west of
126 France. A small proportion of pith residues, which cannot be eliminated during the separation process, is present
127 with the bark. Currently the sunflower bark is not at all valorized. It is left in the field after head harvesting. All the
128 harvesting and industrial valorization chain must be carried out, but this agricultural byproduct presents a very
129 high potential of valorization for agromaterials. In 2017, 550 000 hectares of sunflower have been grown in
130 France. Between 1 and 2 tons of stalks can be harvested per hectare according to the cutting height.

131 The used agroressources are heterogeneous materials consisting essentially of structural compounds (cellulose,
132 hemicelluloses, lignin) and, to a lesser extent, of non-structural compounds (other polysaccharides, proteins,
133 water-soluble organic compounds and inorganic compounds). The chemical composition of an agro-resource

134 depends on its botanical origin, but also on the location of the agrosresource in the plant and on its growth and
135 harvest conditions. These parameters also influence the physical structure of the agrosresource, such as its
136 porosity, its apparent density, and its mechanical strength.

137

138 *Biobased adhesive*

139 In the case of the particleboards prepared without addition of any adhesive, the lignocellulosic compounds
140 contained in the agrosresources act as binders. These lignocellulosic compounds come from the surface or the
141 heart of the agrosresource particles and are activated by various chemical processes thanks to evaporation of the
142 added water during the thermocompression process to create something which can be called an in-situ bond line.
143 The exact nature of all these lignocellulosic compounds is not completely defined, it will be mainly hemicellulose
144 and lignin, and some other non-structural compounds.

145 The other particleboards are bonded by the addition of an adhesive based on casein. The casein is the protein
146 extracted from bovine milk. It is dissolved in a basic solution containing potassium hydroxide (KOH), thus forming
147 a water soluble caseinate. For the quantities used in laboratory, casein and KOH came from Sigma Aldrich. For a
148 larger production, a technical casein could be used directly from dairy plants.

149 Different rates of KOH compared to the mass of casein have been tested on panels formed with small flax shives.
150 Similarly, different addition of casein during panel production has been tested (with fixed KOH rate, based on
151 casein mass). Based on these results, an optimized formulation of the casein-KOH adhesive has been defined.
152 The better results have been obtained with a large excess of alkali salt compared to the neutral solution of casein
153 solubilized by KOH. This adhesive formulation was used to compare panels with various types of agrosresources
154 and binderless panels.

155 In order to compare this caseinate with the intended proportions of alkali salt also a commercial casein salt was
156 used. It is a sodium caseinate purchased from Sigma Aldrich and used in the boards at the same level as the
157 optimized casein-KOH formulation.

158

159 **2.2 Particleboards manufacturing**

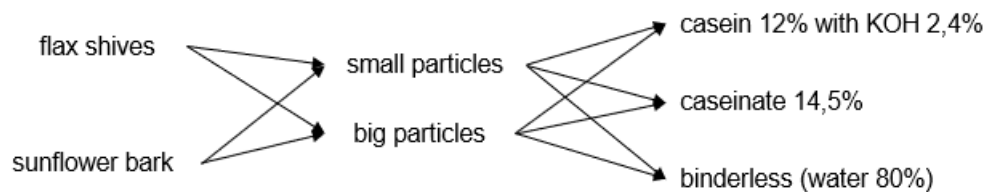
160 The raw particles of flax and sunflower were crushed and then sieved to obtain two batches of particles of
161 different sizes. The small particles were sieved between 0.5 and 2 mm while the big particles were sieved
162 between 2 and 5 mm. The plant particles were conditioned at ambient temperature and 50% relative humidity
163 during at least 48h before being used. In these conditions the particles show a moisture content of approximately
164 8%. In a first step the proportion of casein used in the adhesive and the proportion of KOH added to the casein to
165 form a caseinate were fixed by testing various formulations on boards made of small flax shives only. Table 1.
166 summarizes the different formulations used in order to optimize the adhesive based on casein with KOH.

167 Then, in a second step, particleboards were made with big or small particles of flax shives or sunflower bark and
 168 bounded with either the adhesive system based on casein and KOH at the previously optimized proportions, or
 169 the commercial caseinate-based adhesive or without any binder addition, for a total of 12 different boards. Figure
 170 1 summarizes the various parameters studied in the biosourced particles boards in the second step. The quantity
 171 of material used was calculated in order to obtain a thickness of 15 mm and a density of 500 kg.m⁻³ for all boards.
 172 5 boards were made for each formulation and for each test the samples were taken from all boards of a same
 173 formulation.

174 *Tab.1: adhesive formulations studied in small flax shives boards*

% KOH (compared with casein)					with casein: 12% w/w of the board
2	4	6,7	13,3	20	
% casein (of board mass)					with KOH: 20% w/w of casein
3	6	9	12	15	

175



176

177 *Fig. 1 : Diagram of the parameters varying in the studied boards in the second step*

178

179 A commercial board made of flax shives with a synthetic binder is used as a reference. It is used as door panel,
 180 partition wall and for furniture manufacturing. This reference board is made of three layers: the core layer is made
 181 of big flax shive particles and both face layers are made of small flax shive particles. This commercial board is
 182 bonded with 18% (w/w) of urea-formaldehyde resin (calculated on dry basis) and its density is 530 kg.m⁻³. That is
 183 why we choose a target density of 500 kg.m⁻³ for the new boards that we studied, and we tested biosourced
 184 binder amounts up to 18% (w/w) (15% of casein with 3% of KOH). All the measured properties of the laboratory-
 185 made boards are compared with the same properties of the commercial reference board.

186 The plant particles blended with the bio-based adhesive (14.5% mass/panel mass after optimization) or with water
 187 (80% mass/plant particles mass) were thermocompressed at 190°C in a mold during 20 minutes for the panels
 188 containing casein or caseinate based adhesive and 40 minutes for the panel with water, for boards of 15 mm
 189 thickness. This process needs some heating time because of the water to evaporate. For the binderless boards, a
 190 lot of water is added to the vegetal particles to generate vapor during hot pressing in order to extract some natural
 191 compounds that will act as binder between particles. 80% of the vegetal particles mass for the added water is
 192 reasonable considering that these particles are able to absorb more than 300% of their mass. In the boards using
 193 the biosourced binder, this binder is casein dissolved in basic aqueous solution. Water must be evaporated but
 194 there is less water than in the binderless boards so shorter evaporation time. It must also be considered that the

195 mold used is fully closed, thereby restricting evaporation. In an industrial production, larger presses with open
196 edges are used, speeding up the water evaporation so reducing the hot-pressing time.

197 In the literature some solutions are proposed to reduce the thermopressing time, such as drying the mixture of
198 vegetal particles with aqueous adhesive solution in an oven (during 24h at 100°C) to remove a part of the water
199 before the thermopressing [5]. Another solution, studied by Mati-Baouche et al., is to dry the boards in an oven
200 (during 50h at 50°C) after a short compression of 1 min. In all cases more time is necessary to remove water from
201 binderless boards or from boards made with an aqueous adhesive than to cross-link a synthetic resin.

202 In the laboratory-scale mold, spacers are utilized to stop the closure of the mold in order to obtain a fixed panel
203 volume (150 x 150 x 15 mm) and so the target density. The mat of vegetal particles with the binder of initially
204 approximately 70 mm high (particles compacted by hand) was compressed until the final thickness of 15 mm. The
205 pressure is applied on the spacers and not directly on the vegetal matter, so the pressure applied on the board is
206 not known as soon as the spacers have been reached. Figure 2 shows the surface of the boards made of big flax
207 particles and big sunflower ones bound with the casein-based adhesive.



208
209 *Fig. 2 : Particleboards made of big sunflower bark on the left and made of big flax shives on the right.*

210

211 **2.3 Particleboards characterization**

212 *Mechanical behavior by bending tests*

213 Three-point bending tests were carried out on each particleboard with a universal mechanical property testing
214 machine (TA.XTplus texture analyser). Samples of 15 cm long are put on two supports spaced out by 10 cm. The
215 sample dimensions were 150x30x15 mm³. The ratio between length and thickness of these samples does not
216 allow the internal shear loads to be neglected but we were limited by the mold dimensions and we couldn't made
217 longer boards at laboratory scale. Nevertheless, all measurements were realized in the same conditions, the
218 results are therefore comparable between the studied biosourced boards and the reference board. A deflection
219 rate of 6 min.min⁻¹ was applied in the middle of the sample. The required force to deform them was measured
220 using a 500 N load cell. They were conditioned at 50% relative humidity before testing. The bending tests were
221 performed always on the same side of the boards, in relation to the direction of the thermocompression. Figure 3

222 shows a photography of a flax board sample for the bending test. On picture (a) we can see the surface and the
223 cross section of the sample cut with a bandsaw while picture (b) shows the fracture section after the bending test.
224 The picture on the Figure 3(a) corresponds to a board sample after the bending test. That is why this sample is
225 warped. This distortion is the result of breakage by bending test. To observe the fracture section as shown on the
226 Figure 3(b), a much longer displacement was applied on the sample after the first breakage. The tests were
227 repeated five times, at ambient temperature. The three-point bending test allows determining the modulus of
228 rupture (MOR) and the modulus of elasticity (MOE).

229

230

231

232

233



234 *Fig. 3 : Photography of a flax board sample after the bending test: surface and cross section (a), fracture section*
235 *(b)*

236

237 *Internal bond*

238 Internal bonding strength (IB in $N.mm^{-2}$) corresponds to the energy required to break the sample by z-directional
239 tensile test. It gives an estimation of the fiber-to-fiber bond. The IB was measured on five squared samples
240 ($50 \times 50 \times 15 mm^3$) of each particleboard. Prior to testing, the samples were conditioned at 50% relative humidity
241 then glued onto stainless steel supports with a hot melt. These supports were positioned in the holders of the
242 TA.XTplus texture analyser. A loading rate of $3 mm.min^{-1}$ was applied until failure of the sample. For each test the
243 occurrence of the failure inside the sample and not at the interface between the sample and the steel support was
244 checked. If a failure occurred at the interface, just between the adhesive joint and the sample or between the
245 adhesive joint and the steel support, it was seen as artificial experimental defect, and the test was not considered
246 for the results calculated.

247

248 *Thermal conductivity*

249 The thermal conductivity of the particleboards was measured with a Heat Flow Meter HFM 436 Lamda from
250 Netzch. The sample size was $150 \times 150 \times 15 mm^3$. The measurements were performed in a steady state at $20^\circ C$
251 with a temperature gradient between the hot and the cold plate of $20^\circ C$ and repeated at least 3 times for each
252 material.

253

254 *Hygroscopic behavior*

255 Thickness swelling (TS) and water absorption (WA) were measured on samples of 50x50x15mm³, after fully
256 immersion in 20°C distilled water for 24 hours. After removal from the water bath, excess of water was removed
257 with sorbent paper tissues. The thickness of the samples was measured by a caliper in the middle of each sample
258 before and after the water immersion. The water absorption was determined by weighting the samples before and
259 after the immersion, on a scale with 0.1 mg precision. The measurements were repeated on five samples for each
260 particleboard.

261

262 *Resistance to fire*

263 The resistance to fire of the particleboards made of flax shives and sunflower bark was tested according to EN
264 ISO 11925-2 [24]. The measurements were realized in a dedicated chamber where samples of 90*290*15mm³
265 were exposed to a propane flame inclined by 45° on the lower edge of the sample during 30 s. Measurements
266 were realized in triplicate on each board. After exposure to the flame, the absence of ignition and of flaming
267 droplets was observed and the height of the damaged zone was measured. Figure 4 shows the installation to
268 realize this measurement and an example of the damage zone after the test on a sunflower board.



269

270 *Fig. 4 : installation for test of resistance to fire and example of some boards after the test*

271 **3 RESULTS AND DISCUSSION**

272

273 **3.1 Biobased adhesive formulation**

274 First tests have been carried out to formulate the adhesive based on casein. Casein can be dissolved in water
275 only in a basic solution, where the casein forms a caseinate. In order to fix the proportion of KOH which is
276 required to obtain the best performing casein adhesive, different KOH rates based on casein were tested. The
277 efficiency of the various adhesives was evaluated by comparison of the mechanical properties of the produced

278 boards. For the tests of the adhesive formulations, only small flax shives were used in the boards. Tab. 2 presents
 279 the maximal bending strength (MOR) of the boards containing 12% (mass / panel mass) of casein and various
 280 KOH rates (the proportion of solid KOH is based on solid casein mass) dissolved in 80 ml of water. The pH of the
 281 casein-KOH solution is neutral for 4% KOH but the maximal bending strength of these panels increased
 282 significantly with increasing KOH addition giving alkaline behavior. The better mechanical properties of the boards
 283 made with the casein-based adhesive with high level of KOH can be explained by the lower viscosity of this
 284 adhesive solution. The viscosity of the casein/KOH solution decreases with the increase of the proportion of KOH.
 285 A lower viscosity of the adhesive solution allows better repartition of the adhesive on the flax particle surfaces,
 286 leading to better adhesion and better mechanical properties. According to these results, the highest KOH rate
 287 (20%) gave the highest MOR (10.5 MPa) and was selected for the tests with different addition of casein as
 288 adhesive.

289

290 *Tab.2: MOR and IB of small flax shive boards containing 12% (m/board m) of solid casein with various solid KOH*
 291 *rates and of boards containing 20% (m/casein m) of KOH and various casein rates.*

rate of KOH										
compared with	2		4		6.7		13.3		20	
casein mass (%)										
Casein at 12% of board mass	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>
	5.7	0.5	6.7	0.7	7.1	0.6	8.9	1.0	10.5	0.9
rate of casein										
compared with	3		6		9		12		15	
board mass (%)										
	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>	MOR (MPa)	<i>sd</i>
KOH at 20% of casein mass	4.8	0.4	7.4	0.7	11.2	1.1	10.5	0.9	10.9	0.9
					IB N.mm ⁻²	<i>sd</i>	IB N.mm ⁻²	<i>sd</i>	IB N.mm ⁻²	<i>sd</i>
					0.11	0.02	0.20	0.03	0.20	0.04

292

293 The second step of the adhesive formulation was to fix the casein proportion in the board. The total proportion of
 294 binder in the board (casein + KOH) was limited with 18% (calculated as solid compound versus total board matter
 295 stabilized at 8% RH), which is the same value as for the industrial control panel. In the second part of Table 2, the
 296 MOR of boards containing various mass proportion of casein (always with 20% solid mass of KOH / solid casein

297 mass) is presented. We can observe that the maximal strength increases with the casein rate until 9% casein and
298 then the panel bending resistance is approximately constant between 9% and 15% of casein with 10.5 to 11.2
299 MPa.

300 In order to make a choice between 9%, 12% or 15% casein in the flax shive boards, we compared their IB (Table
301 2). The result obtained with 9% casein was significantly lower than these obtained for both other boards. With
302 12% and 15% casein in the boards, the internal bond was $0.20 \text{ N}\cdot\text{mm}^{-2}$, fulfilling the requirements of EN 15197:
303 minimum IB of $0.13 \text{ N}\cdot\text{mm}^{-2}$ for the first class of boards and 0.20 for the second. Since the IB were the same for
304 12% and 15% casein, the lower addition (12%) was selected for further tests. The selected 20% KOH
305 corresponds to 2.4% of KOH based on board mass containing 12% of casein. Knowing that the adhesive solution
306 of casein/KOH is neutral for 4% KOH (compared to casein mass), this is the quantity used to form the caseinate.
307 It can be considered that the KOH added beyond is in excess in the solution. For the adhesive formulation
308 optimized with 20% KOH compared to casein mass, 16% are excess of KOH. It corresponds to 1,9% of the total
309 board mass, which is free potassium hydroxide. This adhesive formulation was used in the further tests with
310 variations of botanic origin of the particles and of particle sizes. The obtained boards were compared with
311 binderless boards and with boards made with a commercial sodium caseinate based adhesive.

312

313 **3.2 Comparison of board properties with or without adhesive**

314 *Mechanical behavior by bending tests*

315 Table 3 presents MOR and MOE obtained by bending test of the different studied panels. A large difference is
316 observed between the panels bound with the biobased adhesive or without. It seems interesting to realize a
317 particleboard without externally added adhesive because this corresponds to valorization of only the agroresource
318 and its internal composition including inherent chemicals. It has been demonstrated that suitable compounds
319 must be extracted from the plant matter by the vapor and then activated by heat to act as binder and to obtain
320 cohesive bond strength. Pintiaux et al. [25] explain that water extractable compounds are responsible for the self-
321 adhesion capacity of agro-resources during the thermomechanical steam treatment of binderless particleboards.
322 These water extractable compounds come from degradation of cellulose and hemicelluloses during the steam
323 treatment, which can partially hydrolyze them to simple soluble sugars. Lignin is another important chemical for
324 the binderless adhesion process. The joint action of moisture and heating causes on lignin some degradation,
325 softening and plasticization leading to new linkage capability. It is also reported that with heat and pressure lignin
326 melts at the surface of fibers and binds the fibers together [26]. The vapor can be obtained by vaporization of the
327 water previously blended with the plant particles or by direct steam injection into the mold during pressing. Our
328 press is not equipped with system allowing direct steam injection. That's why cold water is added to vegetal
329 particles and heated for a long time in order to generate vapor. Direct steam injection and a press with open
330 edges, facilitating vapor extraction) could reduce the pressing time of binderless boards. Despite too long process

331 time, properties of our binderless boards were studied to highlight the differences to boards with addition of a
332 biosourced binder.

333 In this study the binderless boards showed sufficient cohesion strength to enable manual handling of the pressed
334 boards (they can be manipulated without visible alterations), but the bending test shows that their MOR and MOE
335 are very low with 0.8 to 3.3 MPa for the MOR and 127 to 274 MPa for the MOE. The internal bond is also very low
336 with 0.02 to 0.04 N.mm⁻², showing an important lack of internal cohesion between particles despite a certain
337 adhesion achieved by the extractable compounds during the thermocompression process. Nevertheless, we can
338 notice that mechanical resistance is slightly better for the binderless panels made of big flax shives than for the
339 three others. Comparable results were obtained in a previous study carried out by Mahieu et al. [13] in which flax
340 shives and sunflower bark were used in different proportions in three-layer binderless particleboards. This study
341 showed that with a MOR of 3.8 MPa, binderless boards made of flax shives present interesting mechanical
342 resistance in comparison with flax boards made with UF resins by the same laboratory scale thermopressing
343 process (with MOR of 1.1 MPa). In the present study the same process can lead to panels with very much better
344 MOR when a biobased binder is added.

345 Boards containing the casein based adhesive and made of big plant particles present better MOR and MOE
346 compared to small particles. Commercial three-layer particleboards are mainly made of big particles, both face
347 layers with small particles being used for the surface behavior to limit the access of water, however not for
348 mechanical performances.

349 The results of bending tests also show a difference according to the botanical origin of the plant particles. At the
350 same particle size and same pressing process, the panels made of flax shives always present higher MOR and
351 MOE than the panels made of sunflower bark. The morphology of these agrosources can explain this result.
352 The flax shives are fine and flexible particles (thickness between 0.1 and 0.4 mm) whereas sunflower bark
353 particles are thicker (between 0.3 to 3.5 mm) and hard and brittle. With a maximal bending strength of 8.1 MPa,
354 the panel made of big sunflower bark with casein-based adhesive could be used to replace classical wood-based
355 particleboards in applications for non-load bearing panels (first class of requirements described in EN 15197).
356 Non-load bearing panels can be used for furniture or covering but not for structural applications. With a maximal
357 bending strength of 13.7 MPa and a MOE of 1216 MPa, the panel made of big flax shives with casein-based
358 adhesive presents better bending properties than the commercial reference panel made with three layers of flax
359 shives with UF resin. This board could be used to replace classical particleboards in applications corresponding to
360 the first and the second classes of requirements described in EN 15197. According to this standard, the first class
361 concerns flaxboards for general purpose in dry conditions (usually for filling purposes), while the second class
362 concerns non-load bearing flaxboard for use in dry conditions (usually for further processing, such as
363 veneering). The bending properties of the commercial reference board are closer to that of the biobased board
364 made of small flax shives with casein adhesive. However, IB of the commercial board is higher compared to all
365 biobased bonded boards (0.32 compared to 0.17 to 0.24 N.mm⁻²). EN 15197 requires an IB of 0.13 N.mm⁻² for the

366 first class of application and 0.20 N.mm⁻² for the second. Thus, IB obtained for the biobased boards is in the
 367 range of the limits and principally would envisage use of these boards in replacement of the classical board.
 368 The biobased boards bonded with the sodium caseinate adhesive present slightly better bending properties than
 369 the casein/KOH-based in the case of boards made with sunflower bark (small or big), but the bending properties
 370 of the boards made with flax shives are lower with the caseinate adhesive than with the casein/KOH one. The
 371 internal bond is slightly higher with the sodium caseinate for all boards. Thus, the type of caseinate used in the
 372 adhesive formulation (commercial sodium salt or made with an excess of potassium hydroxide) could be adapted
 373 according to the agresource used and the expected mechanical properties.

374

375 *Tab. 3: Modulus of rupture, modulus of elasticity, internal bond and thermal conductivity of the different studied*
 376 *panels*

adhesive	agro- resource	particle size	MOR (MPa)		MOE (MPa)		λ (mW.m ⁻¹ .K ⁻¹)		IB (N.m ⁻²)	
			average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation
casein (12%)	flax	small	10.5	0.9	1003	109	84.1	0.7	0.20	0.02
	shives	big	13.7	1.1	1216	106	79.7	0.6	0.20	0.02
KOH (2.4%)	sunflower	small	5.8	0.4	692	94	89.3	0.8	0.17	0.03
	bark	big	8.1	1.0	659	79	84.5	0.6	0.18	0.04
casei- nate (14.5%)	flax	small	8.4	1.0	738	93	82.9	0.8	0.23	0.03
	shives	big	12.3	1.0	1106	81	80.3	0.9	0.20	0.03
	sunflower	small	6.5	0.6	769	88	85.3	0.8	0.24	0.02
	bark	big	9.8	0.3	992	81	82.5	0.7	0.22	0.01
binder- less	flax	small	1.2	0.2	165	14	76.7	1.2	0.04	0.02
	shives	big	3.3	0.4	274	22	72.0	1.1	0.04	0.02
	sunflower	small	0.8	0.1	127	18	77.9	1.0	0.02	0.01
	bark	big	1.0	0.0	139	12	72.9	1.1	0.02	0.01
Commercial reference										
flax board with UF resin			11.7	0.4	1040	78	81.6	0.8	0.32	0.02

377

378 *Insulation properties*

379 Thermal conductivity is usually directly connected to material density. The lower the density, the lower the thermal
 380 conductivity, thanks to the air insulation capability. Although all studied panels have the same target density (500
 381 kg.m⁻³) and final densities of 498 +/- 10 kg.m⁻³, the measured thermal conductivities vary. A significant difference

382 is observed between boards made with both biobased adhesive and without binder. As shown in Table 3, the
 383 thermal conductivities of the binderless panels are between 72 and 78 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ whereas these of panels which
 384 contain the biobased adhesives are between approximately 80 and 90 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This can be due to the
 385 formation of thermal bridges by the adhesive but also to the replacement of a part of the plant particles by the
 386 adhesive. The plant particles present a honeycomb structure with fine cavities full of air, the best insulator,
 387 whereas the adhesive is denser. This also explains the results presented in Table 4: the thermal conductivity
 388 increases with the increase of adhesive rate in the panel made of small flax shives. El Hajj et al. [7] come to the
 389 same conclusion on agrocomposites made by casein based binder with flax shives (50% to 70% of binder) when
 390 boards of same densities are compared. Viel et al. [9] well show the influence of the addition of a binder on the
 391 thermal conductivity in particleboards made of hemp shives or corn cob with various binders, but they obtain very
 392 high thermal conductivity for particleboards of density about $500 \text{ kg}\cdot\text{m}^{-3}$ with around $150 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

393

394 *Tab. 4: Thermal conductivity λ of panels made of small flax shives with different casein rates (and 20% (w/casein*
 395 *w) of KOH) at $500 \text{ kg}\cdot\text{m}^{-3}$*

396

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400

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casein rate in the panel (%)	λ ($\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	
	average	standard deviation
9	81.8	0.8
12	84.1	0.7
15	88.2	0.7

402 The particleboards include two types of porosity: the internal porosity of the plant material and the porosity
 403 induced by the arrangement of the particles in the board, which is linked to the board density. At the same board
 404 density, the internal porosity of the plant particles has a more important role in the material insulation capacity
 405 than the external porosity when comparing different plant materials. This observation is confirmed by the
 406 difference observed between thermal conductivities λ of comparable panels made of flax shives or sunflower
 407 bark. The bulk density of the flax shives is $100 \text{ kg}\cdot\text{m}^{-3}$ whereas that of sunflower bark is $180 \text{ kg}\cdot\text{m}^{-3}$. As shown by
 408 Mahieu et al. [25], the flax shives show more uniform pores of homogeneous and finer sizes than the sunflower
 409 bark which is made of pores of various and coarser sizes with thicker walls. This may explain the higher bulk
 410 density measured for the sunflower bark. The sunflower bark includes much less internal porosity than the flax
 411 shives. Knowing that the internal porosity of the plant particles is the basis of the thermal insulation capacity of the
 412 particleboards, it may explain that the boards made of sunflower bark are less insulating and present so slightly
 413 higher λ than these made of flax shives at the same board density if the same quantity of adhesive is used.
 414 Moreover, as shown by Shynar et al. [27] on porous ceramics, the pore size has an influence on the thermal
 415 conductivity at equivalent porosity: a coarser microstructure exhibits higher thermal conductivity than a finer one.

416 In the vegetal particles the finer pores of the flax shives lead to lower thermal conductivity so better thermal
417 insulation capacity for the fax boards than for the sunflower ones, which have coarser pores. The difference of λ
418 between sunflower and flax particles is less significant for binderless boards. The particle size has also an
419 influence on λ at the same board density. In all case λ is lower with big particles than with small ones. On the one
420 hand, the thermal bridges are more numerous with small particles, and on the other hand, due to the crushing, a
421 part of the initial internal porosity disappears in the small particles. A slight decrease of λ can be observed with
422 the sodium caseinate adhesive in comparison with the casein-KOH adhesive but the difference is low. According
423 to an analysis of variance (ANOVA test) the variation of λ between boards with both different adhesives is
424 significant for sunflower boards (with probability values less than 5% : $4 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$ respectively for small and
425 big sunflower bark). However, the λ variation is not significant for the flax boards with probability values more than
426 5% : 0.07 and 0.3 respectively for small and big flaxes shives. The lowest λ is given for the board with big flax
427 shives without binder with $72 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The better λ for the boards bound with an adhesive is reached for the
428 small flax shives with $80 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (average of λ for boards with both adhesives). It is significantly less than the λ
429 of the reference board made of flax shives with UF resin ($81.6 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) with a probability value of 0.008.

430

431 Hygroscopic properties

432 Table 5 presents water absorption (WA) and thickness swelling (TS) after 24h. The plant particles present
433 naturally a high affinity with water and are very sorbent due to their high porosity. In binderless boards the
434 cohesion of the particles is based on wood inherent chemicals extracted during the thermocompression process
435 by water and steam. A smaller part of these water-soluble compounds extracted during the process can further
436 react under influence of temperature and time to give insoluble materials, but the greater part remains soluble.
437 These soluble adhesive components might be again dissolved in water during the immersion, such as sugars
438 from the degradation of hemicellulose or some degradation products of lignin. The binderless boards sorb high
439 quantities of water, 220 to 270% of the board initial mass and swell strongly, from 50 to 100% of the initial
440 thickness, which is not surprising without addition of any hydrophobic agent. Consequently, the binderless panels
441 present very bad cohesion after the water immersion. On the contrary, the panels containing the biobased
442 adhesives present much better cohesion after the immersion. Due to the addition of the biobased adhesives TS is
443 reduced (from 50-100% to 18-38%) and is in the order of magnitude of particleboard based on wood particles but
444 without addition of hydrophobic agents such as paraffin. WA is also reduced but remains still high (100-180%). A
445 significant difference of the hygroscopic properties is observed between panels based on small or big particles. In
446 all cases TS and WA are higher for big particles compared to small ones. This fact can be explained by the bigger
447 size of the pores in the coarse plant particles. Except from the coarse flax shives panel bound with casein-KOH,
448 the panels made of sunflower bark seem to sorb more water and to swell more than the panels made of flax
449 shives. The panels made with the sodium caseinate sorb and swell slightly more than the panels made with the
450 casein-KOH adhesive. Nevertheless we can notice that one biosourced board (with small flax shives bound with

451 casein/KOH adhesive) shows, with 18% of TS and 103% of WA, similar values of TS and WA as the commercial
 452 reference board made of flax shives with UF resin with 15% of TS and 99% of WA. This means that there is a
 453 good chance for this biosourced board to replace boards bonded with synthetic binder. However, the press time
 454 remains to be improved for the introduction of such bio-based boards into industrial production. The board made
 455 of big flax particles, shows good mechanical properties but insufficient behavior towards water. Thus, new
 456 attempts are necessary to improve the resistance towards water to be able to use them in a wet environment. The
 457 panels based on flax shives and sunflower bark with biobased adhesive may still be used for applications in dry
 458 environment according to the standard EN 15197.

459

460 *Tab. 5: Water Absorbtion (WA) and Thickness Swelling (SW) of the different panels after 24h immersion in water.*

adhesive	agro- resource	particle size	Water Absorbtion (%)		Thickness Swelling (%)	
			average	standard deviation	Average	standard deviation
casein (12%)	flax shives	small	103	12	18	1
		big	149	8	23	1
KOH (2.4%)	sunflower bark	small	140	9	26	3
		big	141	14	30	3
caseinate (14.5%)	flax shives	small	133	9	25	1
		big	142	15	30	2
	sunflower bark	small	163	12	35	3
		big	179	9	38	3
binderless	flax shives	small	262	5	53	1
		big	245	11	74	1
	sunflower bark	small	274	18	84	4
		big	221	7	101	8
Commercial reference			99	1	15	1

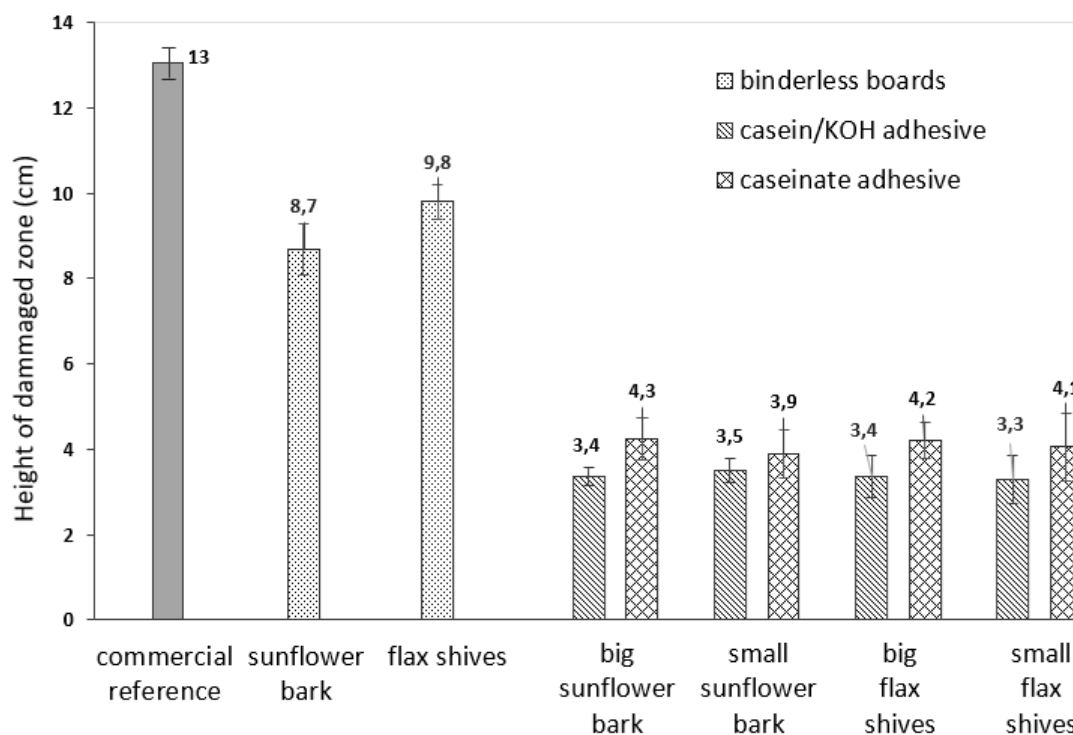
461

462 Resistance to fire

463 As shown by Mahieu *et al.* [13], the height of the damaged zone by fire for the three layers binderless flax board
 464 at 500 kg.m⁻³ is 9.8 cm and 8.7 cm for the sunflower one, whereas for boards bound with UF resin the height of
 465 the damaged zone is 13.0 cm for the flax board and 11.3 cm for the sunflower board. Figure 5 presents the height
 466 of the damaged zone by fire, measured with the same protocol on the commercial reference board and on the
 467 boards bound with the casein-KOH adhesive or the sodium caseinate adhesive. The boards containing casein or

468 caseinate present clearly a much smaller height of the zone damaged by fire. This height decreases from 13 cm
 469 for the reference board (bound with UF resin) to between 9 and 10 cm for the binderless boards [13]. This
 470 decrease is due to a difference of the flame propagation in relation with the nature of the adhesive. The test
 471 consists on measuring the damaged zone by the flame on the board surface and does not necessarily reflect the
 472 degradation of material properties or the thickness of the damaged layer. The adhesive based on components
 473 extracted from water during the thermocompression process seems to react to fire slightly less than the UF resin,
 474 since they do not contain nitrogen, as compared to a UF resin. The height of the damaged zone decreases much
 475 more for the boards containing casein or caseinate down to between 3.3 to 4.3 cm. This result is due to the flame-
 476 retardant property of the casein, as shown by Alongi [21]. For all studied particleboards, there is no significant
 477 difference for the damaged zone height between flax or sunflower or between the particle sizes. A small but
 478 significant difference (probability value of 0.009 by ANOVA test) can be observed between the adhesives: the
 479 boards made with the casein-KOH adhesive present a damaged zone smaller of approximately 0.7 cm than the
 480 caseinate-made boards (average heights of respectively 3.4 cm and 4.1 cm). Whereas the commercial sodium
 481 caseinate contents only 3% of sodium, the excess of KOH in the casein-KOH adhesive leads to an increase of the
 482 flame-retardant property of the casein. This fact might be explained by an action of the excess of hydroxide on the
 483 plant material. This action could be assimilated to the classical use of alkali treatment to improve the surface of
 484 plant fibers, generally leading to improvement of the fiber thermal stability as shown by Parre *et al.* on banana
 485 fibers [28]. This flame-retardant property of the casein-based adhesive consists of a large advantage for the use
 486 of this adhesive in replacement of the synthetic resin in particleboards.

487



488

489 *Fig. 5: Height of the damaged zone caused by fire, for the different boards.*

490

491 **4 CONCLUSION**

492

493 In order to understand the structure-property relationships of particleboards made from agricultural by-products,
494 two agro-resources from different botanical origin (flax shives and sunflower bark) at two different particle sizes
495 and two types of casein adhesive as well as a binderless version have been tested.

496 The mechanical strength of the particleboards depends on the interactions between the surface of the particles
497 and the used binders. Vapor extractable compounds produced by lignin and hemicellulose degradation with
498 steam are responsible for the self-adhesion capacity of the agroresources during thermocompression of the
499 binderless particleboards. By using a biobased adhesive, the mechanical resistance is improved and allows
500 adapting the formulation to the required behaviors of the final material, such as improvement of the water and fire
501 resistance, while keeping good thermal properties.

502 The formulation of biobased adhesive based on casein has been optimized according to the mechanical
503 properties of particleboards made of flax shives. It appears that an excess of KOH in comparison with casein
504 leads to better mechanical properties of the panels due to a lower viscosity of the adhesive. The use of a
505 commercial sodium caseinate showed comparable or partly slightly lower board properties. A proportion of even
506 less than 15% (w/w) of biobased adhesive in the particleboards is enough to obtain sufficient mechanical
507 properties. The comparison of the different boards produced showed that:

- 508 - Big particles provide better mechanical properties than small ones.
- 509 - In all cases flax-shive panels are more resistant to bending than sunflower bark-based panels.
- 510 - Addition of casein and caseinate based adhesives leads to particleboards with much better mechanical
511 properties than binderless ones.
- 512 - Using caseinate adhesive by blend of casein with an excess of KOH leads to slightly better properties than
513 using a commercial sodium caseinate (mechanical properties and resistance towards water and fire).

514 Casein-based adhesive improve the board resistance towards water compared to binderless boards. TS is
515 reduced by factor approx. 3. Nevertheless, TS and WA still need to be improved. The binderless boards show
516 lower thermal conductivity due to the presence of only plant material with a porous structure, whereas in the
517 boards containing some adhesive, some porous plant material is replaced by the adhesive as a denser material.
518 But the binderless boards suffer from too low mechanical and hygroscopical properties and the extremely long
519 press time needed to see at least some bonding effect.

520 Finally, all measured properties demonstrate the interest of using a casein or caseinate-based adhesive in
521 comparison with the binderless boards, especially for their very good flame-retardant property. Both studied

522 aggroresources could be used in particleboards for non-load bearing applications in a dry environment. Big flax
523 shives seem nevertheless more suitable for particleboard manufacturing but need optimization of the formulation
524 and the production process.
525

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