Influence of thermo-pressing conditions on the mechanical properties of biodegradable fiberboards made from a deoiled sunflower cake

Philippe Evon[a,b,*], Justine Vinet[a,b], Laurent Labonne[a,b], Luc Rigal[a,b]

[a] Université de Toulouse, INP, Laboratoire de Chimie Agro-industrielle, ENSIACET, 4 Allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France
[b] INRA, Laboratoire de Chimie Agro-industrielle, 31030 Toulouse Cedex 4, France

Keywords:
Sunflower whole plant
Twin-screw extruder
Lignocellulosic fibers
Proteins
Thermo-pressing
Biodegradable fiberboards

A B S T R A C T

The objective of this study was to manufacture new biodegradable fiberboards by thermo-pressing. The starting material was deoiled cake (only 0.9% oil content), generated during the biorefinery of sunflower (*Helianthus annuus* L.) whole plant in a co-rotating twin-screw extruder. All fiberboards were cohesive mixtures of proteins and lignocellulosic fibers, acting respectively as binder and reinforcing fillers. The molding experiments were conducted using a 400 ton capacity heated hydraulic press. The influence of molding conditions on board density, mechanical and thermo-mechanical properties, thickness swelling, and water absorption was examined. Molding conditions included pressure applied (24.5–49.0 MPa), molding time (60–300 s), and mold temperature (156–204 °C), and these greatly affected board density and thus the mechanical and thermo-mechanical properties. Board density increased with increasingly extreme molding conditions, rising from 1162 to 1324 kg/m^3. The flexural properties increased at the same time (from 12.2 to 27.7 MPa for flexural strength at break, and from 2183 to 5244 MPa for elastic modulus) and also Shore *D* surface hardness (from 69.6 to 79.0°). Conversely, Charpy impact strength was low and quite independent of thermo-pressing conditions. Statistical analysis of the Doehlert's experimental design was conducted to determine optimal thermo-pressing conditions for flexural properties, giving 49.0 MPa pressure applied, 300 s molding time, and 204 °C mold temperature. Density of boards molded under these conditions was 1267 kg/m^3. Flexural strength at break, elastic modulus and Shore *D* surface hardness were 30.3 MPa, 5946 MPa, and 81.5°, respectively, and these corresponded to the highest values for the entire study. Such boards largely complied with French standard NF EN 312, type P4 (i.e., load bearing boards for use in dry conditions) for flexural properties. However, thickness swelling (30%) needs to be slightly reduced to achieve the 21% recommended standard value.

1. Introduction

Twin-screw extrusion technology is an original and powerful solution for the biorefinery of sunflower (*Helianthus annuus* L.) whole plant. The latter is conducted in the presence of water, allowing the aqueous extraction of sunflower oil (Evon et al., 2010a). The twin-screw extruder produces highly effective, mechanical cell lysis in a single step and in continuous mode. The filtration section of the barrel allows an extract (filtrate) and a raffinate (cake) to be collected separately, and oil extraction yield attains 57% under optimal operating conditions. To simplify conservation, cake is first dried because it has a relatively high moisture content of at least 62%. Structurally, it is porous with a majority of lignocellulosic fibers (around 58% of the dry matter), although there is also cell debris from breakdown of the kernels. The soluble molecules (proteins, pectins. . .) and lipids have been partly removed, whereas the structural plant molecules have not been extracted. Because the cake is a mixture of proteins and lignocellulosic fibers, it has been the subject of new valorizations (Orliac et al., 2002, 2003; Rouilly et al., 2001, 2003, 2006a,b).

DSC (differential scanning calorimetry) analysis of the cake indicate that denaturation of proteins is almost complete, and the significant peak observed at high temperature (around 180 °C) in the DMTA (dynamic mechanical thermal analysis) spectrum obtained from a dried and ground sample is associated with the glass transition of proteins (Evon et al., 2010b). And as the cake is a mixture of proteins and lignocellulosic fibers, it can be processed by thermo-pressing into cohesive fiberboards, with the proteins acting as internal binder and giving the agromaterial's cohesion,

* Corresponding author at: Université de Toulouse, INP, Laboratoire de Chimie Agro-industrielle, ENSIACET, 4 Allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France. Tel.: +33 5 62 44 60 80; fax: +33 5 62 44 60 82.
E-mail address: Philippe.Evon@ensiacet.fr (P. Evon).

and lignocellulosic fibers as reinforcing fillers (Evon et al., 2010a,b, 2012a,b,c, 2014a).

Temperature, pressure, and length of time of thermo-pressing all increase fiberboard bending properties (Evon et al., 2010a,b, 2012b,c), and the highest elastic modulus (2.2 GPa) and highest flexural strength at break (11.5 MPa) are obtained with a cake having a dry matter residual oil content of 14.5%, using the following molding conditions: 500 mg/cm^2 cake quantity, 200 °C mold temperature, 31.4 MPa pressure applied, and 60 s molding time (Evon et al., 2010a,b). Fiberboard thickness is just 3.9 mm with quite a high density (1035 kg/m^3). A fiberboard with these flexural properties, could be used in the handling and storage industry as pallet inter layer sheeting, or for furniture manufacture and biodegradable, multi-board containers, e.g., composters, vegetable gardening crates (Evon et al., 2010b). Moreover, another industrial application of fiberboards with lower densities (from 500 to 858 kg/m^3) is heat insulation of buildings (walls and ceilings) (Evon et al., 2014a).

For dense boards, because of the high pressure applied, part of the cake residual oil is expressed through the sidewall vents of the mold during molding (Evon et al., 2010a, 2012a,b,c). Logically, this molding oil expression decreases the fiberboard residual oil content (up to 8.7% of the dry matter for the highest pressure applied) (Evon et al., 2012c). Recuperation of this molding oil would mean filtering it, and then adding a refining step. Possible applications could be as a biolubricant, or transforming it into biodiesel (Amalia Kartika et al., 2013; Evon et al., 2014b). However, it is reasonable to suppose that oil expression during molding could reduce the mechanical resistance of fiberboards, due to defects appearing within the material as the oil escapes. Thus, an improvement in the molding process would be to use a deoiled cake as starting material for thermo-pressing.

This study aimed to manufacture new biodegradable fiberboards, by thermo-pressing from sunflower cake generated during the biorefinery of whole plant, which was then deoiled before molding using a Soxhlet extractor and *n*-hexane as extracting solvent. The influence of thermo-pressing conditions (pressure, time, and temperature) on the boards' mechanical (flexural properties, Charpy impact strength, and Shore *D* surface hardness) and thermo-mechanical properties, their thickness swelling and their water absorption, was then evaluated.

2. Material and methods

2.1. Material

Twin-screw extruder fractionation was applied to a batch of oleic type sunflower (*Helianthus annuus* L.) whole plant (Oxalliance, France) (Table 1), harvested at plant maturity, pre-dried in a ventilated oven (50 °C, 48 h) and then crushed with a hammer mill (Electra VS 1, France) through a 15 mm screen. Powdered plant moisture content was 8.9 ± 0.2% (French standard NF V 03-903).

Table 1
Chemical composition of the sunflower whole plant used for the experiment and of the cake obtained, after its thermo-mechanical fractionation in the Clextral BC 45 twin-screw extruder and after its deoiling using *n*-hexane as extracting solvent (% of the dry matter).

Material	Sunflower whole plant	Cake	Deoiled cake
Minerals	8.01 ± 0.04	7.06 ± 0.09	8.04 ± 0.12
Lipids	24.11 ± 0.04	17.31 ± 0.11	0.92 ± 0.34
Proteins	11.46 ± 0.20	8.34 ± 0.39	11.26 ± 0.39
Cellulose	24.81 ± 0.59	31.25 ± 1.02	38.84 ± 0.88
Hemicelluloses	8.10 ± 0.30	5.16 ± 0.45	5.90 ± 0.69
Lignins	10.27 ± 0.16	15.60 ± 0.49	19.42 ± 0.61
Water-soluble components	18.55 ± 0.40	12.15 ± 0.03	14.40 ± 0.34

Results in the table correspond to the mean values ± standard deviations.

2.2. Analytical methods

The moisture contents were determined according to French standard NF V 03-903. The mineral contents were determined according to French standard NF V 03-322. The oil contents were determined according to French standard NF V 03-908. The protein contents were determined according to French standard NF V 18-100. The three parietal constituents (cellulose, hemicelluloses, and lignins) were estimated using the ADF–NDF method of Van Soest and Wine (1967, 1968). Similarly, the water-soluble components were estimated by measuring the mass loss of the test sample after 1 h in boiling water. All determinations were carried out in duplicate.

2.3. Deoiled cake production by twin-screw extrusion plus deoiling

A Clextral BC 45 twin-screw extruder was used to conduct simultaneously at 80 °C the thermo-mechanical fractionation of whole plant and the aqueous extraction of sunflower oil, and the screw configuration was the same as that previously optimized (Evon et al., 2010a). Operating conditions for cake production were 67.4 rpm for the screw rotation speed, 5.5 kg/h for the inlet flow rate of the sunflower whole plant, and 20.5 kg/h for the inlet flow rate of the water. A filtrate was collected continuously from the filter section, and a cake was generated at the same time. Immediately after its production, and to facilitate conservation, it was dried in a ventilated oven (80 °C, 12 h). Then, residual oil inside the cake was extracted. Oil extraction was conducted for 5 h using a 1 L Soxhlet extractor and *n*-hexane as extracting solvent.

2.4. Particle size distribution

A 500 g test sample mass of deoiled cake was treated in a Retsch AS 300 (Germany) vibratory sieve shaker to determine particle size distribution. Sieve acceleration was 1.5 × *g*, and sieving time 10 min. For the apparent and tapped densities of the deoiled cake, which were also determined, the tapped density measurement used a Granuloshop Densitap ETD-20 (France) volumenometer.

2.5. TGA measurements

Thermogravimetric analysis (TGA) of the deoiled cake was performed with a Shimadzu TGA-50 (Japan) analyzer. Dynamic analysis was conducted under air at a heating rate of 5 °C/min, from 20 to 750 °C. The deoiled cake was first equilibrated in a climatic chamber (60% RH, 25 °C) for 3 weeks, and the test sample mass was about 5 mg. Sample weight was measured as a function of temperature, and the data used subsequently to plot the percentage of undegraded sample (1–*D*) (%) as a function of temperature,

$$D = \frac{W_0 - W}{W_0} \quad (1)$$

where W_0 and W were the weights at the starting point and during scanning (mg). The measurement was carried out in duplicate.

2.6. Thermo-pressing

The deoiled cake was dried in a ventilated oven (60 °C, 12 h) to minimize vapor generation during thermo-pressing thus reducing the risk of defects like blisters inside the fiberboards. Then, molding was by thermo-pressing inside an aluminum mold. A 400 ton capacity Pinette Emidecau Industries (France) heated hydraulic press

was used to produce 150 mm × 150 mm fiberboards. The quantity of deoiled cake for all experiments was 150 g (i.e. 667 mg/cm^2). A Doehlert's experimental design with three variables was made to evaluate the influence of thermo-pressing conditions (including pressure applied, molding time, and mold temperature) on fiberboard properties. Statistical analysis of the results was by NEMROD software, which was also used to plot isoresponse curves.

The best-fit second-order response (Y) obtained to describe each of the fiberboard characteristics (including flexural properties, Charpy impact strength, Shore D surface hardness, thickness swelling, and water absorption) was given by the following formula:

$$Y = a_0 + (a_1 \times X_1) + (a_2 \times X_2) + (a_3 \times X_3) + (a_{12} \times X_1 \times X_2) + (a_{13} \times X_1 \times X_3) + (a_{23} \times X_2 \times X_3) + (a_{11} \times X_1 \times X_1) + (a_{22} \times X_2 \times X_2) + (a_{33} \times X_3 \times X_3) \quad (2)$$

X_1, X_2, and X_3 are the coding values of the experimental design, each varying from −1.0 to 1.0, and relative to the three molding conditions tested (pressure, time, and temperature, respectively), and a_i (i varying from 0 to 3), and a_{ij} (i and j varying from 1 to 3, and $i \leq j$) the coefficients of the polynomial model.

Three fiberboards were produced for all the thermo-pressing conditions. Immediately after molding, these were equilibrated in a climatic chamber (60% RH, 25 °C) for 3 weeks in order to assess their properties using equilibrated materials. A first fiberboard was used to assess thickness, mean apparent density, and mechanical properties for bending. After equilibration, four 30 mm wide test specimens were cut and their thickness measured at three points and their length at two points, with a 0.01 mm resolution electronic digital sliding caliper. Thickness and length mean values were recorded to calculate the specimen volume, and test specimens were all weighed to calculate their density. The thickness (t) and mean apparent density (d) of fiberboard were the mean values of measurements made on the four test specimens. A second fiberboard was used for measuring: Charpy impact strength, Shore D surface hardness, and finally thermo-mechanical properties. The third fiberboard was used for thickness swelling and water absorption.

2.7. Mechanical properties for bending

Measurement of the flexural properties of the 30 mm wide test specimens according to French standard NF EN 310 was undertaken using an Instron 33R4204 (USA) universal testing machine fitted with a 500 N load cell, and the three points bending technique. Test speed was 2 mm/min with 100 mm grip separation. Load was applied equidistant from the two supports, and the loading direction was perpendicular to the upper face of the test specimen. Properties covered energy-to-break (E), breaking load (F), flexural strength at break (σ_f), and elastic modulus (E_f). An estimation of the energy-to-break for each specimen, using the area under the load deformation curve from zero to rupture, was calculated using the trapezium method. All determinations were carried out four times, i.e., from each of the four test specimens cut in each fiberboard.

2.8. Charpy impact strength

The impact strength of the unnotched test specimens according to French standard NF EN ISO 179 was assessed with a Testwell Wolpert 0–40 daN cm (France) Charpy machine, and this also covered absorbed energy (W), and resilience (K). After fiberboard equilibration, twelve test specimens, 60 mm long and 10 mm wide, were cut. To calculate their section, thickness was measured at three points with a 0.01 mm resolution electronic digital sliding caliper, and the mean value (t) recorded. Impact strength measurements were made at 23 °C using the three points bending technique, with 25 mm grip separation. Load was applied equidistant from the two supports, and the loading direction was perpendicular to the test specimen. All determinations were carried out twelve times, i.e., from each of the twelve test specimens cut in each fiberboard.

2.9. Shore D surface hardness

Shore D surface hardness of the fiberboards was assessed using a Bareiss (Germany) durometer according to French standard NF EN ISO 868. The indentation direction was perpendicular to the upper face of the fiberboard. All determinations were carried out 48 times for each fiberboard (24 times for each board side).

2.10. Thickness swelling and water absorption

Four 50 mm × 50 mm samples were used to determine thickness swelling (TS) and water absorption (WA) of the fiberboards. To evaluate these, they were submerged in distilled water at 25 °C for 24 h. TS was determined according to the French Standard NF EN 317 and thickness of each sample was measured at four points, midway along each side 10 mm from the edge before and after soaking in distilled water. Each sample was also weighed to an accuracy of 0.01 g to determine WA values.

2.11. Dynamic mechanical thermal analysis (DMTA)

DMTA analysis was used to evaluate the thermo-mechanical behavior of fiberboards (boards 8, 14, and 7) produced at three different mold temperatures (160, 180, and 200 °C, respectively). DMTA experiments were on a Triton Technology Tritec 2000 (UK) machine. Fiberboards were analyzed using 10 mm wide and 30 mm long samples. Measurements were made using the two points bending technique: 1 Hz frequency, 50 μm displacement, and a 3 °C/min heating rate over a 0–165 °C range. Distance between the two points was 10 mm. Curves for the storage modulus (E') and the loss modulus (E'') were plotted. Four samples were tested for each fiberboard.

3. Results and discussion

3.1. Physico-chemical characterization of the deoiled cake

The cake produced by twin-screw extrusion was a powder consisting of inhomogeneous particles, whose chemical composition is shown in Table 1. It revealed an oil content (17.3% of the dry matter) quite comparable to that of a cake used in a previous study for the manufacture of thermal insulation fiberboards (17.6%) (Evon et al., 2014a). Due to the fact that some lipids and proteins were partly extracted by water during the process, this meant that their residual contents in the cake decreased compared to initial whole plant values (Table 1). Similarly, with hemicelluloses and water-soluble components, the same tendency was also observed. On the other hand, cellulose and lignins were not extracted, because both these biopolymers are insoluble in water. Thus, in parallel, a significant increase relative to their initial values was observed.

Residual oil inside the cake was extracted before thermo-pressing to preserve fiberboard mechanical properties. As expected, the chemical composition of the deoiled cake (Table 1) revealed a large decrease in the oil content (0.9%), meaning that oil extraction using n-hexane was almost complete. Conversely, it logically showed an increase in the content of the other compounds like proteins, cellulose, and lignins.

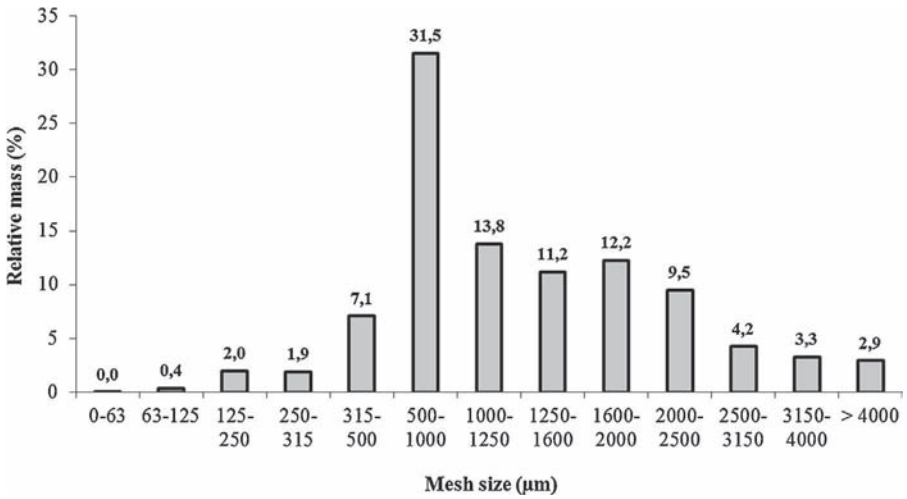

Fig. 1. Particle size distribution in the deoiled cake.

In conclusion, the chemical composition of the deoiled cake (Table 1) confirmed that it was a mixture of lignocellulosic fibers and proteins whose denaturation in the twin-screw extruder was almost complete (Evon et al., 2010b). Therefore, it could be considered to be a natural composite capable of being transformed into fiberboards by thermo-pressing. The particle size distribution inside the deoiled cake (Fig. 1) revealed the presence of large particles (above 1 mm), mainly composed of lignocellulosic fibers originating essentially from the sunflower stalk, and also smaller particles, mean diameter around 500 µm. This second population contained not only smaller fibers but also spherical particles, from the kernel breakdown process. Most of the proteins contained in the deoiled cake were present within this population. Lastly, apparent and tapped densities of the deoiled cake were quite low (215 ± 3 and $233 \pm 1\ kg/m^3$, respectively). Thermogravimetric analysis of the deoiled cake was also conducted, and the TGA degradation curve is shown in Fig. 2. At 100 °C, there is an initial mass loss observed corresponding to water evaporation. After 3 weeks in a climatic chamber, the level of moisture in the deoiled cake was $7.5 \pm 0.1\%$, and the TGA curve mass loss observed corresponded approximately to the same mass percentage. Then, thermal degradation of organic compounds took place essentially in one stage (between 220 and 375 °C) that lead to the loss of 70–75% of the sample dry matter. Finally, another degradation phenomenon was also observed between 425 and 500 °C, however this was associated with a lower mass loss (15–20% of the dry matter in sample).

Using data dealing with the thermal degradation of fibers and sunflower proteins, cited by some researchers in previous studies (Beaumont, 1981; Geneau, 2006; Hatakeyama and Hatakeyama, 2004; Lalou, 1995; Schaffer, 1973), it was logical to infer that the main thermal degradation stage (220–375 °C) could be associated with the simultaneous breakdown of proteins, hemicelluloses, and cellulose. The subsequent stage, beginning about 425 °C, would in this case correspond to the thermal degradation of just the lignins. Following all the measurements, the undegraded sample accounted for less than 9% of the test sample mass, and represented the minerals contained in the deoiled cake.

3.2. Influence of thermo-pressing conditions on mechanical properties of fiberboards

Fourteen fiberboards were manufactured using different thermo-pressing conditions (Table 2). Conditions included pressure applied, molding time, and temperature of the aluminum mold. The pressure applied, in particular, varied from 24.5 to 49.0 MPa. This was comparable to values used in previous studies: up to 31.4 MPa (Evon et al., 2010b), from 31.4 to 35.3 MPa (Evon et al., 2012c), and from 24.5 to 49.0 MPa (Evon et al., 2012b), and

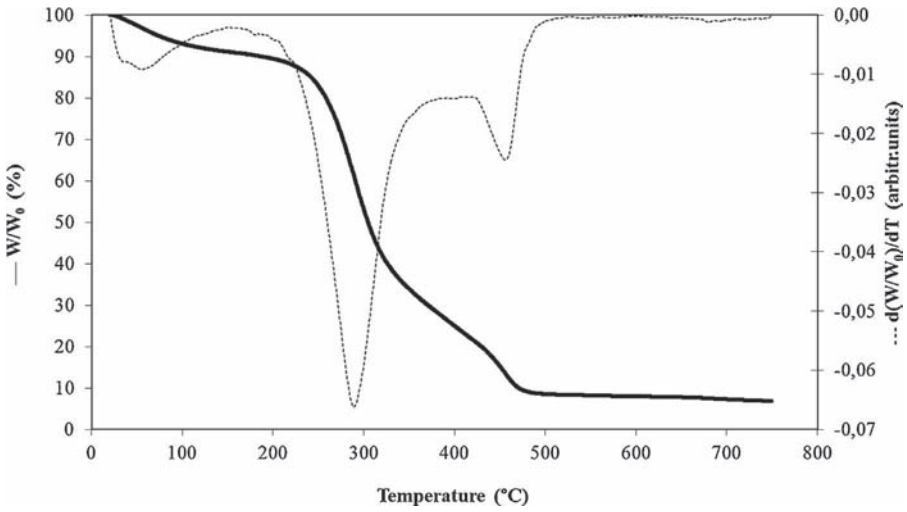

Fig. 2. TGA degradation curve of the deoiled cake.

Table 2
Thermo-pressing conditions for the manufacture of the fourteen fiberboards (Doehlert's experimental design).

Board number	X_1	Pressure applied (MPa)	X_2	Molding time (s)	X_3	Mold temperature (°C)
1	1.000	49.0	0.000	180	0.000	180
2	−1.000	24.5	0.000	180	0.000	180
3	0.500	42.9	0.866	284	0.000	180
4	−0.500	30.6	−0.866	76	0.000	180
5	0.500	42.9	−0.866	76	0.000	180
6	−0.500	30.6	0.866	284	0.000	180
7	0.500	42.9	0.289	215	0.816	200
8	−0.500	30.6	−0.289	145	−0.816	160
9	0.500	42.9	−0.289	145	−0.816	160
10	0.000	36.8	0.577	249	−0.816	160
11	−0.500	30.6	0.289	215	0.816	200
12	0.000	36.8	−0.577	111	0.816	200
13	0.000	36.8	0.000	180	0.000	180
14	0.000	36.8	0.000	180	0.000	180

the objective here was to manufacture dense fiberboards, i.e., with a density up to 1000 kg/m^3. Molding time varied from 60 to 300 s, which was similar to values used in a previous study (Evon et al., 2012b), and was sufficient for sunflower proteins to reach a rubbery state during molding.

Mold temperature varied from 156 to 204 °C. The lowest temperature (156 °C) was chosen to be slightly higher than the protein glass transition temperature. A previous study using the DSC technique, showed that, for sunflower proteins, this temperature was clearly influenced by their water content (Rouilly et al., 2001), with a large drop (from 181 to 5 °C) observed as this protein water content increased from 0 to 26.1% of the dry matter, confirming that water acted as a plasticizer for the proteins. Indeed proteins, like the main biopolymers (starch, pectins, hemicelluloses, and other polysaccharides), contain polar functions (amides) capable of linking the water molecules by hydrogen bonds. The presence of water separates the proteins and facilitates their movement (Rouilly and Rigal, 2002). The thermal and rheological properties of proteins are therefore highly dependent on the amount of water, resulting in variations in their glass transition temperature according to their hydration. Because the cake moisture was only 2.8 ± 0.1% on molding, the glass transition temperature of proteins was therefore estimated to be close to 145 °C. On the other hand, the highest temperature (204 °C) corresponded approximately to that giving the best mechanical properties for bending in a previous study (200 °C) (Evon et al., 2010b). Finally, no temperature higher than 204 °C was tested because thermal degradation of most of the organic compounds in the cake occurs in the 220–375 °C temperature range (Fig. 2).

Deoiled cake quantity for all the experiments was 667 mg/cm^2, and this led to the manufacture of fiberboards with thicknesses after climatic chamber conditioning (at least 5.0 mm, and up to 5.8 mm) (Table 3) comparable to those of other materials from sunflower cake described in previous studies (Evon et al., 2010b, 2012b,c). All fiberboards were cohesive. Proteins acted as an internal binder within the fiberboards, and they contributed to ensuring cohesion of the agromaterial. In addition, the entanglement of lignocellulosic fibers also acted as reinforcement.

The density of the equilibrated fiberboards was clearly influenced by the thermo-pressing conditions used, increasing with increasing conditions (Table 3). This was illustrated by the positive values obtained for the a_1, a_2, and a_3 coefficients of the corresponding best-fit second-order response (Table 4). At the same time, a_{ij} coefficients were negative but their absolute values were all much lower than a_i coefficients. Therefore, logically an increase in pressure applied and/or molding time led to fiberboard densification. But it was the mold temperature that most affected fiberboard density, as shown by the a_3 coefficient which was higher (59.5) than the a_1 and a_2 coefficients (43.7 and 40.9, respectively). And such an evolution, explained the decrease in the moisture content of equilibrated fiberboards with the increase in pressure, molding time, and especially temperature (Table 3). Indeed, water uptake during climatic chamber conditioning was less for denser boards, due to their lower porosity.

The mechanical properties for bending of fiberboards were also clearly influenced by the thermo-pressing conditions. And it was still the mold temperature that most affected the energy-to-break, and especially the breaking load, the flexural strength at break and the elastic modulus (Table 4). Moreover, the higher the fiberboard density, the higher its flexural properties (Table 3). And the most mechanically resistant fiberboard (board 7) was also the densest board. The NEMROD software analysis of the isoresponse curves for flexural strength at break (Fig. 3) and elastic modulus (Fig. 4), perfectly illustrates the increase in mechanical properties for bending of fiberboards with increasing thermo-pressing conditions, especially the mold temperature. Similarly, the Shore *D* surface hardness increased slightly with increasing thermo-pressing conditions (Tables 3 and 4). Conversely, Charpy impact strength was low and relatively independent of thermo-pressing conditions, and such fragility could be explained by the high rigidity of the boards manufactured (Tables 3 and 4).

Since the mold temperature was always higher than the protein glass transition temperature, this change occurred systematically during molding and proteins were thus always in a rubbery state. However, because the protein-based resin became less and less viscous with increasing mold temperature, this meant that the fiber wetting improved progressively. This could explain why the mechanical properties of fiberboards increased as the mold temperature increased, the 200 °C mold temperature logically leading to the most resistant fiberboards of the study (Table 3).

Thickness swelling (TS) and water absorption (WA) of fiberboards were also dependent on thermo-pressing conditions, decreasing as they increased (Table 3), with the greatest effect from mold temperature (Table 4) which, at 200 °C gave the least water-sensitive boards. At such a temperature, TS and WA were only 61–100 and 43–69%, respectively (Table 3). Moreover, as previously observed for flexural properties, thickness swelling, and water absorption were correlated to the board density, and both tended to decrease with its increase. Indeed, an increase in board density resulted in a reduction of its internal porosity, and this contributed to making it less water-sensitive.

DMTA analysis of fiberboards was conducted on boards 8, 14, and 7 (Fig. 5). They were molded at 160, 180, and 200 °C, respectively, and the higher the mold temperature, the higher the storage modulus (E′). This confirmed that fiberboards' internal cohesion increased with increasing mold temperature. Moreover, no significant transition occurred between 0 °C and 118 °C for board 8, up to 129 °C for board 14 and 140 °C for board 7. Thus, no phase

Table 3
Mechanical properties, thickness swelling, and water absorption of the fourteen fiberboards manufactured by thermo-pressing.

Board number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Mechanical properties for bending														
H_{FB}[a] (%)	7.71 ± 0.11	7.44 ± 0.06	7.06 ± 0.04	7.46 ± 0.03	7.25 ± 0.01	6.96 ± 0.00	6.94 ± 0.05	8.00 ± 0.02	7.92 ± .09	7.37 ± 0.10	6.66 ± 0.01	6.84 ± 0.07	6.96 ± 0.04	6.98 ± 0.12
t (mm)	5.18 ± 0.28	5.63 ± 0.21	5.22 ± 0.22	5.71 ± 0.24	5.41 ± 0.20	5.27 ± 0.21	4.98 ± 0.20	5.80 ± 0.25	5.54 ± 0.24	5.49 ± 0.25	5.12 ± 0.23	5.24 ± 0.12	5.32 ± 0.19	5.30 ± 0.26
d (kg/m^3)	1299 ± 33	1200 ± 38	1287 ± 50	1182 ± 37	1247 ± 34	1280 ± 43	1324 ± 17	1162 ± 39	1215 ± 44	1234 ± 28	1299 ± 40	1280 ± 12	1257 ± 20	1275 ± 31
E (mJ)	210 ± 8	174 ± 16	201 ± 15	160 ± 24	193 ± 14	207 ± 14	183 ± 13	132 ± 17	143 ± 11	172 ± 12	164 ± 20	181 ± 21	184 ± 9	171 ± 12
F (N)	136 ± 3	114 ± 7	134 ± 12	104 ± 8	118 ± 8	142 ± 9	137 ± 8	82 ± 7	92 ± 7	103 ± 7	134 ± 5	131 ± 10	112 ± 2	122 ± 4
σ_f (MPa)	25.4 ± 0.6	18.0 ± 2.1	24.6 ± 2.2	15.9 ± 1.1	20.1 ± 1.4	25.6 ± 1.6	27.7 ± 3.1	12.2 ± 1.1	15.0 ± 1.0	17.0 ± 1.2	25.5 ± 0.9	23.8 ± 1.9	19.8 ± 0.4	21.7 ± 0.7
E_f (MPa)	4505 ± 452	3177 ± 151	4220 ± 323	2717 ± 75	3316 ± 284	4262 ± 209	5244 ± 461	2183 ± 226	2673 ± 270	2911 ± 121	4978 ± 248	4212 ± 312	3258 ± 283	3719 ± 258
Charpy impact strength														
W (mJ)	147 ± 11	147 ± 10	164 ± 10	164 ± 12	152 ± 16	169 ± 17	146 ± 12	158 ± 14	145 ± 17	166 ± 15	153 ± 10	172 ± 10	168 ± 11	161 ± 18
K (kJ/m^2)	2.84 ± 0.21	2.61 ± 0.17	3.15 ± 0.19	2.87 ± 0.22	2.81 ± 0.30	3.21 ± 0.33	2.94 ± 0.24	2.73 ± 0.25	2.62 ± 0.31	3.03 ± 0.26	2.98 ± 0.19	3.28 ± 0.38	3.15 ± 0.21	3.03 ± 0.17
Surface hardness														
Shore D (°)	73.7 ± 1.6	71.4 ± 2.8	77.1 ± 2.1	71.3 ± 3.2	72.9 ± 3.3	76.2 ± 2.6	79.0 ± 1.7	69.6 ± 2.7	70.6 ± 3.1	72.0 ± 2.4	77.8 ± 1.7	76.4 ± 2.4	74.2 ± 3.5	74.9 ± 2.6
Thickness swelling and water absorption														
TS (%)	138 ± 15	180 ± 7	130 ± 8	202 ± 17	188 ± 12	129 ± 9	72 ± 6	235 ± 15	232 ± 16	228 ± 7	61 ± 5	100 ± 7	147 ± 7	142 ± 14
WA (%)	96 ± 10	146 ± 17	98 ± 11	208 ± 25	151 ± 16	89 ± 9	52 ± 5	260 ± 15	238 ± 15	213 ± 15	43 ± 4	69 ± 6	109 ± 9	100 ± 8

Results in the table correspond to the mean values ± standard deviations.

[a] H_{FB} is the moisture content of the fiberboard. Fiberboards were equilibrated in a climatic chamber (60% RH, 25 °C) for 3 weeks before moisture measurements.

Table 4
Coefficients of the best-fit second-order response for each of the fiberboard characteristics analyzed, and corresponding correlation coefficient (R^2).

Coefficient	a_0	a_1	a_2	a_3	a_{12}	a_{13}	a_{23}	a_{11}	a_{22}	a_{33}	R^2
Mechanical properties for bending											
d (kg/m^3)	1265.9	43.7	40.9	59.5	−33.4	−5.3	−10.1	−16.3	−17.1	−11.9	0.99
E (mJ)	177.4	16.2	15.8	16.4	−22.6	12.3	−30.6	14.8	12.1	−29.0	0.99
F (N)	116.9	7.9	14.6	25.6	−12.7	0.6	−8.3	8.2	7.1	−9.5	0.98
σ_f (MPa)	20.7	2.9	3.9	6.7	−3.0	0.7	−0.6	1.0	0.8	−1.3	0.98
E_f (MPa)	3488.7	496.0	729.7	1361.0	−370.0	−6.7	194.2	352.1	69.3	211.7	0.98
Charpy impact strength											
K (kJ/m^2)	3.1	0.0	0.2	0.2	0.0	0.0	−0.3	−0.4	0.0	−0.2	0.89
Surface hardness											
Shore D (°)	74.5	1.2	2.5	4.3	−0.4	0.2	0.9	−2.0	0.4	−0.1	1.00
Thickness swelling and water absorption											
TS (%)	144.8	−11.2	934.2	−94.6	8.7	5.6	−18.3	14.1	18.7	6.4	0.99
WA (%)	104.6	−20.3	−45.5	−111.6	38.0	5.4	17.7	16.3	37.3	48.4	0.99

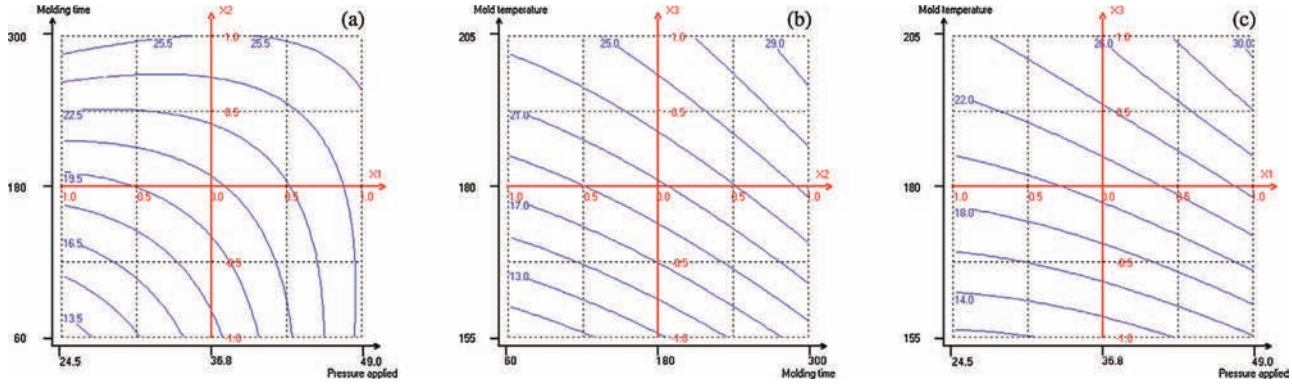

Fig. 3. Isoresponse curves for flexural strength at break (σ_f) of fiberboards at 180 °C mold temperature (a), at 36.8 MPa pressure applied (b), and for 180 s molding time (c).

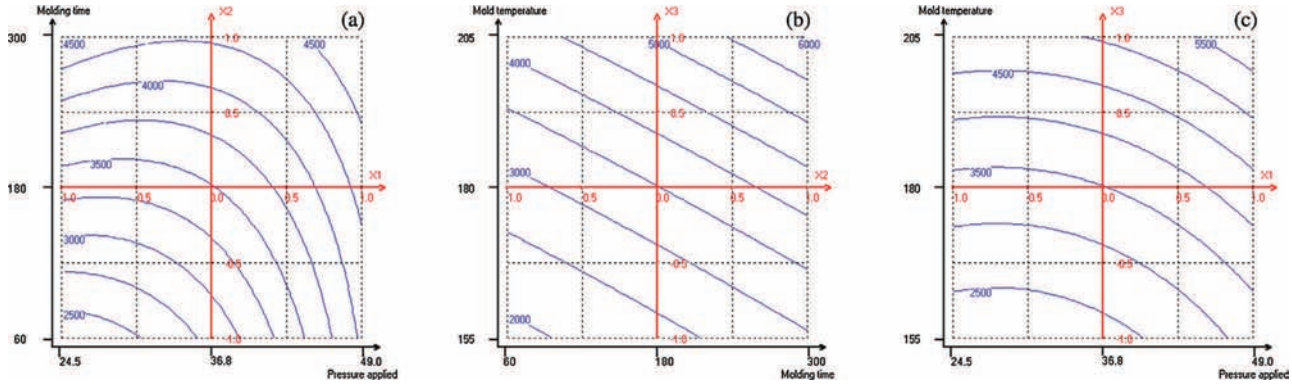

Fig. 4. Isoresponse curves for elastic modulus (E_f) of fiberboards at 180 °C mold temperature (a), at 36.8 MPa pressure applied (b), and for 180 s molding time (c).

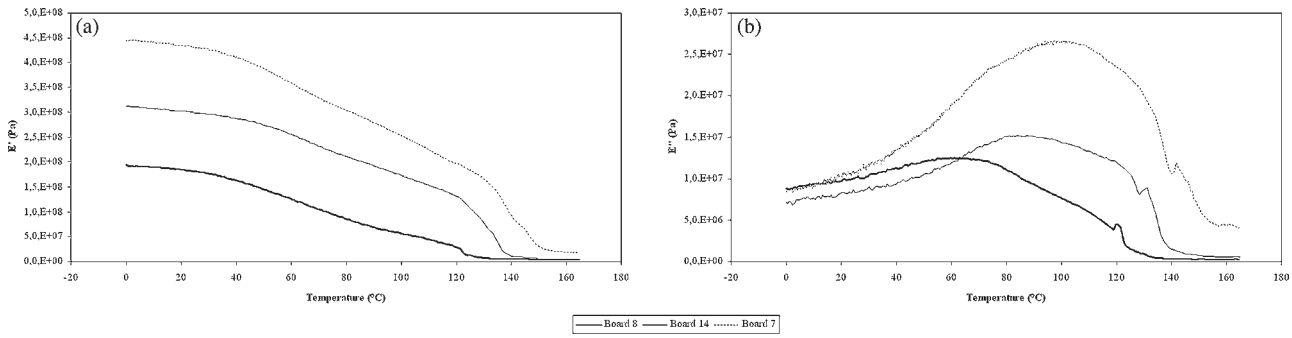

Fig. 5. DMTA curves of boards 8, 14, and 7: storage modulus (E') (a) and loss modulus (E'') (b).

Table 5
Optimal thermo-pressing conditions for each of the fiberboard characteristics analyzed, and corresponding optimal response ($Y_{optimal}$).

Thermo-pres-sing conditions	X_1	Pressure applied (MPa)	X_2	Molding time (s)	X_3	Mold tempe-rature (°C)	$Y_{optimal}$[a]
Mechanical properties for bending							
d (kg/m^3)	1.00	49.0	−0.08	171	1.00	204	1336
E (mJ)	1.00	49.0	−1.00	60	1.00	204	258
F (N)	1.00	49.0	−1.00	60	1.00	204	163
σ_f (MPa)	1.00	49.0	1.00	300	1.00	204	31.9
E_f (MPa)	1.00	49.0	1.00	300	1.00	204	6526
Charpy impact strength							
K (kJ/m^2)	0.00	36.8	−1.00	60	1.00	204	3.31
Surface hardness							
Shore D (°)	0.26	39.9	1.00	300	1.00	204	82.7
Thickness swelling and water absorption							
TS (%)	−0.11	35.4	1.00	300	1.00	204	23
WA (%)	0.25	39.8	0.25	209	1.00	204	36

[a] The optimal response is the maximal one for fiberboard mechanical properties (including flexural properties, Charpy impact strength, and Shore D surface hardness), and the minimal one for thickness swelling and water absorption.

Fig. 6. Photograph of test specimens from fiberboard produced under optimal thermo-pressing conditions.

change took place in these temperature ranges, and proteins still ensured panel cohesion in all three cases. Then, a rapid decrease in the storage modulus was observed, and at the same time a peak appeared in DMTA loss modulus (E'') curves (Fig. 5). This transition was associated with the protein's glass transition, and the corresponding temperature was around 120 °C for board 8, 131 °C for board 14, and 142 °C for board 7. These differences can be explained by the decrease in moisture content of equilibrated fiberboards with increasing mold temperature (Table 3), thus re-illustrating the plasticizing effect of water for proteins. And logically, because panel cohesion was no longer ensured by the protein-based resin beyond the protein's glass transition temperature, the storage modules were negligible at higher temperatures. Polynomial models were used to determine the optimal responses for each fiberboard characteristic analyzed, i.e., mechanical properties for bending, resilience, Shore D surface hardness, thickness swelling, and water absorption. All optimal responses are given in Table 5, as well as relevant thermo-pressing conditions. The X_3 coding value was always 1.00, i.e., 204 °C mold temperature, confirming that this was the thermo-pressing condition that most affected fiberboards' mechanical properties, thickness swelling, and water absorption. Moreover, optimal flexural strength at break (31.9 MPa) and elastic modulus (6526 MPa) were both obtained under the same thermo-pressing conditions, i.e., 49.0 MPa pressure applied, 300 s molding time, and 204 °C mold temperature. Such conditions were considered as the optimal ones.

So, a fifteenth fiberboard was molded using these conditions, and Table 6 shows fiberboard characteristics calculated from best-fit second-order equations, plus experimental data. The board obtained (Fig. 6) was a little less dense (1267 kg/m^3) than expected from the polynomial model. However, flexural strength at break and elastic modulus were 30.3 and 5946 MPa, respectively, relatively close to the expected values. Shore D surface hardness was 81.5° instead of the 81.6° expected value, and the fiberboard molded under optimal thermo-pressing conditions was indeed the strongest board of the entire study for bending stress and surface hardness. The only significant difference between the model and the experiment was Charpy impact strength where excessive panel rigidity significantly altered its impact resistance. Conversely, thickness swelling and water absorption (30 and 23%, respectively) were better than expected, meaning that the optimal board was not very water-sensitive.

Therefore, this optimal fiberboard largely complied with French standard NF EN 312, type P4 (i.e., load bearing boards for use in dry conditions) for flexural properties (recommendations of 16 and 2200 MPa for flexural strength at break and elastic modulus respectively, for boards with a thickness of between 4 and 6 mm) but not exactly for thickness swelling (recommendation of 21% after 24 h immersion in water). An additional process such as preheating, chemical, or steam treatment would probably improve this dimensional stability parameter (Halvarsson et al., 2009; Okuda et al., 2006; Saadaoui et al., 2013; Widyorini et al., 2005).

Another fiberboard was molded using the optimal thermo-pressing conditions with sunflower cake before deoiling, retaining cake quantity at 667 mg/cm^2. Part of the oil was expressed during molding, due to pressure applied, representing 66% of the oil inside the cake. Nevertheless, the resultant fiberboard still contained oil (7.1 ± 0.1% of the dry matter). It remained cohesive like the others, but its mechanical properties were particularly low compared with those of the optimal board from deoiled cake (Table 6): 10.1 ± 0.7 MPa for flexural strength at break, 2163 ± 153 MPa for elastic modulus, 1.32 ± 0.15 kJ/m^2 for Charpy impact strength, and 67.5 ± 3.1° for Shore D surface hardness. At the same time, thickness swelling and water absorption were higher (54 ± 5% and 45 ± 5%, respectively). Thus, oil expression during molding reduced both board mechanical and water resistance, due to defects appearing within the material as the oil escaped.

To conclude, all fiberboards from deoiled cake were self-bonded composite materials, entirely derived from a renewable resource and also biodegradable. The proteic resin ensured the board's cohesion and lignocellulosic fibers further acted as reinforcement. Moreover, the use of the deoiled cake for thermo-pressing significantly improved the molding process, leading to more resistant

Table 6
Fiberboard characteristics calculated from best-fit second-order equations for 49.0 MPa pressure applied (1.00 for X_1), 300 s molding time (1.00 for X_2), and 204 °C mold temperature (1.00 for X_3), and obtained from the experiment under these conditions.

Fiberboard characteristic	Calculated from best-fit second-order equation[a]	Obtained from the experiment[b]
Mechanical properties for bending		
d (kg/m^3)	1316 (99%)	1267 ± 25[c] (96%)
E (mJ)	183 (71%)	190 ± 13 (104%)
F (N)	150 (92%)	149 ± 9 (99%)
σ_f (MPa)	31.9 (100%)	30.3 ± 2.6 (95%)
E_f (MPa)	6526 (100%)	5946 ± 272 (91%)
Charpy impact strength		
K (kJ/m^2)	2.62 (79%)	2.33 ± 0.21[d] (89%)
Surface hardness		
Shore D (°)	81.6 (99%)	81.5 ± 0.8 (100%)
Thickness swelling and water absorption		
TS (%)	40	30 ± 4
WA (%)	90	23 ± 2

Results obtained from the experiment (right column in the table) correspond to the mean values ± standard deviations.
[a] The number in parentheses in the second column is the ratio of the response calculated from the best-fit second-order equation to the associated optimal response ($Y_{optimal}$) (%).
[b] The number in parentheses in the third column is the ratio of the fiberboard characteristic obtained from the experiment to the one calculated from the best-fit second-order equation (%).
[c] 4.95 ± 0.16 mm for the thickness of the equilibrated fiberboard.
[d] 115 ± 10 mJ for absorbed energy.

and less water-sensitive boards compared with those produced from sunflower cake before deoiling. Fiberboards produced under optimal thermo-pressing conditions (49.0 MPa pressure applied, 300 s molding time, and 204 °C mold temperature) largely complied with the French standard NF EN 312, type P4 regarding mechanical properties for bending, while this was slightly less valid for thickness swelling. However, these optimal boards had low dimensions (150 mm × 150 mm). Therefore, significant work is still needed to produce commercial products, i.e., with a width from 1 to 4 m, while maintaining the same properties.

When comparing the optimal boards to most conventional ones, there was no necessity to add any external binder such as a thermosetting resin in order to obtain a cohesive panel. Further, the inclusion of lignocellulosic fibers revealed a promising ability for mechanical reinforcement. Essentially originating from the by-products of sunflower culture, i.e., the stalks and heads, these fibers are not commercially available for the moment, the sunflower harvest concerning only the seeds. Thus, this could, in the future, justify their harvest in the field and provide farmers with the potential benefits from an additional source of income.

4. Conclusion

New biodegradable and cohesive fiberboards were manufactured using a heated hydraulic press, from a deoiled cake generated during the biorefinery of sunflower whole plant in a twin-screw extruder. Proteins acted as an internal binder, and entanglement of lignocellulosic fibers also acted as reinforcement. The thermo-pressing conditions had an important influence on board density and on mechanical properties for bending. Statistical analysis of the Doehlert's experimental design revealed that the optimal thermo-pressing conditions for flexural properties corresponded to the highest values of pressure applied (49.0 MPa), molding time (300 s), and mold temperature (204 °C). Density of the fiberboard produced under these conditions was 1267 kg/m^3. Flexural strength at break and elastic modulus were 30.3 and 5946 MPa, respectively, and these values were the highest for the entire study. At the same time, thickness swelling and water absorption were 30% and 23%, respectively. Such boards largely complied with French standard NF EN 312, type P4 (i.e., load bearing boards for use in dry conditions) for flexural properties but not entirely for thickness swelling. It is anticipated that one additional process such as preheating, chemical, or steam treatment could achieve the recommended thickness swelling value, i.e., 21%.

References

Amalia Kartika, I., Yani, M., Ariono, D., Evon, P., Rigal, L., 2013. Biodiesel production from jatropha seeds: solvent extraction and in situ transesterification in a single step. Fuel 106, 111–117.
Beaumont, O., 1981. Pyrolyse Extractive Du Bois. Ph.D. Thesis. Ecole Nationale Supérieure des Mines de Paris, Paris, France.
Evon, P., Vandenbossche, V., Pontalier, P.Y., Rigal, L., 2010a. The twin-screw extrusion technology, an original and powerful solution for the biorefinery of sunflower whole plant. Ol. Corps gras Lipides 17 (6), 404–417.
Evon, P., Vandenbossche, V., Pontalier, P.Y., Rigal, L., 2010b. Thermo-mechanical behaviour of the raffinate resulting from the aqueous extraction of sunflower whole plant in twin-screw extruder: manufacturing of biodegradable agromaterials by thermopressing. Adv. Mater. Res. 112, 63–72.
Evon P., Rigal L., Pontalier P.Y., Vandenbossche V., 2012. Procédé de fabrication d'un matériau solide à partir d'une plante oléagineuse et matériau solide obtenu, French Patent FR, 2967, 689.
Evon, P., Vandenbossche, V., Rigal, L., 2012b. Thermo-pressing of cake meal from sunflower whole plant, one only operation for two actions: expression of residual oil and molding of biodegradable agromaterials. In: Proceedings of the 18th International Sunflower Conference, Mar del Plata Argentina, pp. 937–942.
Evon, P., Vandenbossche, V., Rigal, L., 2012c. Manufacturing of renewable and biodegradable fiberboards from cake generated during biorefinery of sunflower whole plant in twin-screw extruder: influence of thermo-pressing conditions. Polym. Degrad. Stab. 97 (10), 1940–1947.
Evon, P., Vandenbossche, V., Pontalier, P.Y., Rigal, L., 2014a. New thermal insulation fiberboards from cake generated during biorefinery of sunflower whole plant in a twin-screw extruder. Ind. Crops Prod. 52, 354–362.
Evon, P., Amalia Kartika, I., Rigal, L., 2014b. New renewable and biodegradable particleboards from jatropha press cakes. J. Renew. Mater. 2 (1), 52–65.
Geneau, C., 2006. Manufacturing Process of Agromaterial Natural Composite by Twin-screw Extrusion and Injection Moulding from Sunflower Cake. Ph.D. Thesis. INP, Toulouse, France.
Halvarsson, S., Edlund, H., Norgren, M., 2009. Manufacture of non-resin wheat straw fiberboards. Ind. Crops Prod. 29, 437–445.
Hatakeyama, T., Hatakeyama, H., 2004. Thermal Properties of Green Polymers and Biocomposites. Kluwer Academic Publishers, Dordrecht.
Lalou, A., 1995. Mise Au Point D'un Procédé D'extraction Des Hémicelluloses À Partir D'un Substrat Végétal Ligno-cellulosique: Application Au Cas Des Coques De Tournesol. Ph.d. Thesis. INP, Toulouse, France.
Okuda, N., Hori, K., Sato, M., 2006. Chemical changes of kenaf core binderless boards during hot pressing. I: influence of the pressing temperature condition. J. Wood Sci. 52, 244–248.
Orliac, O., Rouilly, A., Silvestre, F., Rigal, L., 2002. Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. Polymer 43 (20), 5417–5425.
Orliac, O., Rouilly, A., Silvestre, F., Rigal, L., 2003. Effects of various plasticizers on the mechanical properties, water resistance and aging of thermo-moulded films made from sunflower proteins. Ind. Crops Prod. 18 (2), 91–100.

Rouilly, A., Orliac, O., Silvestre, F., Rigal, L., 2001. DSC study on the thermal properties of sunflower proteins according to their water content. Polymer 42 (26), 10111–10117.
Rouilly, A., Rigal, L., 2002. Agro-materials: a bibliographic review. J. Macromol. Sci. Polym. Rev. 42, 441–479.
Rouilly, A., Orliac, O., Silvestre, F., Rigal, L., 2003. Thermal denaturation of sunflower globulins in low moisture conditions. Thermochim. Acta 398 (1–2), 195–201.
Rouilly, A., Orliac, O., Silvestre, F., Rigal, L., 2006a. New natural injection-moldable composite material from sunflower oil cake. Bioresour. Technol. 97 (4), 553–561.
Rouilly, A., Mériaux, A., Geneau-Sbartaï, C., Silvestre, F., Rigal, L., 2006b. Film extrusion of sunflower protein isolate. Polym. Eng. Sci. 46 (11), 1635–1640.
Saadaoui, N., Rouilly, A., Fares, K., Rigal, L., 2013. Characterization of date palm lignocellulosic by-products and self-bonded composite materials obtained thereof. Mater. Des. 50, 302–308.
Schaffer, E.L., 1973. Effect of pyrolytic temperatures on the longitudinal strength of dry Douglas-fir. J. Test. Eval. 1 (4), 319–329.
Van Soest, P.J., Wine, R.H., 1967. Use of detergents in the analysis of fibrious feeds. IV. Determination of plant cell wall constituents. J. AOAC Int. 50, 50–55.
Van Soest, P.J., Wine, R.H., 1968. Determination of lignin and cellulose in acid detergent fiber with permanganate. J. AOAC Int. 51, 780–784.
Widyorini, R., Xu, J., Umemura, K., Kawai, S., 2005. Manufacture and properties of binderless particleboard from bagasse. I: effect of raw material type, storage methods, and manufacturing process. J. Wood Sci. 51, 648–654.