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100% BIOBASED PARTICLEBOARDS BASED ON NEW AGRICULTURAL WASTES

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Abstract
The agriculture in France offers exceptional wastes that can be recycled and turned into biomaterials. This paper presents a comparison between the properties of particleboards made from different agricultural wastes (hemp and flax shives, sunflower bark and rape straw) and those of classical particleboards based on wood. The use of these new agroresources as materials could increase the potential supplies for this application and could provide an additional source of income for farmers. The particleboards are made by thermocompression without synthetic binder addition. Thermal insulation, mechanical and hygroscopic properties of the panels are measured and discussed with regard to the used agricultural resources.

Keywords:
particleboards, hemp shives, flax shives, sunflower bark, rape straw

1 INTRODUCTION

The building sector, main consumer of particleboards, is now changing. New technical regulations aim to reduce 1) the emissions of greenhouse gases, 2) the energy consumption and 3) the resource depletion. The development of environment- and health- friendly materials is a priority and these new materials have to match new criteria such as better performance insulation, renewable material resources, recyclability and moderate cost.

Wood is traditionally the major resource for the particleboard manufacturing but today it is subject to strong competition between construction and energy industries. In this context, the development of particleboards based on agricultural wastes, such as annual plants stems or crop by-products, is an attractive alternative due to the abundance, availability and renewability of these new resources. Moreover, the production of these particleboards can preserve wood resources, which is desirable considering the increasing worldwide wood fiber shortage. Another advantage is that these residues can provide good insulating properties to materials [Wei 2015, Mati-Baouche 2014]. Many studies present agricultural residues as raw material for particleboards such as wheat straw, corn pith [Wang 2002], rice straw, coir fibers [Zhang 2014] and sunflower stalks [Khristova 1998, Binici 2014]. A trade-off between the availability and cheapness of these agricultural by-products versus particleboard mechanical properties allows using them in various industrial applications. High-density particleboards made from agricultural fibers have found applications in floor, wall and ceiling panels, furniture, cabinets, counter tops and desk tops. Limited information is available for low density application in insulation, packagings, or lightweight core materials [Wang 2002].

Currently, particleboard industry depends on synthetic adhesives to manufacture panels. Most of the particleboard formulations contain urea-formaldehyde (UF) or phenol formadehyde (PF) resins as synthetic binders, even though the formaldehyde emission is an environmental and health issue. Other synthetic binders based on diisocyanate were studied [Zhang 2014, Pan 2006]. They offer several benefits for particleboard manufacturing: high reactivity, high binding quality and no formaldehyde emission. However, the disadvantages of diisocyanate adhesives include their rather high price and the high toxicity of the uncured resin. Replacing the currently used synthetic adhesives with environmentally friendly and inexpensive ones is of great interest for the particleboard industry. The use of natural binders such as lignin [Privas 2013], tannins [Pizzi 2009], proteins [Pizzi 2006, El Hajj 2012, Lasko 2013], rice bran [Pan 2006] or polysaccharides [Sun 2013] have been already studied for the realization of 100% biobased particleboards.

Another possibility to obtain totally biobased particleboards is to make panels without any binder. The vegetal stems can be considered as natural composite because they are formed by the association of different tissues with different functions, morphological structures and chemical compositions (various proportions of cellulose, hemicellulose, lignin ...). The lignocellulosic compounds contained in the used agricultural wastes, extracted and activated by both humidity and heating during panels pressing, can act as binder. This method makes possible the manufacturing of ecological (no toxic synthetic binder derived from petroleum resources) and low cost particleboards.

Steam-injection treatment in addition to hot-pressing treatment can optimize particleboards properties [Xu 2004, Widyorini 2005]. According to these authors, the dimensional stability of the steam-pressed boards is due to the following factors: 1) degradation of hygroscopic hemicelluloses to free sugars, which may undergo reversion reactions to form less hygroscopic polysaccharides; 2) degradation of hemicelluloses to soluble sugars, which in turn form an adhesive during pressing; 3) relaxation of internal stresses in the plasticizing action of the steam. Moreover, the lignin contained in agroresources particles contributes also significantly to the adhesive effect by plasticization with water and heating [Bouajila 2005]. The effects of compression at high temperature and high raw particle water content can be compared to changes occurring during steam injection treatment because steam is generated from initial moisture during processing [Pintiaux 2015]. It was also reported that adhesive bonding between fibers in binderless panels can be improved by oxidative treatment which activates fiber surfaces [Halvarsson 2009]. Biological pre-treatment with enzymes such as laccase or peroxidase, which activates lignin present on particule surface, is another way to improve the self-bonding properties of the biocomponents used [Ghaffar 2014]. The major drawbacks of this type of particleboards include relatively long pressing times and low water absorption resistance of these panels. Nevertheless the binderless particleboards do not emit formaldehyde and can be produced at a considerable lower raw material cost than conventional wood-based boards.

In this study, four co-products of important crops in France have been identified. Two are co-products of crops dedicated to the production of fibers: hemp shives and flax shives. They are obtained by grinding stalks of hemp and flax. The remaining co-products, sunflower bark and rape straw, come from oilseed industry. The use of these agricultural residues for particleboard manufacturing will improve the agriculture's economy and give new market opportunities thanks to the diversification of supply sources. It will also create an additional source of income for farmers and the possibility to adjust the particleboard composition according to the locally available resources.

The objective of this research was to characterize the physicochemical properties of low-density particleboards made from hemp shives, flax shives, sunflower bark or rape straw, without binder addition. The particleboards were 100% biobased. The study was focused on characterization of thermal insulation, hygroscopic behavior and mechanical properties (MOR – modulus of rupture and MOE – modulus of elasticity) of these panels.

2 MATERIALS AND METHODS

2.1 Raw materials

Hemp shives

In France, mainly in the East of France, about 11 000 hectares of hemp (Cannabis Sativa) are cultivated each year and generate 7 tons of stems per hectare. This leads to approximately 56000 tons per year of hemp straw. Hemp shives represent the woody part of the stems. The agricultural sector of hemp shives valorization is already operational. They are used as animal litter and in many projects in the building sector. The hemp shives used for these experiments were supplied by La Chanvrière De l'Aube (LCDA, Kanabat).

Flax shives

Two kinds of flax are grown in France: the fiber flax (75 000 ha), produced for textile uses, and the oilseed flax (11 000 ha). Like hemp shives, flax shives represent the woody part of plant stems and its industrial sector is already operational (animal litter). The shives used in this study are by-products of fiber flax and came from Seine-Maritime, a department in the Northwest of France.

Sunflower bark

In France 700 000 hectares are cultivated for the sole purpose of obtaining sunflower oil. Currently the stems are left in the field after head harvesting and then are buried. Sunflower straw yield is about 2 tons per hectare. A sunflower stem is composed of pith in the center and bark in the periphery. The bark was the considered resource for this study. It came from the Southwest of France. The bark was separated from the pith but a small proportion of pith residues couldn't be eliminated from the sunflower bark used.

Rape straw

In France, 1 400 000 hectares of rape are cultivated for the oilseed industry. The stems are left in the field. The yield of straw is about 2 tons per hectare. The rape stem is composed of pith in the center and bark in the periphery with a much lower pith proportion than in sunflower stem. The pith cannot be separated from the bark in rape. The used rape straw particles came from the Northwest of France. They were obtained by cutting mill. The section mesh of the grid was 1 cm^2 in order to obtain the same particle size as the particles from other resources. The four different types of raw particles were dusted and sieved to obtain two homogeneous batches of different particle sizes: one with particles diameter between 0.5 and 2 mm and the other one between 2 and 5 mm. The moisture content of all the raw particles was lower than 10%. Figure 1 shows samples of each type of raw particle.

Fig. 1 : Sample of hemp shives (a), flax shives (b), sunflower bark (c) and rape straw (d).

2.2 Experimental

The conventional wood particleboards are made with urea-formaldehyde adhesive. Thus, the reference for the evaluation of the performances of the materials based on other agroresources was a wood particleboard shaped with urea formaldehyde adhesive (20% w/w) by our laboratory-scale process. To achieve this material, commercial wood chips were ground and sieved using the same process as rape straw.

Particleboards were constituted of three layers [Hiziroglu 2005]. A core layer of big particles (2-5 mm), which represents 2/3 of the panel mass, was inserted between two layers of small particles (0.5-2 mm), that represent each 1/6 of the total mass. Particleboards measured 150*150*15 mm^3 with a target density of 350 kg.m^{-3}. All boards were prepared with a hydraulic hot press (SCAMEX). The pressing module consisted of two heating plates of 300*300 mm. For the flax and hemp shives, sunflower bark and rape straw formulations, no binder was added. A high amount of water was sprayed onto the particles (80% of the initial particle mass) in order to generate steam which contributes to extract and plasticize the lignocellulosic compounds contained in the agroresources [Bouajila 2005, Pintiaux 2015]. These binderless particleboards were pressed at 170°C during 50 min (for water evaporation) while woodboards were pressed at 180°C during 5 min (for synthetic binder setting).

2.3 Particleboards characterization

Thermal conductivity

Thermal conductivity (λ) is the heat flow (W) crossing a homogeneous material of one meter thickness in a direction perpendicular to isothermal planes, induced by a difference of 1 K between both planes. Thermal conductivity is expressed in W.m^{-1}.K^{-1} and is a function of the material's mean temperature and its moisture content. The lower the thermal conductivity value is, the more the material is insulating. Heat flow-meter HFM 436 Lamda (Netzsch) was used for measuring the thermal conductivity. The sample size was 150 * 150 mm^2 and 15 mm thick. The measurements were performed in a steady state at 20°C with a temperature gradient of 20°C. The measurements were repeated at least twice for each material.

Sorption isotherms

The hygroscopic behavior is determined by the static gravimetric technique, based on the measurement of the sample mass over time in conditions of relative humidity and set temperature. The tests were performed at six different relative humidities (8, 33, 53, 73, 85, 93%) and at 23°C. The relative humidity of 8% was controlled by a saturated solution of KOH placed in a desiccator. The other five relative humidities were generated by a climatic chamber (Vötsch VC18). The sample size was 5*5*1.5 cm^3. Previously, samples were dehydrated by conditioning in a desiccator with P_2O_5 until stabilization of their mass. Similarly, the transition to the higher relative humidity is achieved when the mass is stable. The tests were repeated three times. The water sorption isotherms of the materials were obtained by plotting the mass of absorbed water at equilibrium, as a function of the relative humidity of the atmosphere.

Measurement of elasticity modulus

The bending tests induce a stress distribution having both a gradient and a stress distribution of tension and compression. These tests determine the deformability of a material on two supports with an application of the effort in the midway. The bending tests were carried out using an Instron 8801 testing machine equipped with a 3 points bending bench. A constant speed (5 mm/min) was applied on the central cylinder and the required force to deform the sample was measured using a 5 kN load cell. The specimens dimensions were L = 150, b = 30, e = 15 mm. The tests were repeated five times. The mechanical properties (MOR and MOE) were determined according to EN standards methods (EN 310: 1993).

The modulus of rupture (corresponding to maximal flexural strength) was determined by:

$$MOR = \frac{3FL'}{2be^2} \quad (1)$$

where F is the total load applied to the flexural strength (in N) and L' the distance in mm between the axes of the cylindrical support (100 mm).

The modulus of elasticity was determined on the linear part of the curve (between 10 and 40% of the maximum stress). It was given by:

$$MOE = \frac{L'(F_{40\%} - F_{10\%})}{4be^3(f_{40\%} - f_{10\%})} \quad (2)$$

where f is the deflection of the test piece (mm).

3 RESULTS AND DISCUSSION

3.1 Thermal conductivity

The thermal conductivity, denoted by λ, is a performance indicator in a thermal insulation material. Table 1 shows the thermal conductivity results for the five types of panels.

Tab. 1: Thermal conductivity of panels and bulk density of corresponding raw particules

Agroresource	λ at 20°C ($mW.m^{-1}.K^{-1}$)	Bulk density ($kg.m^{-3}$)
Hemp shives	64 ± 8	106 ± 7
Flax shives	68 ± 6	113 ± 3
Sunflower bark	70 ± 3	135 ± 3
Rape straw	67 ± 4	78 ± 1
Wood particles	74 ± 5	160 ± 5

Depending on the agroresource, the thermal conductivity varies from 64 to 74 $mW.m^{-1}.K^{-1}$. The thermal conductivity values obtained for all materials are low, indicating that the materials are thermal insulators. The panel based on wood particles which required the addition of urea-formaldehyde adhesive presents a thermal conductivity of the same order of magnitude as the other materials. The panels made of agricultural wastes without binder are as efficient as traditional wood particleboards in terms of thermal insulation.

Little variations of thermal conductivity are observed between the studied panels. Density is the major factor that influences the thermal conductivity of a material. However all the materials developed in this study have the same density (350 kg m^{-3}) whereas the bulk density of the raw particles differs (Table 1). The relationship between the conductivity of the panels and the bulk density of the plant material is difficult to establish because of the high standard deviations of the measured λ. The hemp shives, flax shives and rape straw show lower bulk densities than the sunflower bark and wood particles. The same trend is noticed for thermal conductivities. The values obtained for the sunflower bark based panels (70 $mW.m^{-1}.K^{-1}$) and the wood based ones (74 $mW.m^{-1}.K^{-1}$) are slightly higher than those obtained for the materials based on the hemp shives (64 $mW.m^{-1}.K^{-1}$), flax shives (68 $mW.m^{-1}.K^{-1}$) and rape straw (67 $mW.m^{-1}.K^{-1}$). The bulk density of the rape straw is the lowest unlike the thermal conductivity of the corresponding panel. Indeed the presence of pith in the rape straw is the cause of its low bulk density but the pith is more compressed than the bark during panel processing so the presence of pith doesn't affect the thermal conductivity.

The thermal conductivity of the materials depends on two parameters: panel density and raw material intrinsic porosity. The spaces between particles in the panel define the panel porosity and the spaces inside particles define the particle porosity. This double porosity gives insulation properties to the final material.

3.2 Water vapor sorption

Figure 2 shows the sorption isotherms of the five studied materials. The evolution of the sample mass was measured at six different relative humidities.

All the isotherms have a sigmoidal shape. This isotherm shape is observed when the interactions between the penetrant (water) and the polymer (particle backbone) are strong. The fixation mechanisms of the water molecules in the material network depend on the relative humidity:

- at low RH (<8%), the water molecules are adsorbed by the polar groups of the backbone. They cover the surface of the backbone in a single layer;
- then, when the relative humidities are between 8 and 75% the water molecules are adsorbed by a polymolecular way, covering the initial monolayer;
- finally, at high RH (> 75%) a capillary condensation occurs. The water molecules of the layers merge forming aggregates of water molecules.

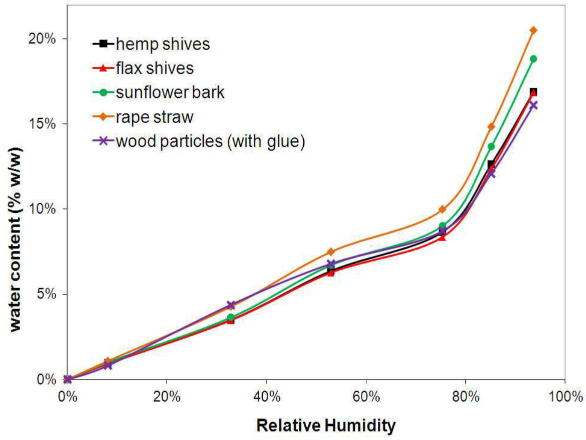

Fig. 2 : Sorption isotherms of the studied panels.

The behavior of the materials differs only at high relative humidities. Beyond 75% RH, the curves begin separating. At 93% RH, the panels based on the rape straw and the sunflower bark absorb a little more water (respectively 19% and 20.5% for the sunflower and the rape panels compared to between 16 and 17% for the three others panels). The observed variations are essentially due to the presence of pith in these two agroresources. The pith particles present in the sunflower bark are the residues of the sorting method applied on the sunflower milling in order to separate pith from bark. For the rape no method allows to separate the pith from the straw. Pictures taken with a scanning electron microscope (SEM) show an alveolar structure (Fig. 3a) for the pith and a vascular structure (Fig. 3b) for the other particles (bark and shives). Cell walls in alveolar structures are finer and thus present more surfaces for water absorption.

We also have to note that the water absorption of the wood particles based panel prepared with UF binder is close to that of the panels without synthetic binder. Thus in this case the synthetic binder does not protect the material from humidity.

3.3 Mechanical properties

The results of the bending tests are presented in Figure 4. The mechanical properties of the boards are commonly expressed with the use of the maximal flexural strength, generally called "modulus of rupture" in literature and noted MOR and the modulus of elasticity, noted MOE. These two parameters are correlated. However the MOE is more representative of the intrinsic material behavior while the MOR is the most commonly used parameter for description of particleboard characteristics. The MOE (Fig.4 (a)) and the MOR (Fig.4 (b)) of each material are compared.

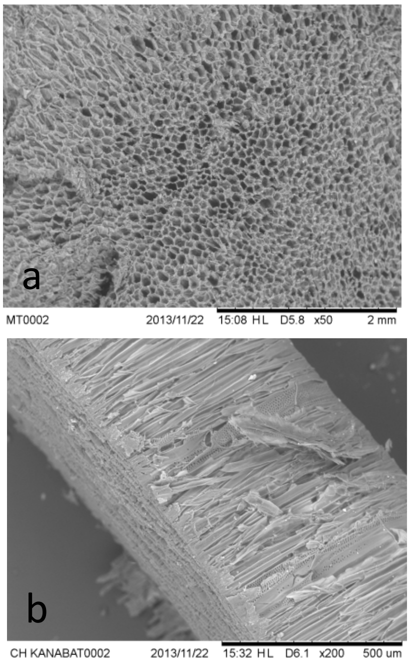

Fig. 3 : SEM pictures of sunflower pith (a) and hemp shives (b).

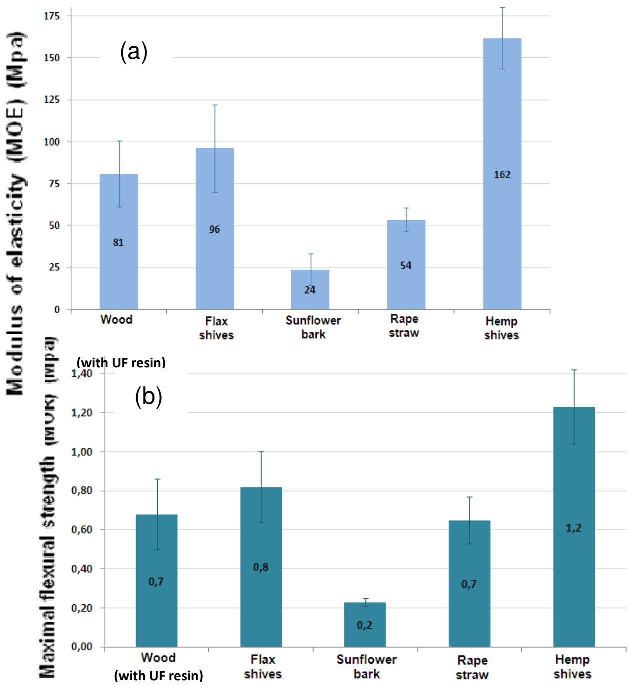

Fig. 4 : Modulus of elasticity (a) and maximal flexural strength (b) of the different panels in bending tests.

The MOE of the hemp shives based panel is the highest with 162 +/-19 MPa. The panels based on the flax shives and the wood particles follow with respectively 96 +/-26 MPa and 81 +/-20 MPa. The MOE of the rape straw and the sunflower bark based panels are lower with respectively 54 +/-7 MPa and 24 +/-10 MPa. The MOR follows the same evolution than that of the MOE for the different materials with results between 0.23 +/- 0.02 MPa for the sunflower bark panel and 1.2 +/- 0.2 MPa for the hemp shives panel. We should notice that two materials made of agricultural wastes without addition of any binder (the hemp and the flax panels) are more resistant in bending test than the reference panel based on wood particles with UF adhesive. These results demonstrate the feasibility of the particleboards based on agricultural wastes without binder and the efficiency of the thermocompression process that gives cohesion to the particleboards.

The fracture surfaces of the tested samples show that the fracture occurs at the interface between particles and not inside them, for all the materials. Thereby the resistance to breaking is strongly dependent of the adhesion performance between the particles. The adhesion depends itself on the contact surface between the particles and on the interactions between the molecules released from the raw particles during the thermocompression process with water. The surface of contact between particles varies according to the agroresource. Indeed large differences between the bulk densities of the studied raw materials are observed (Tab.1). All panels have the same density but the volume occupied by the matter differs in function of the matter bulk density, leading to variations in the contact surface. The higher the bulk density, the less the contact surface. The order of the bulk densities is as follows: Rape straw < hemp shives ≈ flax shives < sunflower bark < wood particles. The bending resistance of the panels follows the same order for the raw materials without pith: hemp panel > flax panel > wood panel. The superiority of the hemp panel resistance can be explained by the quantity of adhesive molecules released and/or by the rigidity of the raw particles. Indeed while the hemp shives, sunflower bark and wood particles have “sticks” shape, are rigid and have a thickness up to 2 mm, the flax and the rape particles look more like “flaxes”, are more flexible and have a thickness of less than 0.5 mm. The inferiority of the rape and the sunflower panel resistances can be explained by the presence of pith. The pith is a type of “foam”, it is a little rigid and probably contains fewer extractible compounds capable of causing adhesion. The high bulk density of the sunflower bark associated to the presence of pith can explain the very low MOR and MOE of the sunflower panel. The proportion of pith in the rape straw cannot be quantified because the pith is locked inside the straw. In spite of the pith, the very low bulk density of the rape straw explains the higher MOE of the rape panel than the sunflower panel ones. The flexibility of the rape straw particles (in form of “flaxes”) is probably the reason why the MOR of the rape panel is closer to the flax panel ones than its MOE is.

So the rigidity of the final panels at equivalent densities is the result of a combination between the bulk density of the agroresource, the rigidity of the particles and the adhesion performance of the particles between them. According to different authors [Widyorini 2005, Bouajila 2005], the molecules present in lignocellulosic raw material that can act as binder are hemicellulose and/or lignin. In future work we will seek to identify and quantify these components in our raw particles. From this study we will retain that particleboards made of agricultural wastes and more precisely of hemp shives and flax shives without synthetic binder addition present higher mechanical resistance than wood particleboards with UF resin made by the same process.

4 CONCLUSION

The objective of this study was to compare four agricultural resources through the study of the physicochemical properties of 100% biobased particleboards. The thermal conductivity measurements show that the developed materials have interesting insulation properties. The thermal performance is due to the natural porosity of these plant materials. Sorption measurements and mechanical properties show that the panels made of two of the four agroressources exhibit comparable or higher performances than that of the reference material prepared with wood particles and UF resin. Thus the agroressources studied here seem good candidates for replacing wood for the manufacture of low-density panels. Nevertheless hemp shives are clearly the best agricultural waste raw material for manufacturing of 100% biobased particleboards.

This study demonstrated the importance of the natural characteristics of plant materials (structure, porosity, composition) for the properties of the final panel. In further studies single layer panels based on different homogeneous particle sizes will be studied in order to attain a better understanding of the effects of particles dimensions. The relation between the composition of each agroresource and the adhesion capacity of these particles should also be investigated.

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