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ELABORATION AND PHYSICAL CHARACTERIZATION OF AN AGRO-MATERIAL BASED ON SUGAR BEET PULP AND POTATO STARCH.

H. Karaky[1, 2*], C. Maalouf[1], C. Bliard[2], G. Polidori[1].

[1] Research Group in Engineering Science, *GRESPI*, SFR Condorcet FR CNRS 3417, University of Reims Champagne Ardennes, Moulin de la Housse, BP 1039, 51687 Cedex 2, France.

[2] Institute of Molecular Chemistry in Reims, *ICMR-UMR 7312 CNRS*, University of Reims Champagne Ardennes, Moulin de la Housse, BP 1039, 51687 Cedex 2, France.

*Corresponding author; e-mail: hamze.karaky@etudiant.univ-reims.fr

Abstract
In this paper, we describe a potential route to improve the value of the sugar beet pulp in the manufacture of ecological lignocellulosic insulation concrete panels. These panels could on the one hand, reduce the energy consumption of buildings and therefore the associated CO_2 emissions, and on the other hand, could ensure a good thermal, hygrothermal and acoustic insulation of buildings. This study aims to describe the making and characterization of a 100% vegetable agro-material based on the sugar beet pulp and potato starch. Chemical analysis of the beet pulp was carried out using the sequential extraction method with different solvents (cyclohexane, ethane, water, soda, HCl ...), to determine the pulp components, its behavior, and its chemical and physical characteristics. Mixtures of the sugar beet pulp, potato starch and saturated lime water were prepared for different starch / pulp mass ratios, then the drying method was optimized since pulps can withhold large quantities of water and lead to important deformations of the panels. For this reason several drying methods were investigated: freeze drying, drying under vacuum, ventilated or static oven at 40 °C, or drying in a controlled humidity chamber.

Keywords: Sugar beet pulp, potato starch, chemical properties, hygrothermal properties.

1 INTRODUCTION

The building sector in France is responsible for 43% of energy consumption and 25% of total greenhouse gas emissions. In this context, we must contribute to sustainable development to meet the needs of the present without compromising the future. It seems interesting to offer an innovative building material that would link the domain of the building to the agro-resources available in our region.

Generally, the process of producing beet sugar generates large quantities of waste and by-products (Mathlouthi, 2005). One of these by-products is the sugar beet pulp (*Beta vulgaris var. saccharifera*), which is well grown in France (1,300,000 tons / year). Due to its high nutritional value and excellent palatability, the sugar beet pup is recognized as an excellent feed for livestock (Legrand, 2005). In recent years, beet pulp has become an important source of gelling pectin. The pectin is extracted from the pulp of the sugar beet from various extraction procedures (Hughes, 1998), (L. Phatak. K.C. Chang, 1988), (Hai-ming Chen, 2015) and used in food and cosmetics industries. It has also been used as a bio-adsorbent for the removal of heavy metals (V.M. Dronnet, 1997).

Various chemical and physical treatments have been carried out on sugar beet pulps, one treatment using cement in association with linseed oil was the best to reduce the potential of the pulps to absorb large quantities of water and swell (P. Monreal, 2011).

In this context, a potential route to improve the value of the sugar beet pulp would be to use it in the manufacture of ecological lignocellulosic concrete with a binder based on potato starch. This concrete could reduce the energy consumption of buildings and the associated CO_2 emissions, while ensuring a good thermal, hygrothermal and acoustic insulation of buildings.

Starch is the main carbohydrate reserve of higher plants. It represents a significant weight fraction in many agricultural raw materials such as cereals (30% to 70%), tubers (60% to 90%) and legumes (25% to 50%). Starch is composed of two polymers of different primary structure: Amylose, (linear molecule), and amylopectin (branched molecule). (Boursier, 2005).

The industrial outlets for starch are mainly the food industry through the drink industry, confectionery and bakeries industry, and the chemical industry which uses it in fermentation processes to produce bioethanol, surface treatments, formulation of adhesives, encapsulation of pharmaceutical products, cosmetics, paper stationery and biodegradable plastics (Wertz, 2011).

In this work, we describe a new agro-composite based on sugar beet pulp and a bio-sourced binder based on potato starch. The physico-chemical characterization of the sugar beet pulp and the fabrication of the agro-composite via different methods and techniques are presented.

2 MATERIALS

2.1 Sugar beet pulp

The sugar beet pulps were provided by Cristal Union factory (Pomacle route de Bazancourt, France).

Figure 48: beta vulgaris.

In the factory, clean beets emerge from the washhouse and fall into the root cutter, whose knives, driven by a large diameter disk, cut the roots into thin, rigid straps called *fresh pulp*. After extraction of the sugar, the pulps are generally pressed to 20-30% of dry matter, and are called *pressed pulp*. (Mathlouthi, 2005)
To ensure proper conservation in the lab fresh pulps were dehydrated by freeze drying immediately. In the industrial process pulps are dried to 18% humidity and agglomerated as 8-10 mm diameter dried pellets.
In this paper, fresh pulps were used to determine their physicochemical characteristics, and to develop the pulp / starch composite.

2.2 Potato starch

The pulps were blinded together using potato starch from ROQUETTE* (Lestrem France).
The starch is a mixture of two families of glucose homopolymers linked by alpha-glucosidic linkages (1-4) and 1-6): amylose and amylopectin.
The potato starch has higher polymerization degree than that of the other types of starch such as cereal starch, which provides good mechanical strength and high dynamic viscosity.

2.3 Water

The difficulty in designing of our agro-composite is often related to the existence of a competition of water between the pulp and the binder. To overcome this problem, the amount of water was decreased when mixing the two components, using the fresh pulp genuine water to swell the added dry native starch in an autoclave.

2.4 Lime water

A solution of $Ca(OH)_2$ from SIGMA ALDRICH, was used to create a basic medium to both reduce microbial attack and improve adhesion between the matrix and the fibers.

3 CHARACTERIZATION OF SUGAR BEET PULP

3.1 Aggregate morphology.

It is important to consider the morphology of the beet pulp, which can influence the adhesion of the latter to the matrix, as well as the mechanical properties of the elaborated composites. The morphology was studied by a microscopic view (x2) and an image analysis software.

Microscopic view.

A Vernox microscope with enlargements x2 and x4 allows to visualize the granules of the freeze-dried fresh pulp in the microscopic state. The microscope is equipped with a camera that allows to capture microscopic photos to be analyzed.

Image analysis.

The computer analysis program (ImageJ) allowed to process and analyze plain macroscopic images taken from the pulp of the beet, and determine the geometrical characteristics of individual centimeter size pulp chunks and model regular geometrical shapes such as rectangle, ellipse. The experimental device comprises (see figure 2):
• A 16 Mpx camera (Samsung) with 4GB storage.
• A high-resolution 2560 x 1440-pixel screen for processing black-and-white images on 256 levels of gray (0 is black and 255 is white).
• A PC using ImageJ software.
• A support that provides the camera with a plane parallel to the plane board on which pulp chunks were spread out.

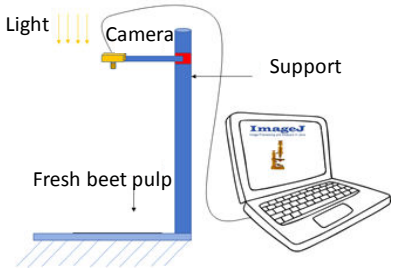

Figure 49: The device for capturing images.

More than 300 particles were dispersed in such a way that they don't touch each other. The resulting image were processed and analyzed using the software.

3.2 Beet pulp density

Knowledge of the bulk density of aggregates is important for the manufacture of composites in a volume assay. The density is generally defined as the mass of a unit volume of a material. In the case of a granular medium, the bulk density is obtained from the following expression:

$$\rho = m/V$$

With ρ: the bulk density of the aggregates in kg / m^3.
M: the mass of the aggregate in kg.
V: the volume of the aggregate in m^3.

The measurements were carried out using a 250-mL measuring glassware. The pulps were poured into the

container until the given volume, but without compacting in any case. The measured bulk density is then equal to:

ρ_{bulk} = *(total mass - mass of the container) / V Container.*

By processing the images taken from the pulps, the surface of each pulp was calculated by the software. This surface was considered uniform per height, so the thickness of each pulp was taken equal to 1 mm as measured with a sliding caliper, thereafter the calculated volume is equal to calculated surface x 1 mm. As having the mass of the aggregates and their estimated volumes, therefore the bulk density is calculated:

$$\rho_{bulk} = M / \Sigma_{i=1 \rightarrow n} (S_i \times 1mm).$$

This density does not represent the actual apparent density of individual dried pulp chunk, because the measured volume contains interstitial air. The dried pulp density is represented by the following formula:

$$\rho = M / (V - V_a).$$

With M: the mass of pulps.

V: the volume occupied by the sum of individual pulp chunks volume.

V_a: the volume of the air between individual pulp chunks.

A measurement of the apparent density of the pulp was carried out using < 250µm sand, which eliminates the voids surrounding the beet pulps in the container. A volumetric flask of volume 250 ml was filled together with sand and a given mass of dried pulp (M) of the pulp. The system was well packed manually by gently knocking the top of the flask with a soft wood stick, then using a vortex (Heidolph Top-Mix 94323) until the settled given volume. The system was then weighed by a balance with an accuracy of 10^{-3}g.

The volume of the aggregates equals: The volume of the flask (250cm3) - volume of sand.

The measured sand density was (1680.11 kg / m3):

$$(M_T - M) / \rho_{sand}.$$

With M: the mass of the pulps in kg.

M_T: the mass of the system in kg.

ρ_{sand}: the density of the sand.

Thus, the pulp volume becomes equal to 250- (MT-M / ρsand), consequently the pulps apparent density is equal to:

$$\rho_{real} = M / [250 \times 10\text{-}6\text{-} (MT\text{-}M / \rho_{sand})].$$

The actual mass does not represent the absolute density of the pulps matter, because the sand cannot penetrate the air cavities within each pulp chunk. Another measurement is made using a pycnometer. The pycnometric flask was filled with a given mass of dried pulp and half its volume with cyclohexane, which is a non-polar solvent and does not affect the pulp composition and mass (M). The system is kept under reflux (see Figure 4) for 6 x 10 min boiling then cooling cycles, during which air is released from the pulps voids and replaced by cyclohexane, and during the 6th cycle the system is kept under Argon atmosphere to avoid humidity. At ambient temperature (20 ° C) the flak was filled to the top and corked. The system was then weighed with a of 10^{-3} g accuracy. The absolute density is calculated per this formula:

$$\rho_{absolue} = M \times \rho_{cyclohexane} / M\text{-} (M_2\text{-}M_1).$$

With $\rho_{cyclohexane}$: the density of cyclohexane.

M: mass of dry aggregates.

M_1: the mass of the pycnometer (cyclohexane).

M_2: the mass of the pycnometer (cyclohexane + saturated aggregates).

Care was taken to avoid the accumulation of eventual residual humidity in the reflux system.

Each measurement was carried out at least 3 times to be considered representative.

3.3 Particle size analysis by sieving.

The pulp was sieved to analyze the particle size distribution.

The sieves sizes are shown in Table 1.

After sieving, the aggregates retained in each sieve are weighed and the cumulative masses are then calculated with their mass percentages. The granulometric curve is plotted by representing on the ordinate the cumulative mass percentages as a function of the sieves size in logarithmic scale.

3.4 Composition study

Several methods, techniques and chemical operations were used to analyze the chemical composition of the pulp.

Calcination

The calcination of the beet pulp was carried out using the protocol of Micard (V. Micard, 1996). Nine samples of 4 g were calcined at 550◦C for 8 hours and then one hour at 900◦ C in a pyrolysis oven to determine the residual mineral matter.

Sequential Extraction with solvents of increasing polarity and extracting media

The sequential extraction with solvents of increasing polarity allows to selectively extract the components of increasing polarity in the pulp. A hierarchical extraction was carried out on fresh lyophilized pulps, in such a way that the solvent would not affect the structure or the composition of the remaining of the pulp. The extractions carried out are shown in FIG. 3.

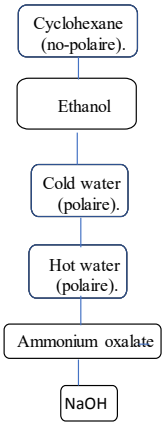

Figure 50:The sequential extraction with solvents.

5g samples of the lyophilized fresh beet pulp were weighed and placed in a filtering paper sack, placed in a Soxlet extractor and then subjected to a series of extractions with different solvents, under reflux, for a minimum of twenty cycles. The extract was concentrated by evaporation of the corresponding solvent using the Rotary Evaporator. The residue was analyzed by NMR to identify its molecular structure.

4 ELABORATION OF THE COMPOSITE

4.1 Composite Preparation Methods

Several drying and molding techniques were carried out since beet pulps and potato starch are both very hydrophilic.

The fresh pulps were mixed with dry potato starch powder, with a weight ratio S/P = 10%, and 5% by adding 2.66 g in order to have a saturated molar concentration equal to 36 mMol, then the mixture was placed in an autoclave and heated for 30 minutes to jellify the starch granules.

The molds used were in the form of a 20 x 10 x 5 cm^3 brick, with a piston on the upper part to compact the mix and provide a flat surface on each side for a volume of 1000 cm^3. Another mold was constructed to accelerate the permeation of the moisture from the sample through a series of 1mm bit holes. To keep the compaction level steady during the drying the piston was kept in a custom made clamp a system consisting in two long screws holding two pieces of wood pressing on to the piston. A layer of the cardboard was placed between the piston and the mixture to diffuse the water vapor released from the sample (see. Fig 4 &5).

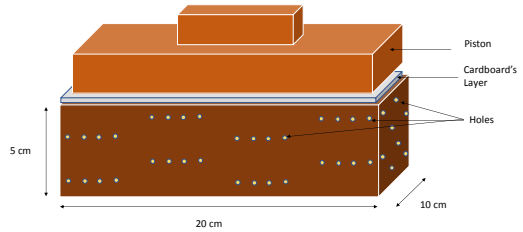

Figure 51: presentation of wooden molds and piston used.

Once the preparation is finished, the mixture is poured into wooden molds. The molds were dried by various technics:

1. Drying in the oven at 100°C.
2. Drying in the vacuum oven at 40°C.
3. Freeze drying.
4. Ventilated oven at 40°C.

Figure 52: Photos of wooden molds used to make composite.

4.2 Moisture Buffering Value (MBV)

For this test, the edges and the back-sides of samples were sealed to obtain a one-dimensional moisture flow. Samples were stabilized at 23°C and 50% RH in a climatic chamber and weighted until they reach equilibrium. After stabilization, the protocol defines cyclic step-changes in relative humidity between high (75%) and low (33%) values for 8 and 16 h, respectively. The moisture buffering value (MBV) was calculated according to this equation (Rode, 2005):

$$MBV = \Delta m / A \times (HR_{high} - HR_{low}).$$

A (m^2) is the area of the sample that is in contact with air, HR_{high} and HR_{low} respectively represent high relative humidity (75% RH) and low relative humidity (33% RH) and Δm represents the change in mass during the absorption / desorption phase (g).

5 RESULTS AND DISCUSSION

5.1 Aggregate morphology.

The pulps have a cavernous shape, an irregular and rough surface which allows to provide a good adhesion with the matrix (see. Fig. 6).

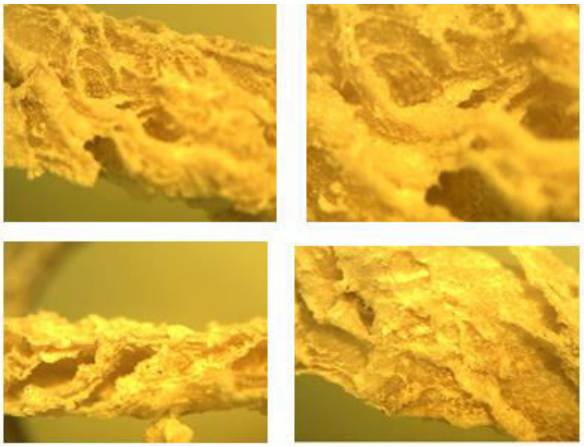

Figure 53:Microscopic photos of pulp x2.

The cavities filled with air in the pulps can reduce the thermal conductivity of the composite to be elaborated and in addition reduce its apparent density, which result in a lightweight composite with good thermal insulation.

In macroscopic view, the image software allowed to calculate the surfaces and perimeters of each pulp, the lengths and widths of the smallest rectangle containing the aggregate, as well as the major and minor axis of the ellipse assimilated to each particle. The surface has an average of 33 mm^2, and a perimeter 39.07 mm. The surfaces and the perimeters of the geometric shapes were calculated, as well as the quadratic error of each parameter (FIG. 7&8). The error on the surface of the rectangle is large, because the pulps have angles. The best calculated model for the pulp shape was the elliptical form.

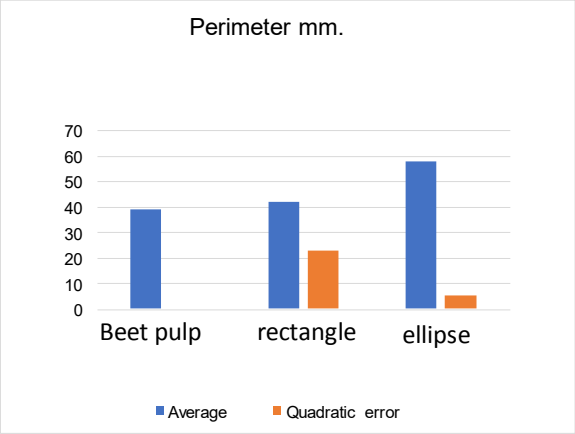

Figure 54: Perimeter of pulp chunks and the geometric forms.

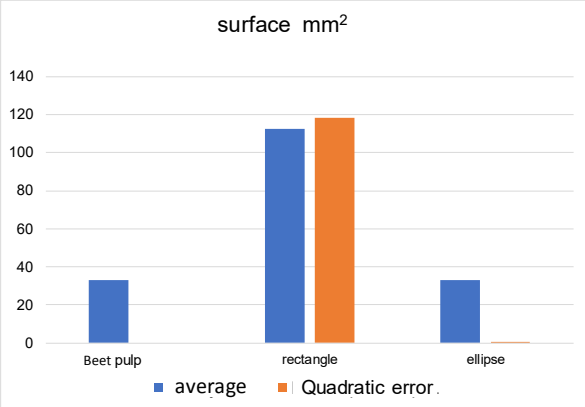

Figure 55: surface and perimeter of Pulp chunks, and geometric forms in mm2.

Figure 56:The photo of the pulp chunks.

5.2 Beet pulp density

Measurements of the density of the fresh sugar beet pulp were calculated in Kg/m^3. (Table 1).

Table 24: Measurements of fresh pulp density

$\rho_{apparent}$	$\rho_{apparent}$ (image analysis)	ρ_{real}	$\rho_{absolute}$
134.22	427.84	558.41	1230.74

5.3 Particle size analysis by sieving.

The results presented in figure 8 and 9, show that the particle size is continuous, that no granulometric fraction is missing. The largest fraction is between 2 and 4 mm with 55% of the beet particles. The beet pulp has a shape larger than that of the hemp, which offers a larger perimeter and has a better adhesion with the matrix.

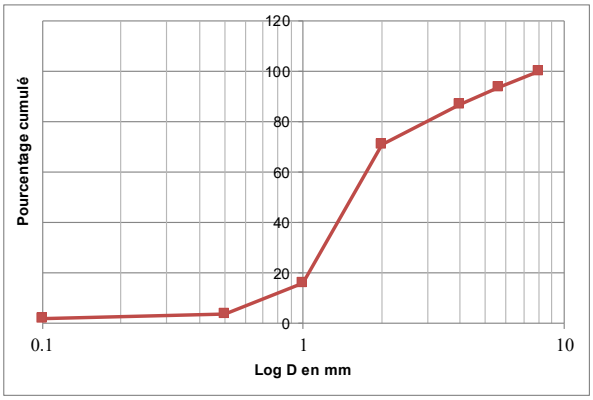

Figure 57: The granulometric curve.

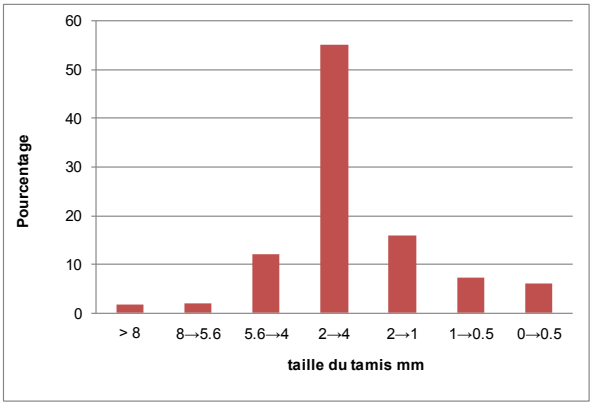

Figure 58: The distribution of the aggregates on the various sieves.

In Table 2 the results of the pulp calcination are compared to the ones obtained with other fiber sources.

Table 25: The results of the calcination of the beet pulp.

	Sugar beet pulp	Nettle fibers	Hemp shiv
Organic materials %	93	90	98
Mineral materials %	7	10	2

The beet root is growing in the ground, a mineral-rich medium (Ca, Na ...) while hemp stems are aerial parts of the plant and is less rich in mineral components. Beet

Pulps like nettle fibers have the potential to absorb more minerals from the ground and diffuse them throughout the plant.

5.4 Composition study

The extraction of the pulp from beet with various solvents (see. Fig 10), allowed to extract lipids, fats, certain sugars, pectin, hemicelluloses and part of lignin. The pulp contains 20% of sugars which correlates well with the bibliography (Mathlouthi, 2005).

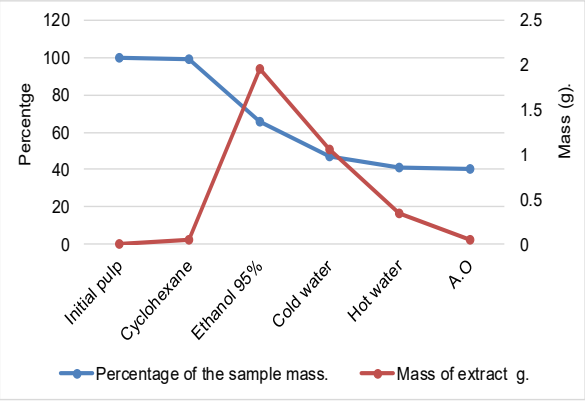

Figure 59: The percentage of the mass of fresh pulp during the various extraction stages.

5.5 Composite results.

Morphology

During the drying of the samples, microscopic cracks appear on the composite surface due to extensive shrinkage. As both the beet pulp and starch are highly hydrophilic, water gradients inside and anisotropy of the drying within the composite sample probably cause

irregular shrinkage of the composite. Large dimensional variations were observed after drying in the oven at 100 °C (see Fig 14), the sample underwent a (33%) retraction, which caused large millimeter size cracks. Drying under vacuum at 40 °C(see FIG 13) resulted in much more regular shapes, the composite retracted, there were no macroscopic cracks observed and the surface was more flat. The same result was obtained with the lyophilized specimen, in addition the color of the composite was whiter.
The pulp / starch composites dried under vacuum and in the ventilated oven are rigid and light, but still present important dimensional deformations and irregular surfaces.

Figure 60: Photos of the dried samples in (left) ventilated furnace with pierced mold, (right):

Figure 61:The photos of the dried samples in (right) ventilated oven with mold not drilled 20x10x5 cm, (left) oven 100 C with 20x20x5 cm.

Therefore, drying with the ventilated oven at 50 ° C. and with the vacuum oven at 40 ° C. Seemed to be the best choice, since the lyophilize costs more and is not practical for the manufacture of composites.

Composite density

The calculated apparent bulk densities are presented in the following table in Kg/m^3. (see. Table 3).

Table 26: Densities composites with different drying methods in kg/m3.

ρ Vacuum oven	ρ freezer drier	ρ ventilated oven
425.40	362.27	424.27

The composite was freeze dried without keeping the compaction of the mixture, therefore it represents a larger volume and hence a smaller bulk density. The dried composite obtained with a mold with walls perforated by a series of 1mm holes has a smaller density than the one obtained in an unperforated mold, since, after drying, the composite releases the water more regularly, and consequently retracts less, this implies a Larger volume ($\rho_{apparent}$ =420.48 Kg/m^3).

Composite MBV

Two formulations were made to measure their preliminary MBV. The formulations had a beet pulp / potato starch ratio equal 10%, 20% respectively, and a thickness equal 2, 4 cm respectively. The results presented in figure 15 clearly show that the composite beet pulp / potato starch is an excellent regulator of the relative humidity of the environment (MBV> 2 g/m^{-2}. %RH^{-1}). The difference between the MBV values is due to the difference of thicknesses between each sample. It must be noted that the samples had dimensional deformations during the testing of the MBV.

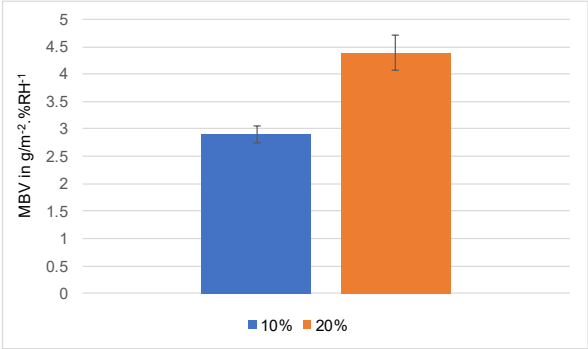

Figure 62: The MBV values of two formulations 10 and 20%.

6 CONCLUSIONS

The pulp of sugar beet has a cavernous surface, with air cavities, leading to a light composite and good thermal insulation for applications in the field of building. Its rough surface improves the adhesion of fibers with the binder based on potato starch.

The pulp granulates can be assimilated to ellipsoids. They have an average surface area of 33 mm^2. The corners in the aggregates converge to a large perimeter (39 mm) which allows the binder to spread well over the aggregates.

The most important part of the aggregates was obtained between the mesh screens 2 and 4 mm.

The sugar beet pulp and the potato starch are very hydrophilic, so during the drying of the samples, the water gradients cause cycles of swelling and shrinkage because of cracks on the superficial surface of the composites.
Drying manually compacted samples in 20x10x5 cm^3 molds, in a ventilated oven or under vacuum at 40 °C, resulted in a light and rigid composite without any cracks but with dimensional deformations due to the shrinkage of pulp and starch.

Beet pulp/ potato starch is an excellent regulator of relative humidity.

Physicochemical treatments such as linseed oil, will be carried out to attenuate the water sensitivity of beet pulps, to prevent swelling and shrinkage of the composite during drying. The fight against microbial attack is an important aspect of our work.

The next step relates to the mechanical characteristics of the composite, such as resistance to compression, tension and bending, as well as its hygrothermal characteristics, such as MBV, sorption isotherm, thermal conductivity, vapor permeability.

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