USE OF CELLULOSE FIBERS FROM HEMP CORE IN FIBER-CEMENT PRODUCTION. EFFECT ON FLOCCULATION, RETENTION, DRAINAGE AND PRODUCT PROPERTIES

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ABSTRACT

The aim of this paper is to study the feasibility of using cellulose fibers obtained from an agricultural waste, hemp core *(Cannabis Sativa L.)*, through different new environmental friendly cooking processes for fiber-cement production. The physical and mechanical properties of the fiber reinforced concrete, which depend on the nature and morphology of the fibers, matrix properties and the interactions between them, must be kept between the limits required for its application. Therefore, the morphology of the fibers and how its use affects the flocculation, retention and drainage processes in the fiber-cement manufacture, and the mechanical and physical properties of the fiber-cement product have been studied.

The use of pulp obtained by means of the hemp core cooking in ethanolamine at 60% concentration at 180 ºC during 90 minutes resulted in the highest solids retention and the best mechanical properties among the studied hemp core pulps.

Keywords:

Fiber-cement; Pulping conditions; Hemp core; Agricultural wastes; Flocculation.

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1. INTRODUCTION

The use of agricultural wastes as reinforcement of composite materials is one of the most important targets in today's materials research (Ahankari et al., 2011; Ashori and Nourbakhsh, 2010; Rabi et al., 2009). The present research is concerned with the use of the wastes from the industrial hemp, *Cannabis Sativa L.*, to obtain useful cellulose fibers to manufacture fiber-cement products for roofing. Industrial hemp is one of the crops having a highest yield among those of temperate zones, being at the same time one of and less intensive ones. It is highly self-compatible what means that it requires crop rotation. Similar to other lignocellulosic fibers, hemp is biodegradable and environmentally friendly (Mutjé et al., 2007). This, together with its high strength and durability and low density, explains the increase in the use of hemp fibers in the manufacture of composite materials (Carver, 1941; Hayo, 2004). The most common material obtained from hemp is its fibers, especially the coarse ones which are extremely strong and durable. As the most valuable fibers are located in the phloem, they must often be separated from the xylem material ("hemp core"), which is considered a waste in the hemp industry (Sedan et al., 2008; Troëdec et al., 2011).

The use of cellulose fibers as reinforcing agents in composite building materials offers many advantages over glass fibers, such as the possibility to manufacture products with low density and good biodegradability (Joshi et al., 2004; Li et al., 2006; Mwaikambo and Ansell, 2003). However, cellulose fibers also have some disadvantages, for instance, they present low modulus of elasticity, high moisture absorption, they decompose in alkaline environments and are susceptible to biological attack, and they have variable mechanical and physical properties (Swamy, 1990). Some of these disadvantages could be overcome by using fibers

from hemp core with a higher durability than the traditional cellulose fibers from pine and with a specific tensile strength of 0.750 GPa, and specific modulus of elasticity of 60 GPa. These properties make hemp fibers a candidate material with potential as reinforcement fiber (Li et al., 2004).

Many authors have studied the use of hemp fibers as reinforcement for building materials based on cement (Dalmay et al., 2010; Placet, 2009; Sedan et al., 2008; Troëdec et al., 2011). However, the use of hemp core fibers for this purpose has not been yet reported. This research aims to contribute to fill this lack of knowledge.

In general, cell wall polymers and their matrices determine the mechanical and physical properties of natural fibers. In view of this, a number of researchers have reported the chemical composition of natural cellulose fibers and some of them have recommended improving the natural cellulose fiber properties by modifying the cell wall polymers (Golbabaie, 2006; Wielage et al., 2003; Young, 1997). Furthermore, the incorporation of cellulose fibers in a polymer or mineral matrix can involve an interface incompatibility between fibers and matrix, which may be overcome through the chemical pretreatment of fibers, with the aim of modifying either the chemical nature of the fiber surface or the surface properties (e.g., electrostatic charge, conformation of adsorbed polymers). The effect of this treatment is probably a modification of the interactions between the mineral matrix and fibers, which increases the efficiency with which stress is transferred from the matrix to the fiber (Negro et al., 2005; Ouajai and Shanks, 2005).

The process through which fibers are obtained from natural sources determines the properties of the fibers surface and, therefore, it affects the interface matrix-fiber surface. To study the effect of this stage on the final product two different

treatments, namely a semi-chemical pulping process and a chemical pulping process, both at different cooking conditions have been applied to obtain the cellulose fibers from the hemp core.

First, a comprehensive study of the morphology of the fibers was carried out (Jarabo et al., 2012); then, the effect of using these fibers on the fiber-cement manufacture process was determined through the study of the flocculation, retention and drainage of the fiber-cement suspensions prepared with the different fibers. Finally, the effect of using the obtained fibers on the physical and mechanical properties of fiber-cement probes was determined.

2. MATERIALS AND METHODS

2.1. Materials

The raw material used for this study was the hemp core, waste from the culture of *Cannabis Sativa L*. grown in Spain and supply by the LEPAMAP Group.

The hemp fiber is constituted by 43% cellulose, 16% hemicellulose and 8% lignin. Hemp straw is a sub-product in the process to obtain hemp strands from stalk of the plant. This stalk can be separated, or decorticated, into two main components: fibers and core fibers. The initial length of these core fibers lies between 5 and 10 mm (Mutjé et al., 2007; Barberà et al., 2011).

Tables 1 and 2 show the cooking conditions used to obtain hemp pulp by a semi-chemical process and a chemical (organosolv) process employing NaOH and ethanolamine as solvents, respectively and the yield obtained in each case.

The ethanolamine PA-ACS solution was supplied as a commercial product by Panreac.

Organosolv pulping were performed in a 25-L stainless steel rotator digester with a heat exchanger system and pressure control. The pulping conditions were

maintained constant as follows: liquor to solid ratio: 6:1 and digester pressure 5–7 bars. Selected experimental conditions were: solvent concentration, temperature and pulping time.

The pulping with NaOH was carried out in the same digester but with a solution of NaOH having 1.4 g/L of anthraquinone as a catalyzer of the chemical reaction.

The cooked pulps were defibred in a hydrapulper and screened through a Somerville vibratory flat screen with 0.15 mm slot size; the screened pulp was washed, pressed, crumbled and stored at 4 ºC.

The conditions chosen in these tables are the result best from a previous study carried out to optimize these cooking processes for hemp core fibers (Barberà et al., 2011).

Refined unbleached pine Kraft pulps (35 ºSR) were used as reference since this pulp is commonly used to provide cellulose fibers in the manufacture of fiber-cement through the Hatschek process.

A Portland cement (type II / AV 42.5) containing 12% fly ash was used for the probes. It is a fine powder with a wide distribution of particle sizes, being the 80% of the particles in the interval from 2 µm to 50 µm.

Microsilica was also used to manufacture of the test probes. The type of microsilica employed was composed of ultra-thin amorphous spheres of SiO_2 with a particle size around 0.5 µm containing small amounts of crystalline quartz (less than 0.5%) as impurities.

The flocculant employed to study the behavior of fiber-cement suspensions and to prepare the fiber-cement probes was an anionic polyacrylamide (APAM) commonly used in the industrial Hatschek process (Negro et al., 2006) with a molecular weight of $7.4 \cdot 10^6$ g/mol and a charge density of 13.4%. The flocculant

was dissolved in distilled water to prepare solutions of APAM with a concentration of 1.5 g/L.

The composition of the prepared fiber–reinforced cement slurries is summarized in Table 3. Five fiber-cement slurries were prepared, being the source of cellulose the only difference between them: M1 was prepared using pulp P1 as a source of cellulose fibers, M2 was prepared with P2, M3 with P3, M4 with P4 and the pine Kraft pulp was used to prepare the fiber-cement slurry MR, which was used as a reference.

Although in air curing fiber-cements synthetic fibers (PVA) are normally used due to their capacity to withstand degradation due to environmental conditions, in the present research, no synthetic fibers were used to prepare the probes so as to avoid interferences in the determination of the fiber-cement properties that can be ascribed to the use of cellulose fibers.

2.2. Methods

2.2.1. Density of the fibers

The fiber density was measured by using a gas pycnometer (Multipycnometer). Helium was the gas employed because its small atomic radius enables it to enter into crevices and pores approaching one Angstrom (10^{-10}m).

Before the measurement, the samples were dried in an oven at 60 ºC for 24 h. The volume of each sample was determined five times applying Equations 1-2 to the pressure and volume values measured:

$$Vp\ (cm^3) = V_c - V_r\ ((P_1/P_2) - 1) \quad [1]$$

$$\text{Density}\ (g/cm^3) = W/V_p \quad [2]$$

Where: V_p is the sample volume, V_c is the volume of the sample holder (16.163 cm^3), V_r is the reference volume (8.068 cm^3), P_1 is the pressure measurement after pressurizing the reference volume (PSI), P_2 is the pressure measurement after including V_c (PSI) and the W is the dry weight of sample.

2.2.2. Morphological characterization of fibers

The morphological characterization of the fibers was carried out by using a fiber and pulp morphological analyzer, Morfi, V7.9.13.E (Techpap, France).

This characterization is based on an image analysis system, consisting of a diode that emits unpolarized light and a microcamera. Imaging is performed until the equipment counts 5000 fibers, which is the optimum value for subsequent statistical analysis, which is performed using a computer software. The images were analyzed using a specific program to determine different parameters of the fibers and pulps: fibers, arithmetic length, length weighted in length, average length weighted in area, average width, coarseness, number of microfibrills and fines length.

Fines are generated mainly during the beating stage when the pulps were defibred. There are differentiated from the fibers by their dimensions. The equipment was programmed to consider fiber length values between 100 and 10000 μm, width between 5 and 75 μm, fines length below 100 μm and width below 5 μm (Jarabo, et al., 2012; Moral et al., 2010).

The samples for morphological characterization were prepared by adding 1 g of dry fibers to 600 mL of water and homogenizing the suspension in a laboratory disintegrator ENJO- 692. The characterization was done in duplicates.

2.2.3. Flocculation of fiber-cement suspension

A commercial focused beam reflectance measurement probe (FBRM) M500L, manufactured by Mettler Toledo, USA, was employed to monitor the flocculation process and to determine the properties of the flocs. The FBRM device measures the chord length distribution on real time over a wide interval of solid concentrations. A laser beam is generated by a diode and focused on a focal point in the plane next to the external surface of the probe window, which is inside the suspension. The focal point describes a circular path at a constant speed of 2000 m/s due to the rotation of the focusing lens. When a particle intercepts the focal point path, the reflected light reaches the detector through the probe and the optical fiber. The detector receives light pulses. A chord length of the intercepting particle is determined as the product of the time duration of the light pulse by the linear speed of the focal point movement. Thousands of particles can be measured each second. In this way, a chord length distribution is obtained from the light pulses received during the measurement time (set in 5 s in this case). Each distribution is a function of the size and shape of particles in suspension. The evolution of the chord size distribution reflects the aggregation or dispersion of particles. Many statistical parameters can be calculated from the distribution to follow its evolution, e.g., the mean chord size and the total number of counts measured per second (Blanco et al., 2002; Hubbe, 2007; Kerekes and Schell, 1992; Negro et al., 2007).

In the present study, the flocculation trials were carried out immersing the probe in a 400 mL fiber–cement suspension, prepared with water saturated in $Ca(OH)_2$, and stirred at 800 rpm. After 10 min, stirring intensity was reduced to 400 rpm. 100 ppm of APAM was added 5 min later, to induce flocculation, and the evolution of the flocs was studied at 400 rpm for 4 min. After that, the stirring intensity was

increased to 800 rpm to break down the flocs formed (deflocculation) for 2 min and, finally, stirring intensity was reduced again to 400 rpm to induce the reflocculation of the system (Jarabo et al., 2010).

2.2.4. Retention and drainage of fiber-cement suspension

The equipment used for measuring the retention and drainage was a vacuum drainage tester (VDT). It has two jars separated by a barrier: the upper jar keeps the fiber–cement suspensions stirred up to the addition of the flocculant dosage. The second jar contains a mesh in the bottom to carry out the dewatering of the suspension and it is connected to a vacuum pump and to a probe in which the filtrate is stored and weighted in real time. The final volume of filtrate is measured. In a typical trial, 400 mL of fiber–cement suspension, prepared with water saturated in $Ca(OH)_2$, were stirred at 600 rpm during 6 min in the upper jar. Then, stirring intensity was decreased to 300 rpm and, 5 min later 100 ppm of APAM were added. After 15 s of contact time between flocculant and mixture, the stirring was stopped, the barrier was removed and the suspension was drained to the second jar in which an 18 mesh wire was placed. The suspension was drained under vacuum (0.2 atm) through the filter and a computerized balance recorded the mass of drained water over time. The drainage curve was analyzed in order to obtain the drainage rate for the different flocculants. Retention and cake humidity were determined gravimetrically after the analysis of the formed cake (Fuente et al., 2010).

2.2.5. Preparation of fiber-cement probes

Fiber reinforced cement probes were prepared in the laboratory through a slurry vacuum de-watering technique. The matrix materials were added and dispersed in $Ca(OH)_2$ saturated water with a solids concentration of 20%. The slurry was

transferred to an evacuable 200 x 200 mm^2 casting box and a vacuum (~60 KPa gauge) was exerted until excess water was removed and a solid cake was formed. The pad was pressed at 3.2 MPa, so that the rest of the water was removed. After pressing, the plates were sealed in a plastic bag at room temperature. Three pads were prepared in this way for each formulation. After two days; the pads were removed from the bags and placed in water. Twenty-six days later, the pads were removed from the water and four 200 x 50 mm^2 flexural test specimens were diamond wet-sawn from each pad. Eight pads were prepared to provide sufficient specimens for the determination of mechanical properties and four pads were prepared for the determination of physicals properties.

2.2.6. Mechanical properties of fiber-cement probes

Mechanical tests were performed in the universal testing machine Emic DL-30,000 equipped with 1 KN load cell. A four point bending configuration was employed in the determination of modulus of rupture (*MOR*), limit of proportionality (*LOP*), modulus of elasticity (*MOE*) and specific energy (*SE*) of the specimens following calculations specified in Equations 3-6.

A span of 100 mm and a deflection rate of 0.5 mm/min were used in the bending test (Savastano et al., 2000). Test data were digitally recorded and reduced using automatic data collection and processing facilities. Eight flexural specimens were tested for each composite formulation.

$$MOR\ (MPa) = (L_{MAX} / (b \cdot h^2)) \cdot (S_{down} - S_{up}) \quad [3]$$

$$LOP\ (MPa) = (L_{LOP} / (b \cdot h^2)) \cdot (Sd_{own} - S_{up}) \quad [4]$$

$$MOE\ (kPa) = tg\ \alpha\ (L_{MAX} / \delta) \cdot (S_{down} - S_{up})^3 / (b \cdot h^3) \quad [5]$$

$$SE\ (kJ/m^2) = Absorbed\ energy / (b \cdot h) \quad [6]$$

Where L_{MAX} is the maximum stress, L_{LOP} is the stress at the upper point of the linear portion of the stress-strain curve, ($S_{down} - S_{up}$) is the major span, b and h are the specimen width and thickness respectively, tgα is the initial slope of the stress-strain curve and δ is the deflection of the composite.

The absorbed energy is the area under the stress-strain curve to the point corresponding to a reduction in carrying capacity to the maximum stress (Tonoli et al., 2010).

The mechanical properties of the probes were measured 28 days after the construction of the sheet.

2.2.7. Physical properties of fiber-cement suspension

Water absorption, bulk density and porosity values at 28 days were obtained from the tested flexural specimens following the procedures specified in ASTM C 948-81 (ASTM C 948-81).

Four specimens were used to determine these properties.

3. RESULTS

3.1. Morphological characterization of pulps

The results of the morphological characterization of hemp core fibers and pulps obtained by both semi-chemical and organosolv process are shown in Table 4. Kraft pine pulp was also characterized for comparison.

It is noticeable that the length of the fibers and fines obtained from the hemp core is much shorter than that of the pine fibers. Therefore, the number the fibers per gram on hemp pulps are higher than that on pine pulp. This could improve their dispersion in the matrix.

P1 and P3, presented lower values of fibers arithmetic length, length weighted in length, average width and coarseness along which lower fines length than those for the pulps P2 and P4. This can be due to the more aggressive cooking conditions used to obtain pulps P1 and P3, which increase the probability of fibers degradation during the process.

Regarding the effect of the process (semi-chemical or organosolv), the organosolv pulps (P3 and P4) had slightly shorter fibers and with lower coarseness than the semi-chemical pulps.

NaOH used in semi-chemical process is well-known to remove amorphous materials, such as hemicelluloses and pectins, from the surface of hemp fibers (Troëdec et al., 2009); this reduces the coarseness of the fibers, which is lower for P1. However, the coarseness of the organosolv fibers is even lower than that of P1. Organosolv process consists of dissolving lignin, extractives, hemicelluloses and pectin in ethanolamine but in such way that they can be used to obtain valuable chemical products. The efficiency of the organosolv process in removing these compounds from the fiber surface is high even when soft cooking conditions is applied.

The percentage of microfibrills is similar in pulps P2, P3 and PR and higher than in the two other pulps. This could increase the interaction among the fibers and the matrix and, consequently, improve the properties of the fiber-cement.

It has been demonstrated that a fiber analyzer (MorFi) can gain quick and reliable results (Bartl and Pico, 2009; Pico and Bartl, 2011).

3.2. Flocculation of fiber-cement mixtures

Fig. 1 shows the evolution of the mean chord size of particles and flocs in cement suspensions.

After 600 s of stirring at 400 rpm, the value of the mean chord size was constant. 900 s after starting the trial, the addition of flocculant to the suspension caused a fast increase in the mean chord size due to the aggregation of particles to form larger flocs. A maximum value of this parameter was reached at ten or fifteen seconds and then it started decreasing with different rate depending on the stability and strength of the flocs in such hydrodynamic conditions (evolution of flocs). When the stirring was increased to 800 rpm, part of the remaining flocs was broken, thus decreasing the mean chord size (deflocculation). The reflocculation ability of the system is shown by the increase in the mean chord size when the stirring was decreased to 400 rpm again.

It can be observed that the largest maximum mean chord size was reached in the MR suspension. This value, however, is not to different from those reached in suspensions M2 and M4 and the evolution of the mean chord size in these two cases indicates that the flocs formed were more stable than those formed from MR. Moreover, after the deflocculation and reflocculation stages, the mean chord size in M2 and M4 remained larger than in the case of the MR suspension. The maximum mean chord size values reached in M1 and M3 were lower than those reached in the other cases, but after the evolution stage the values obtained were slightly lower than those in MR.

The results indicate that the flocculation process and floc properties are more affected by the cooking conditions than by the cooking reagent used, and that the use of soft cooking conditions favored the formation of larger and more stable flocs when APAM was added to the fiber-cement pulp.

3.3. Retention and drainage of fiber-cement suspensions

Fig. 2 shows the drainage curves of the fiber-cement suspensions considered in this research.

Drainage took place in two steps: first, the suspension was filtrated and a cake was formed with a fast water removal, which corresponds to the first part of the drainage curves (linear part with a high slope); secondly, the cake was compressed and thickened and water removal rate decreases towards zero. During the first stage, only the water between flocs was removed, while part of the water inside the flocs was removed during the compression stage. Most of the solids loss with the filtrate takes place during the first stage while the second stage determines the final humidity and the formation properties of the cake. Drainage time can be obtained as the time required to reduce the drainage curve slope to zero.

There are notable differences between the drainage curves of the fiber-cement suspensions containing hemp core fibers and the one for MR. The initial drainage rate was notably affected by the intensity of cooking conditions of the pulp and it took the lowest values for M1 and M3 suspensions. There was no appreciable compression stage in the drainage curves of M2 and M4. The final weight of recovered filtrate was also higher in these cases and in the case of M1.

Table 5 shows that the solids retention was very low when the cake was formed from suspensions M2 and M4, taking its maximum value in the case of suspensions M1 and M3. These values, together with the drainage curves, indicate that most of the mineral solids, were lost with the water drained during the first drainage stage in the case of M2 and M4 with only some of the mineral solids remaining in the cake and the majority of fibers, whose high hygroscopicity explains the high humidity of the cakes formed in these two cases.

These differences can be explained from the chord size distribution of particles in suspension after the flocculation process (Fig. 3) and from the floc properties.

Fig. 3 shows that the chord size distributions of flocculated suspensions M2, M4 and MR were similar, and that the flocs formed were much larger than in the case of M1 and M3. Therefore, the spaces among the flocs are also larger and water can drain very fast. This explains the high initial drainage rate observed by M2, M4 and MR. However, the flocs formed from MR are much weaker than those formed from M2 and M4 and, therefore, they were broken, deformed and compressed by the vacuum forces causing the spaces among the flocs to diminish, which implies a decrease in the drainage rate (compression stage) and a higher retention of mineral solids.

The chord size distributions of M1 and M3 show that there were numerous small flocs and particles present in these suspensions. The spaces among the flocs were, therefore, smaller, what contributes to an increase in the retention of solids, but causes a decrease in the drainage rate. The humidity of the cake decreases when retention increases, and this is due to the higher mineral content of the cake (water absorbed by the mineral particles is much less than water absorbed by the fibers).

3.4. Mechanical and physical properties of the probes

Fig. 4 shows the stress-strain curves of the specimens at 28 days. The curve obtained with M3 resulted to be the most similar one to that obtained with MR is, although it is worth noticing that the maximum elongation before the failure of the probe was higher in the case of M3, while the maximum stress was lower. This mechanical behavior, high elongation and stress reached, and the large area under the curves can be associated with a good array of the fibers and solid particles into

the composite. The other probes were more rigid than M3 and MR, as shown by their low strain values.

Therefore, the probes prepared from M3 may be the ones with the best mechanical properties among the fiber-cement probes prepared with hemp core fibers.

Fig. 5 shows the results of the mechanical properties: modulus of rupture, limit of proportionality, elastic modulus and specific energy of the probes of fiber-cement made of hemp pulps with the two applied processes.

These figures show that, among the mixtures with hemp core fibers, M3 yielded the probes with the highest modulus of rupture, limit of proportionality and specific energy, although these values were lower than the values obtained with the reference MR. It is worth pointing out that the fibers used in the preparation of MR were refined fibers. Refining increases the presence of microfibrills and degrade fiber surface, which enhances the interaction among fibers and matrix.

Pine fibers and fines lengths are notably greater than those of hemp core fibers and these parameters also have a significant effect on the mechanical properties of the probes. Fines do not contribute significantly to fiber–cement strength but act more as filler and, in most cases, influence negatively the drainage of the suspension (Tonoli et al., 2009).

Furthermore, Fig. 5 shows that the elastic modulus of the probes prepared from M4 were the highest, even higher than the values obtained for the reference probes. This is due to the high value of tgα.

A larger number of fibers per gram could be associated with a better distribution of fibers in the matrix and thus fewer loads bearing capability. However, this was not the case when hemp core fiber was used. Despite on the lower number of fibers per gram, the use of pine improved the mechanical properties of the final product

and it may be attributed to both the superior fiber quality and the beating process, which produces fibrillation and consequently improved fiber matrix bonding (Savastano et al., 2000).

Despite of the large differences observed in mechanical properties, the physical properties (water absorption, bulk density and porosity of the probes) are similar (Fig. 6) between the composites considered. Therefore, they do not explain the effect of the use of fibers from hemp core on the mechanical properties. These effects are probably related to the interaction between the fibers and the matrix.

One of the drawbacks of the use of cellulose in fiber-cement is its ability to absorb moisture from the environment. Due to the hydroxyl and oxygen-containing groups, moisture is retained through hydrogen bonding. This causes a swelling and dimensional change of the fibers affecting the composites.

The water absorption of the probes prepared from M3 and M4 was slightly lower than those from M1, M2 and MR. The main reason for moisture absorption is attributed to hemicelluloses (Golbabaie, 2006), whose removal through the organosolv process was more efficient than those for semi-chemical and Kraft processes.

The results obtained with hemp core and pine fibers fall within the limits of physical and mechanical properties according to the Chilean Standard and the Decreto Nº 21341-MEIC.

4. DISCUSSION

The effect of using hemp core fibers in the Hatschek process for fiber-cement suspensions and probes is closely related to the fibers morphology and to the flocculation process, which themselves depend on the cooking conditions. The addition of APAM to the fiber-cement suspensions prepared with the pulps

obtained at hard cooking conditions (M1 and M3) induced the formation of small flocs (Fig. 1 and 3), which slowed down the drainage process (Fig. 2) and an enhancement of the compression stage due to the lower strength of the flocs. This increased the retention of solids (Table 5), part of them by means of their interaction with the fiber and the other part through blocking the small voids among flocs. This indicates a better performance in mechanical properties of M1 and M3 fiber-cement probes comparing with the fiber-cement suspensions M2 and M4; however, the drainage is affected.

Albeit a high retention solid was obtained for both M1 and M3, the mechanical properties of the probes obtained from M3 were better than those for M1. This can be explained considering the fibers morphology. Although the main effect on the process is related to the cooking conditions, the pulping process affects the percentage of microfibrills, the length, and the coarseness; therefore, it affects the interaction between fibers and matrix and the dispersion of fibers in the matrix. The increase in the number of microfibrills, and the slight decrease in the length and coarseness increase the surface area, which is available for chemical bonding between the fibers and the matrix. This leads to a more homogeneous surface made of cellulose, which will enhance the adhesion between the fibers and the matrix making this fiber-cement probe be better formed.

In addition, there are other mechanisms and phenomena that may explain the higher modulus of rupture of M3 probes induced by the increase in the microfibrills:

- At the level of the microfibrils, the longitudinal tension in the fibers could involve not only tensional stresses, but also torsion effects as well. This

torsion stress, which initially impedes the tension, could subside or relax as a result of the repeated stress.

- It is also probable that rearrangements and re-orientations of the cellulose microfibrils and/or changes in the crystalline fraction occur in the fibers (Placet, 2009).

5. CONCLUSIONS

The novelty of this paper lies in the use of agricultural waste materials, particularly, industrial hemp straw (*Cannabis Sativa L.*), as eco-friendly and renewable source of cellulose fibers in the manufacture of fiber-cement through new environmentally friendly cooking processes.

The cooking process and cooking conditions used to prepare the pulp from the hemp core determined the feasibility of the use of the pulps obtained as source of fibers for fiber-cement manufacture. Cooking the hemp core in ethanolamine at 60% at 180 ºC during 90 minutes was the optimal pulping process among the options studied for hemp core pulping. These conditions provided the best mechanical properties for hemp core fiber fiber-cement probes. However, a more thorough optimization of the pulping process and pulp conditioning (e.g. refining) based on the effect of fibers on the fiber-cement mechanical properties would be required.

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REFERENCES

Ahankari, S.S., Mohanty, A.K., Misra, M., 2011. Mechanical behaviour of agro-residue reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV) green composites: comparison with traditional polypropylene composites. Compos. Sci. Technol. 71, 653–657.

Ashori, A., Nourbakhsh, A., 2010. Bio-based composites from waste agricultural residues, Waste Manage. 30, 680–684.

ASTM (American Society for Testing and Materials) 2000. ASTM C948-81, Standard test method for dry and wet bulk density, water absorption, and apparent porosity of thin sections of glass-fiber reinforced concrete, West Conshohocken, USA.

Barberà, L., Pèlach, M.A., Pérez, I., Puig, J., Mutjé, P., 2011. Upgrading of hemp core for papermaking purposes by means of organosolv process. Ind. Crops Prod. 34, 865– 872.

Bartl A., Pico D., 2009. Characterization of Short Fibers, Chem. Eng. Transactions. 17, 741-746.

Blanco, A., Fuente, E., Negro, C., Tijero., J, 2002. Flocculation monitoring: focused beam reflectance measurement as a measurement tool. Can. J. Chem. Eng. 80, 734–40.

Carver, G.W., 1941. Auto Body Made of Plastics Resists Denting Under Hard Blows. Popular Mechanics Magazine. 76 (6).

Cornejo, D.N., Jason, L.H. (Eds), Building Materials: Properties, Performance and Applications, Chapter 9, pp. 299-342.

Dalmay, P., Smith, A., Chotard, T., Sahay-Turner, P., Gloaguen, V., Krausz, P., 2010. Properties of cellulosic fibre reinforced plaster: influence of hemp or flax fibres on the properties of set gypsum. J. Mater. Sci. 45, 793–803.

Decreto Nº 21341-MEIC, 1992. Láminas planas de fibrocemento. Especificaciones. NCR 193:1992. La Gaceta Nº 127.

Fuente, E., Jarabo, R., Moral, A., Blanco, A., Izquierdo, L., Negro, C., 2010. Effect of sepiolite on retention and drainage of suspensions of fiber–reinforced cement. Constr. Build. Mater. 24, 2117-2123.

Golbabaie, M., 2006. Applications of Biocomposites in Building Industry. Department of Plant Agriculture. University of Guelph.

Hayo, M.G. van der Werf, 2004. Life Cycle Analysis of field production of fibre hemp, the effect of production practices on environmental impacts, Euphytica, 13–23.

Hubbe, M.A., 2007. Flocculation and redispersion of cellulosic fiber suspensions: a review of effects of hydrodynamic shear and polyelectrolytes. BioResour. 2 (2), 296-331.

Jarabo, R., Fuente, E., Moral, A., Blanco, A., Izquierdo, L., Negro, C., 2010. Effect of sepiolite on the flocculation of suspensions of fibre-reinforced cement. Cem. Concr. Res. 40, 1524–1530.

Jarabo, R., Monte, M.C., Blanco, A., Negro, C., Tijero, J., 2012. Characterisation of agricultural residues used as a source of fibres for fibre-cement production. Ind. Crops Prod. 36, 14– 21.

Joshi, S.V., Drzal, L.T., Mohanty, A.K., Arora, S., 2004. Are natural fibres composites environmentally superior to glass fibres reinforced composites?. Compos. Part A. 35, 371–376.

Kerekes, R.J., Schell, C.J., 1992. Characterization of fiber flocculation regimes by a crowding factor. J. Pulp paper Sci. 18(1), 32-38.

Li, Z., Wang, L., Wang, X., 2004. Compressive and Flexural Properties of Hemp Fiber Reinforced Concrete. Fibers Polym. 5 (3), 187-197.

Li, Z., Wang, X., Wang, L., 2006. Properties of hemp reinforced concrete composites. Compos. Part A. 37, 497–505.

Moral, A., Monte, M.C., Cabeza, E., Blanco, A., 2010. Morphological characterization of pulps to control paper properties. Cell. Chem. Technol. 44 (10), 473-480.

Mwaikambo, L.Y., Ansell, M.P., 2003. Hemp fibres reinforced cashew nut shell liquid composites. Compos. Sci. Technol. 63, 1297–1305.

Mutjé, P., López, A., Vallejos, M.E., López, J.P., Vilaseca, F., 2007. Full exploitation of Cannabis sativa as reinforcement/filler of thermoplastic composite materials. Compos. Part A. 38, 369–377.

Negro, C., Sánchez, L.M., Fuente, E., Blanco, A., 2005. Effects of flocculants and sizing agents on bending strength of fiber cement composites. Cem. Concr. Res. 35, 2104 – 2109.

Negro, C., Blanco, A., San Pío, I., Tijero, J., 2006. Methodology for flocculant selection in fiber cement manufacture. Cem. Concr. Res. 28, 90-96.

Negro, C., Blanco, A., San Pío, I., Tijero, J., 2007. In-line flocculation monitoring in a Hatschek machine for fiber–cement manufacture. Compos. Part A – Appl. Sci. Manuf. 38, 26–33.

Norma Chilena, 2006. Fibrocemento - Planchas - Parte 1: Planchas planas - Requisitos. NCh186/1-2003.

Ouajai, S., Shanks, R. A., 2005. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. Polym. Degrad. Stab. 89, 327–335.

Pico D., Bartl A., 2011. Image analysis for simultaneous determination of spherical and fibrous particles. Chem. Eng. Transactions. 24, 619-624.

Placet, V., 2009. Characterization of the thermo-mechanical behaviour of Hemp fibres intended for the manufacturing of high performance composites. Compos. Part A. 40, 1111–1118.

Rabi, J.A., Santos, S.F., Tonoli, G.H.D., Savastano, H.J., 2009. Agricultural wastes as building materials: properties, performance and applications, in:

Savastano, J.H., Warden, P.G., Coutts, R.S.P., 2000. Brazilian waste Fibres as reinforcement for cement-based composites. Cem. Concr. Compos. 22, 379-384.

Sedan, D., Pagnoux, C., Smith, A., Chotard, T., 2008. Mechanical properties of hemp fibre reinforced cement: Influence of the fibre/matrix interaction. J. Eur. Ceram. Soc. 28, 183–192.

Swamy, R.N., 1990. Vegetable fibre reinforced cement composites - a false dream or a potential reality? In: Sobral, H.S. (Ed), Proceedings, 2nd International

Symposium on Vegetable Plants and their Fibres as Building Materials. Rilem Proceedings 7. Chapman and Hall, London, 3-8.

Tonoli G.H.D., Fuente E., Monte C., Savastano Jr. H., Rocco Lahr F.A, Blanco A., 2009. Effect of fibre morphology on flocculation of fibre–cement suspensions. Cem. Concr. Res. 39, 1017–1022.

Tonoli, G.H.D., Santos, S.F., Joaquim, A.P., Savastano, J. H., 2010. Effect of accelerated carbonation on cementitious roofing tiles reinforced with lignocellulosic fibre. Constr. Build. Mat. 24, 193–201.

Troëdec, M., Peyratout, C.S., Smith, A., Chotard, T., 2009. Influence of various chemical treatments on the interactions between hemp fibres and a lime matrix. J. Europ. Ceramic Soc. 29, 1861–1868.

Troëdec, M., Rachini, A., Peyratout, C., Rossignol, S., Max, E., Kaftan, O., Fery, A., Smith, A., 2011. Influence of chemical treatments on adhesion properties of hemp fibres. J. Colloid Interface Sci. 356, 303–310.

Young, R.A., 1997. Utilization of natural fibers: characterization, modification and applications. In: Leao, A.L., Carvalho, F.X., Frollini, E., (Eds), Lignocellulosic-plastics composites. Brasil: USP.

Wielage, B., Lampke, T., Utschick, H., Soergel, F., 2003. Processing of natural fibre reinforced polymers and the resulting dynamic-mechanical properties. J. Mater. Process. Technol. 139, 140–6.

Table 1

Table 1. Cooking conditions of hemp core using semi-chemical process.

Pulps	*T (ºC)*	*Time (min.)*	*NaOH (%)*	*Yield (%)*
P1	180	90	25	49.1
P2	140	30	15	68.8

Table 2

Table 2. Cooking conditions of hemp core using organosolv (chemical) process.

Pulps	*T (ºC)*	*Time (min.)*	*Ethanolamine (%)*	*Yield (%)*
P3	180	90	60	28.2
P4	155	30	40	53.6

Table 3. Composition of the fiber–cement suspensions studied.

Raw materials	*Dry weight (%)*
Cellulose	5%
ASTM II cement	91%
Microsilica	4%

Table 4

Table 4. Morphological characterization of pulps.

PROCESS	Semi-chemical		Organosolv		Kraft
PULPS	**P1**	**P2**	**P3**	**P4**	**PR**
FIBERS					
Fibers (10^6/g)	32.0	61.2	45.2	28.5	10.8
Arithm length (µm)	356	389	345	352	456
Length weighted in length (µm)	539	574	459	497	1129
Average length weighted in area (µm^2)	583	617	472	526	1344
Average width (µm)	19.2	29.0	24.0	27.3	25.5
Coarseness (mg/m)	0.08	0.40	0.06	0.10	0.18
Microfibrills (%)	1.38	1.66	1.68	1.48	1.62
FINES					
Fines number	13149	30470	8947	15474	49192
Fines length (%)	25.4	32.7	19.5	25.1	40.3

Table 5

Table 5. Retention and humidity of fiber-cement suspensions.

Fiber-cement suspension	*Source of fibers*	*Retention (%)*	*Humidity (%)*
M1	P1	66.5 ± 1.87	46.8 ± 2.05
M2	P2	29.1 ± 4.90	63.7 ± 0.80
M3	P3	64.7 ± 1.57	50.5 ± 0.90
M4	P4	18.5 ± 5.70	64.7 ± 1.33
MR	Unbleached Kraft pine	57.3 ± 2.30	57.9 ± 1.20

Figure 1

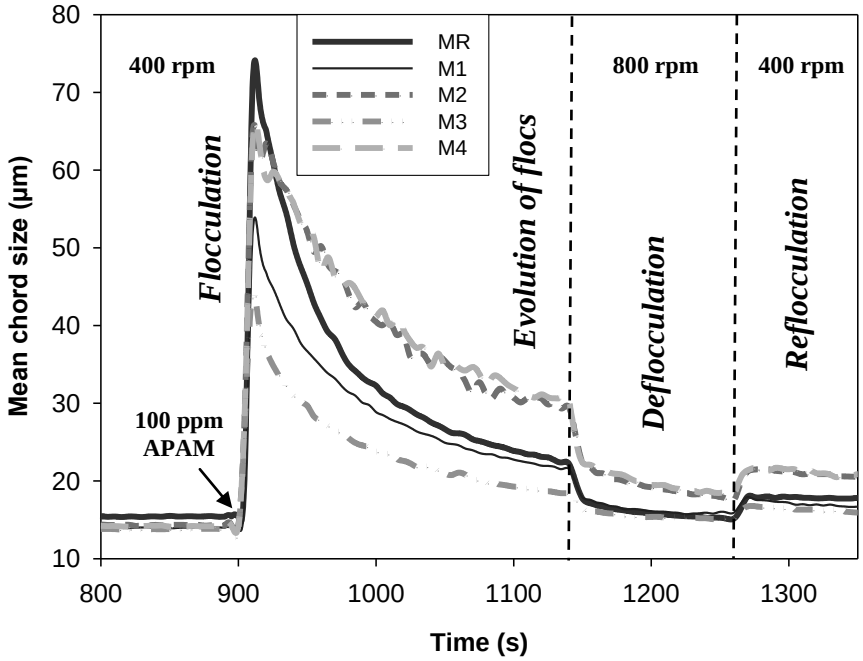


Fig. 1. Evolution of the mean chord size during the flocculation, deflocculation and reflocculation of the fiber-cement suspensions.

Figure 2

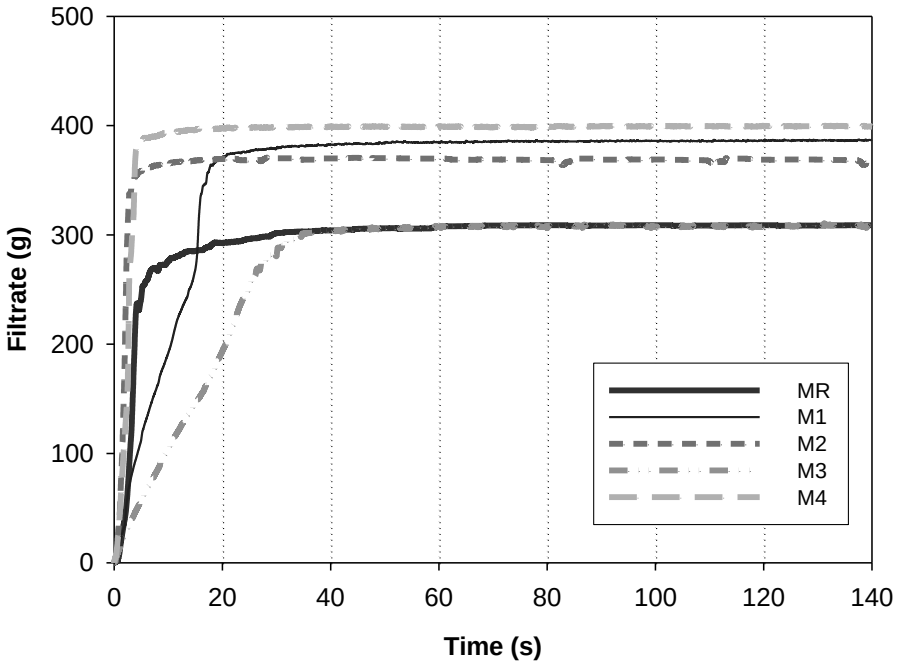


Fig. 2. Drainage curves of the fiber-cement suspensions.

Figure 3

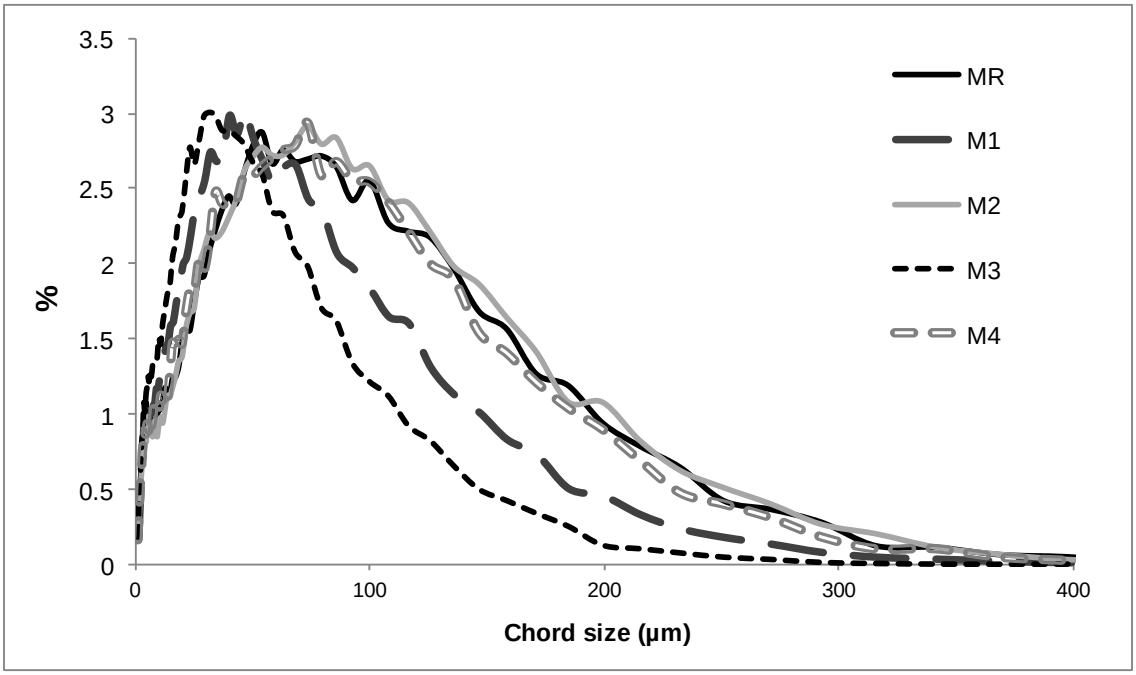


Fig. 3. Chord lengths distribution of the fiber-cement suspensions after the addition of the APAM.

Figure 4

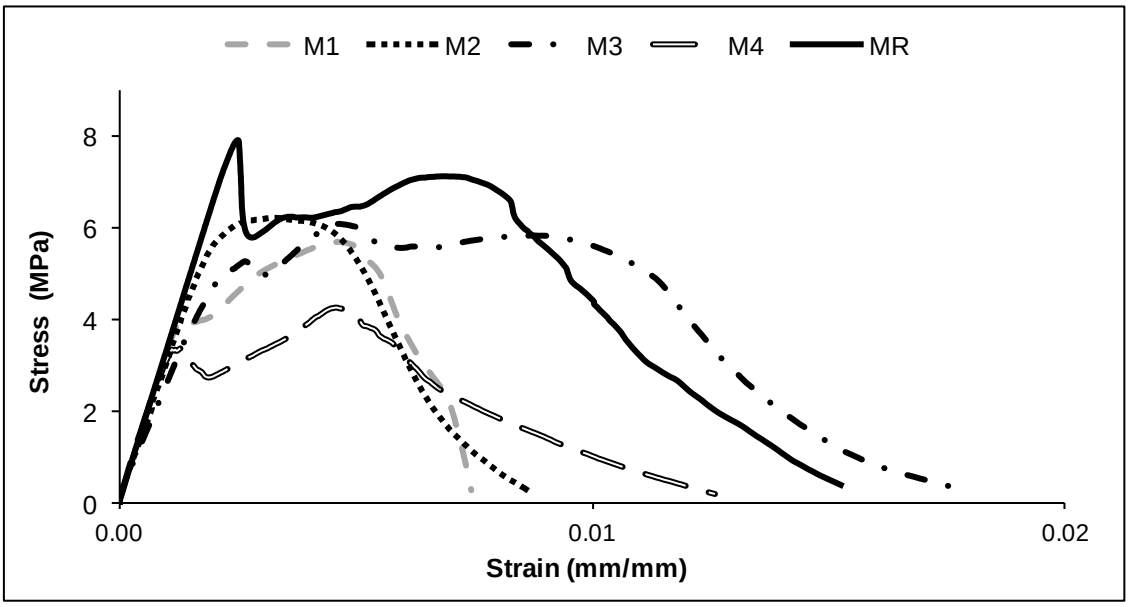


Fig. 4. Stress-Strain curves of the composite reinforced with hemp.

Figure 5

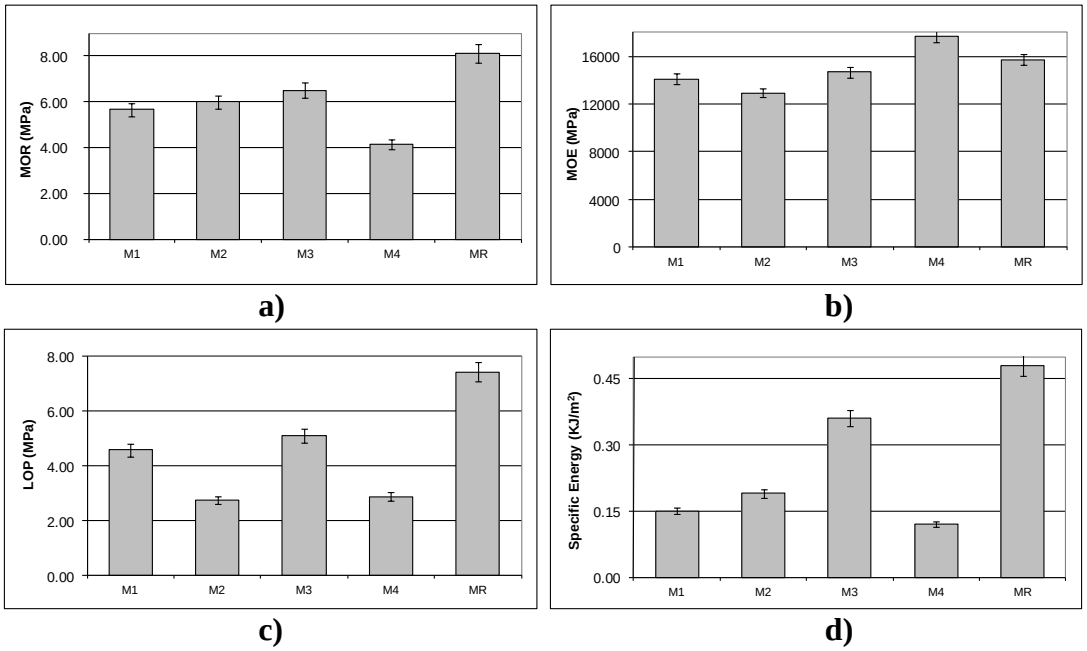
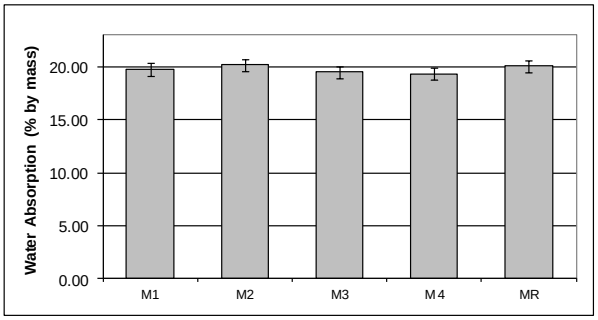
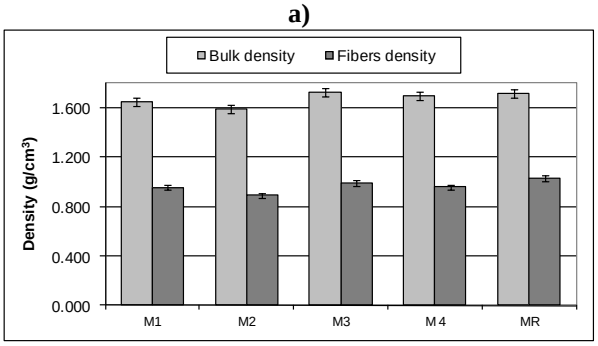


Fig. 5. Effect of the hemp on the mechanical properties: a) modulus of rupture, b) modulus of elasticity, c) limit of proportionality and d) specific energy.

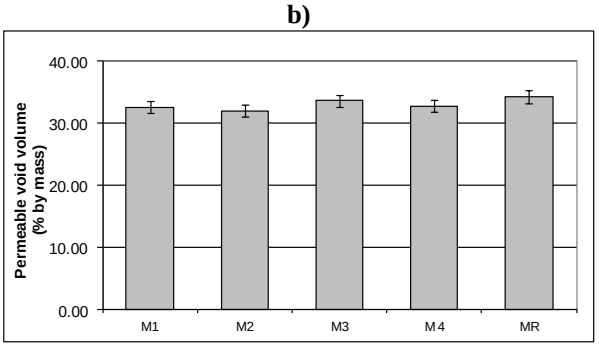
Figure 6



a)



b)



c)

Fig. 6. Effect of the hemp on the physical properties: a) water absorption, b) bulk density and c) permeable void volume.