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Original Research Article

Evaluation of pre-treatment efficiency on sugarcane bagasse fibers for the production of cement composites

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ABSTRACT

In the present study, physical, chemical, morphological, crystallographic analysis of the non-treated and treated (100 °C during 30 min) sugarcane bagasse fibers were examined. Sugarcane bagasse fibers pre-treatment effect on the Portland cement hydration was monitored by inhibition tests and differential scanning calorimetry in the first 24 h. Furthermore, 28 days age physical-mechanical properties of cement composite materials with sugarcane bagasse fibers were also evaluated. Inhibition index of treated sugarcane bagasse fibers was 5.9%, while for the non-treated sugarcane bagasse fibers it was 67.3%. Cement composites containing treated sugarcane bagasse fibers showed lower physical properties (water absorption and thickness swelling) than the cement composites reinforced with non-treated sugarcane bagasse fibers ($p < 0.05$). Likewise, mechanical properties under flexure (modulus of rupture, MOR, and modulus of elasticity, MOE) of cement composites with treated sugarcane bagasse fibers showed higher values than the cement composites with non-treated sugarcane bagasse fibers ($p < 0.05$), thus proving the pre-treatment efficiency on sugarcane bagasse fibers for cement composites.

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1. Introduction

Brazil is the world's largest producer of sugarcane, with an annual crop around 658.7 million tons [1]. Thus, a large amount of residual sugarcane bagasse by-products remains after crushing. The main compounds of sugarcane bagasse are cellulose, hemicellulose and lignin, which can be applied as a reinforcement in cement composites [2].

The major target of using vegetable fibers reinforcement in cement composites is to impart additional energy absorbing capability, by turning a brittle material into a pseudo ductile one. Vegetable fibers in cement composites can also contribute to reduce crack propagation [3]. Moreover, according to Mármol et al. [4], the use of the vegetable waste to produce cement composites is an interesting strategy to handle the environmental and social-economic issues generated by these by-products.

However, the use of sugarcane bagasse fibers as reinforcement for cement composites introduces challenges for manufacturing. The Portland cement (PC) hydration processes is more complex when the vegetable fibers are used as reinforcement of the composites.

PC is basically composed of tricalcium silicate (C_3S, alite), dicalcium silicate (C_2S, belite), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF ferrite). After the water addition, C_3A reacts with water forming an aluminate rich gel. Thereafter, the gel reacts with the sulfate rich solution forming the ettringite (AFt), with a small rod-like structure [5]. Subsequently, C_3S and C_2S take part in a hydration reaction to form calcium silicate hydrate (C–S–H) gel and calcium hydroxide [$Ca(OH)_2$]. These phases are considered as the principal contributors to the mechanical properties of PC composites [5].

Nevertheless, all of these hydration reactions of the PC can be disturbed by the addition of sugarcane bagasse fibers, causing a deceleration of the setting time. Particularly, extractives and impurities may affect the PC hydration reaction equilibrium, resulting in low quality PC composites [6].

Previous studies [6,7] suggest significant decrease on the PC hydration due to the hydrophilic characteristics of the vegetable fibers due to the water uptake by the capillary porous, and subsequent water release during the curing period. Additionally, the released water can contain extractives leading to a protective layer on the cement grains blocking further hydration [8].

The most recent studies have shown that extractives effect in the PC hydration decrease is due to their absorption on the surface of the hydrating cement grains, or on the hydrated products. Chakraborty et al. [9] states that dissolved extractive may form a protective layer on the partially hydrated cement grains. This layer forms a temporary barrier on the cement grains for further hydration. In addition, extractives reduce the PC hydration temperature, acting as an inhibitor of the formation of hydrated products of PC [7]. As a measure to avoid this negative effect, Ferraz et al. [10] suggest to remove extractives and impurities from vegetable fibers by a hot water (100 °C) pre-treatment.

The aim of the present study is to evaluate the effect of hot water (100 °C during 30 min) pre-treatment efficiency on sugarcane bagasse fibers to produce PC composites. Pre-treatment effects will be investigated, either on the sugarcane bagasse fibers, as well as on the physical-mechanical properties of PC composites.

2. Material and methods

2.1. Materials

The Portland cement (PC) used for this research was a Type CP V-ARI PC (High Early Strength), according to the Brazilian Standards NBR 5733 ([11], ABNT, 1991) and equivalent to the PC Type III ASTM C150. High early strength PC contains 0–5% from mineral additions (blast furnace slag or pozzolans). It was selected because it minimizes the influence of those additions on the hydration reactions in conjunction with the sugarcane bagasse fibers. Chemical compositions (% by mass of oxides) of the PC were determined using X-ray fluorescence spectrometry and are presented in Table 1. The sugarcane bagasse used was collected from an industrial sugarcane mill plant located in the state of São Paulo, Brazil.

2.2. Sugarcane bagasse fibers processing and pre-treatment

Sugarcane bagasse was crushed using a mill (Model DPC-1, Cremasco) and then sieved with the aid of an automatic shaker (Model G, Produtest) to obtain approximately 8 mm of length fibers, (Fig. 1).

Pre-treatment of the processed sugarcane bagasse fibers were carried out according to the methodology described by Cabral et al. [2] as shown in Fig. 2. The water was heated up to 100 °C in a 30 L container capacity (Fig. 2a) and then, the sugarcane bagasse fibers were introduced in a ratio of 31.25 g per L of water (Fig. 2b). The immersed fibers were kept into the 100 °C water during 30 min (Fig. 2b). The recovered fibers were washed with tap water (at ~20 °C) (Fig. 2c). Finally, the fibers were placed in a 60 °C oven with forced ventilation for 72 h (Fig. 2d), until the moisture content reached ~8% by mass.

2.3. Chemical characterization

The methodology proposed by the French Standards NF V03-040 ([12], AFNOR, 1993) was followed in order to determine the cellulose, hemicellulose, lignin and extractives content from non-treated and treated sugarcane bagasse fibers. The determination of ash and humidity contents followed the procedures described by Morais et al. [13].

Table 1 – Chemical composition of PC (% by mass of oxides).

	Ca	Si	S	Fe	Al	K	Mg	Sr	Ti	Mn	Zn	Zr
PC[a]	78.73	6.72	4.75	3.9	2.3	1.8	0.9	0.26	0.25	0.10	0.07	0.01

[a] NBR 5733 (clinker + gypsum = 100–95% by mass; carbonate material = 0–5%).

2.4. Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) (TM-3000, Hitachi) at 15 kV (accelerating voltage) was employed to study the morphology of the non-treated and treated sugarcane bagasse fibers (oven-dried at 60 °C, 24 h) without a metallic coating and without epoxy resin impregnation. Both types of fibers were fixed to metallic holders ("stub") and images were generated by the acquisition of backscattered electrons in different fields, magnifications (1.0 and 5.0×) with a working distance (WD) of 5.80 mm.

2.5. Contact angle measurements

Contact angle (CA) between liquid and solid surface can be measured by different methods (e.g. sessile drop method, capillary rise method, Washburn method, or Wilhelmy method) [14]. However, vegetable fibers are variable and irregular along its length, diameter and surface. For all the abovementioned reasons, Wilhelmy method is the most indicated to measure wettability between vegtable fibers and water [15]. This test was conducted on a tensiometer DCAT21 model, Data-Physics Instruments GmbH. Sugarcane bagasse fibers (oven-dried at 60 °C for 24 h) perimeter was measured using an optical microscope (AxioImager.A2m Model, Zeiss) and an image analysis software (AxioVision Rel. 4.8. Model, Zeiss). Then, the fiber was inserted into the spring-loaded immersion clip. A 5-mm immersion/extraction depth was selected and a speed of 8 mm/s was assigned to allow sufficient data points collection. This test was conducted with the water temperature at 20 °C [15], and the contact angle was determined according to Eq. (1).

Fig. 1 – Processed sugarcane bagasse fibers.

$$F(h) = P \cdot \gamma \cdot \cos\theta - \rho \cdot A \cdot h \cdot g \quad (1)$$

where F is the force needed to balance the fiber weight, P is the wetted perimeter of the fiber, γ is the surface tension of the liquid at the liquid/air interface, θ is the contact angle, ρ is the liquid density, A is the cross-section area, h is the immersion length of the fiber, and g is the acceleration due to gravity. The value of the contact angle is determined by linear extrapolation of the curve when the immersion length of the fiber is zero.

For this test 30 repetitions were conducted by each fiber (non-treated and treated), and a statistical analysis was performed to confirm if the mean values of the contact angle of the non-treated sugarcane bagasse fibers and treated sugarcane bagasse fibers are statistically different. The mean values were analyzed by the Tukey test with probability of 5%. Data was analyzed with the SAS program, 2.5.1.

2.6. Crystallographic analysis (X-ray diffraction)

X-ray diffraction measurement was carried out with a diffractometer (AXS Analytical X-Ray system D5005 model, Siemens) operated at 1600 W (40 kV and 40 mA) and Cu-Kα radiation (1.54056 Å wavelength) inherent in the copper tube, and 2θ range from 10° to 50° with goniometer speed of 10° min^{-1}. A Wiley mill (Model 4, Thomas Scientific) was used to reduce fibers size below 1 mm, subsequently, the fibers were oven-dried (60 °C, 24 h). The crystallite size was determined by the Scherrer equation described by Langford and Wilson [16], as presented in Eq. (2).

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

where D is the perpendicular size of the structure represented by the peak of the plane (011), K is a constant related to the shape of the crystals and plan reflectance indices (011), λ is the beam wavelength incident in the experiment diffraction, β is

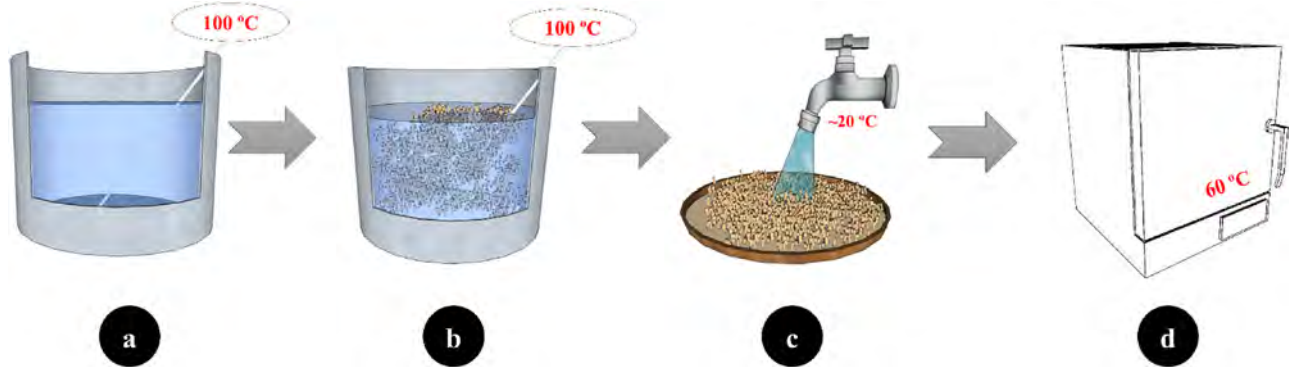

Fig. 2 – Sugarcane bagasse fibers pre-treatment procedure.

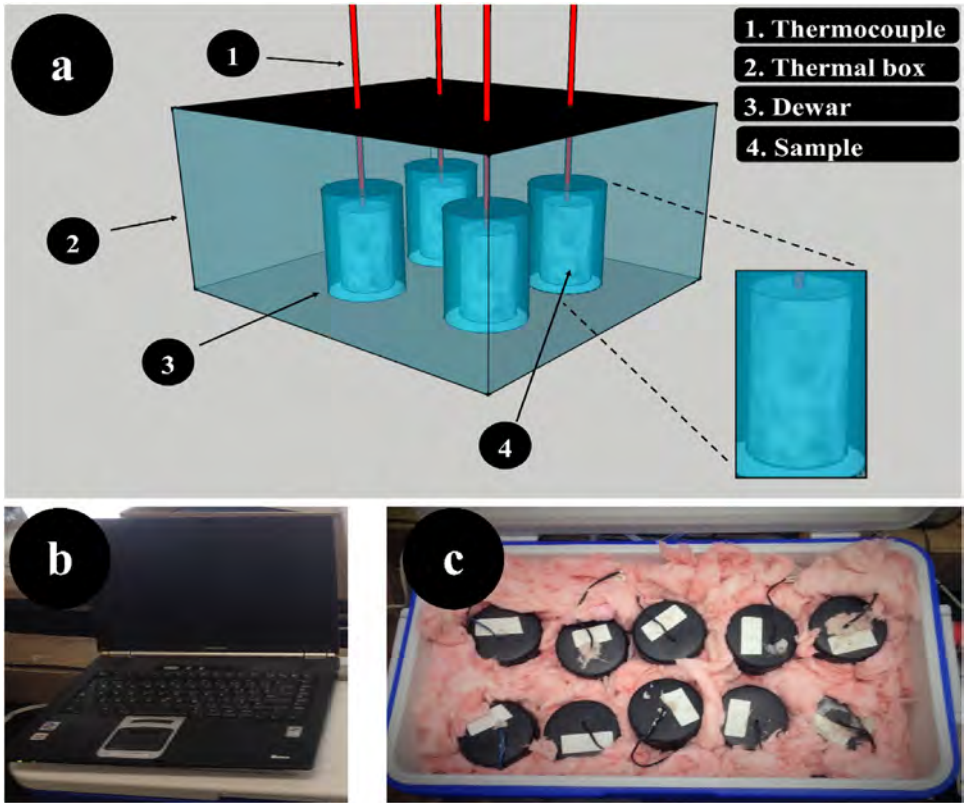

Fig. 3 – Inhibition index test: (a) Schematic representation of test set up; (b) Data acquisition system; and (c) Adiabatic system set up for sample containers.

the width at half height (pwhm) in radians and θ is the peak position (half of the value θ).

In this study, the cellulose crystallite size has been calculated by the experimental and theoretical diffraction patterns. The procedure to adjust the crystallography information file (CIF) was executed according to the methodology proposed by French [17], using unit cell dimensions and fractional coordinates from the free software Mercury. The crystallinity index (CI) was calculated by Buschle-Diller and Zeronian [18] method (Eq. (3)).

$$CI = 1 - \frac{I1}{I2} \tag{3}$$

where $I1$ is the intensity at the minimum (2θ value between 18° and 19°), and $I2$ is the intensity associated with the crystalline region of cellulose (2θ value between 22° and 23°).

2.7. *Inhibition index test*

Inhibition index test method used was the same as described by Okino et al. [6] in an adiabatic system (Fig. 3a). Sugarcane bagasse fibers (non-treated and treated) and PC were used. Water (90.5 mL) was added to a PC mixture (200 g) and sugarcane bagasse fibers (15 g oven dry basis) in a polyethylene bag for 5 min. The amount of water added was based on experiments reported by Weatherwax and Tarkow [19] which suggested the use of 2.7 mL of water per gram of vegetable fiber (adjusted to oven dry basis) and additional 0.25 mL of water per gram of PC.

The final mixture (PC, sugarcane bagasse fibers and water) was placed in a wide-mouth insulated flask with a thermocouple type "J" (Model Omega, Stamford) inserted into each mixture and connected to a data acquisition system (Model Data 21X, Campbell Scientific) (Fig. 3b). The flask was sealed with wrapping tape and introduced in a 500-mL stainless steel vessel insulated by a vacuum double wall. All vessels were placed into a 45.4 L thermal box (Model Coleman, Wichita) filled with fiber glass insulation (Model R-40, EcoTouch) in order to avoid heat exchange with the external environment (Fig. 3c).

Eq. (4) was used to calculate the inhibitory index (I) of the samples.

$$I = 100 * \left(\frac{T - T'}{T}\right)\left(\frac{H' - H}{H}\right)\left(\frac{S - S'}{S}\right) \tag{4}$$

where I is the inhibition index (%), T is the maximum temperature of PC/water mixture (°C), T' is the maximum temperature of sugarcane bagasse fibers/PC/water mixture (°C); H is the time to reach maximum hydration temperature of PC/water mixture (h), H' is the time to reach maximum hydration temperature of sugarcane bagasse fibers/PC/water mixture (h), S is the maximum temperature increment in the PC/water mixture (°C/h); S' is the maximum temperature increment in the sugarcane bagasse fibers/PC/water mixture (°C/h). The inhibitory index was classified according to Table 2 [6].

Three replications were conducted to each treatment of sugarcane bagasse mixtures (PC + sugarcane bagasse fibers + water) and to the control (PC + water). They were fabricated

as a control required by inhibition test method. All the experiments of this study were conducted at room temperature that ranged from 23 up to 29 °C.

2.8. Differential scanning calorimetry

The PC hydration products were evaluated by differential scanning calorimetry (DSC) in the first 24 h of hydration. To perform the DSC analysis, samples were prepared with the same amount of PC, sugarcane bagasse fibers and water used to perform the inhibition tests (Section 2.3).

DSC analysis was carried out in samples extracted from control (PC), PC with non-treated sugarcane bagasse fibers and PC with treated sugarcane bagasse fibers in periods of 12 and 24 h of hydration. The samples were crushed and sieved (0.106 mm) after insertion in acetone to stop the PC hydration process [2].

In order to define each hydration product around 25–200 °C and its corresponding percentage, the deconvolution curves were undertaken with the math function Gauss-area to quantify the mass loss corresponding to each different stage of dehydration/dihydroxylation using PEAK FIT software.

2.9. Production of cement composites with sugarcane bagasse fibers

Non-treated and treated ~8 mm length sugarcane bagasse fibers (8% water content) were used for producing PC composites. Bonding agent used was commercial PC as described in Section 2.1. Formulations adopted 30% by mass of sugarcane bagasse (treated and non-treated) with 70% by mass of PC. The reference (control) series was performed by 100% pure PC (without fiber addition).

The PC composites with sugarcane bagasse fibers were produced according to the methodology described by Cabral et al. [2]. The predetermined amount of sugarcane bagasse fibers and water was blended in a planetary mixer. PC was subsequently added and the constituents were mixed for 5 min to prevent agglomerations. Water amount used in the mixture was calculated using an equation applied by Okino et al. [6], as shown in Eq. (5). Where, Wa is the volume of water added to the mixture (L), C is the quantity of PC (kg); FHC is the water content (oven-dry basis) of the fibers and F is the oven-dry fibers mass (kg).

$$Wa = 0.35C + (0.30 - FHC)F \quad (5)$$

After the homogenization, the mixture was manually placed and casted in a wooden mold (300 mm × 300 mm) to provide a density as uniform as possible and pre-pressed to a thickness of approximately 40 mm. Then, the pre-pressed sample was placed in a hydraulic press (Model PHH100T, Hidral-Mac®) and subjected to the pressure of 5 MPa for 24 h at room temperature. The PC composite samples under study were produced with a 1250 kg/m^3 target density and 10 mm final thickness. Reference composites with pure PC (control) were also manufactured. A total of 12 PC composite pads were fabricated: four pads for the reference (control) composites; four pads for the composites of PC with non-treated sugarcane bagasse fibers; and four pads for the composites of PC with treated sugar fibers. To enhance hydration after manufacturing, the PC composites were conditioned at 23 °C in saturated air environment (i.e. sealed in plastic bags) for 27 days.

Physical tests of Thickness Swelling (TS, after 24 h immersed in water) and Bulk Density (BD) were determined according to European Standard [20] and [21].

Mechanical bending tests were performed on the PC composites specimens (28 days old) in equilibrium with the temperature and air humidity of the laboratory using the mechanical testing machine (Model DL 30000, Emic).

The prismatic specimens were prepared using a diamond saw blade, having nominal dimensions of 250 mm × 50 mm × 10 mm. In order to record the average values of these physical and mechanical variables with their respective standard deviations, 16 specimens were used as repetitions for each property, with four of them randomly extracted from each PC composite pad. Fig. 4 shows the prismatic specimens (250 mm × 50 mm × 10 mm) of the composites fabricated after 28 days for the mechanical tests.

The mechanical properties of Modulus of Rupture (MOR), Specific Energy (SE), Modulus of Elasticity (MOE), in three-point bending test with configuration of major span of 200 mm were determined for the different treatments and then compared with control composites using the recommendations of the [22].

Analysis was evaluated in a completely randomized design (CRD) with 1 factor (treatment) composed by 3 sub-levels (control, composites containing non-treated sugarcane bagasse fibers and composites containing treated sugarcane bagasse fibers). The results were analyzed using SAS program by the Tukey test probability (5%).

Table 2 – Inhibitory index used to PC setting compatibility.

Inhibition index (%)	Grade of inhibition
1–10	Low
10–50	Moderate
50–100	High
>100	Extreme high

Fig. 4 – Prismatic specimens (250 mm × 50 mm × 10 mm) of the composites fabricated for the mechanical tests.

Table 3 – Chemical composition of sugarcane bagasse fibers (Standard deviations in parentheses).

Compound (%)	Non-treated sugarcane bagasse fibers	Treated sugarcane bagasse fibers
Cellulose	38.1[a] (0.6)	38.3[a] (0.2)
Hemicellulose	28.1[a] (0.5)	25.0[a] (0.2)
Lignin	24.8[a] (0.2)	24.8[a] (0.2)
Extractives	9.0[a] (0.5)	7.1[a] (0.1)
Humidity content	7.1[a] (0.1)	7.1[a] (0.1)
Ash	0.9[a] (0.1)	0.5[a] (0.1)

[a] Each value represents the mean of three replicates.

3. Results and discussion

3.1. Chemical characterization

Cellulose, hemicellulose, lignin and water-soluble extractives content of non-treated sugarcane bagasse fibers and treated sugarcane bagasse fibers used in this study are shown in Table 3. The treatment on the sugarcane bagasse fibers favored the decrease of extractives and ash contents while cellulose, hemicellulose and lignin contents remained stable. Similar results were reported by Fan et al. [23].

The extractives are inhibitory substances to the PC hydration reaction. These inhibitory substances consist of sugars, tannins, gums, starches, colorings, fats, resins and other components, which can be removed with hot or cold water, or organic solvents, like ethanol, toluene, acetone or dichloromethane [23]. Such substances (extractives) can decrease the PC hydration temperature [7]. However, as shown in Table 3 the treatment evaluated have decreased the extractives content on both analyses (23 and 100 °C) as well as decreased the ash content in the treated fibers. Additionally, the treatment on the sugarcane bagasse fibers resulted in a mass loss of ~12% based on the initial dry mass before the procedure.

3.2. SEM analysis

SEM analysis of non-treated sugarcane bagasse fibers and treated sugarcane bagasse fibers assessed the longitudinal (Fig. 5a and b) and cross section of the fibers (Fig. 5c and d).

The sugarcane bagasse commonly presents certain amount of foreign materials and dirt, as well as extractives which produces an inhibitory effect on the PC hydration temperature [8]. By SEM analysis impurities removal by the pre-treatment is seen. Fig. 5a and c show the presence of residues on the surface and in the pores of the nontreated sugarcane bagasse fibers which are not seen in Fig. 5b and d for the treated sugarcane bagasse fibers.

3.3. Contact angle measurements

Contact angle (CA) can be used as a parameter to measure the hydrophilicity of the vegetable fibers by the surface energy in water. Contact angles smaller than 90° represent hydrophilic materials. Contrarily, hydrophobic materials can be associated to contact angles greater than 90° [24].

Treated sugarcane bagasse fibers has shown a higher contact angle (Table 4). The higher contact angle indicates both greater difficulty in forming a monolayer of water on the fiber surface and lesser water adsorption.

The pre-treatment of sugarcane bagasse fibers caused a decrease in their wettability as the value of the contact angle increased from 61.6° for non-treated sugarcane bagasse fibers to 90.4° for the treated fibers. These results represent an increase of ~50% in relation to the initial value. Contact angle over 90° means that the fiber is said more difficult to absorb water. Due to this behavior, the treated sugarcane fiber provides a better hydration of the PC composite.

3.4. X-ray diffraction analysis

To determine the crystallite size by the Scherrer equation of the non-treated and treaded sugarcane fibers the experimental diffraction patterns were used (Figs. 7a and 6b respectively). Peak widths at half maximum (pwhm) of 0.1 for the crystalline structure, 2.5 for the non-treated sugarcane bagasse fibers, and 4.4 for the treated sugarcane bagasse fibers were standardized. This standardization was necessary in order to adjust the theoretical semi-crystalline cellulose model close to the experimental model of the non-treated and treated sugarcane bagasse fibers [17].

Cellulose profile was obtained in 0.1 pwhm and the patterns were maintained indicating a possible pattern similarity of boot profiles of sugarcane bagasse fibers (non-treated and treated). Additionally, this similarity is found once both fibers under study have the same origin, planting and soil conditions, weather and processing [17]. However, just for the non-treated sugarcane bagasse fibers it was still necessary the use of 0.5 March-Dollase (MD) factor to adjust the theoretical and experimental profiles.

As shown in Table 5, cellulose crystallite size decrease is associated with the disappearance of some crystal planes such as: (001) and (1–31) (Fig. 6) in the treated sugarcane bagasse fibers.

Crystallite size decrease was observed. This fact can be related to the structural modifications in the amorphous cellulose, lignin, hemicellulose and extractives, the formation of intramolecular hydrogen bonds and the occurrence of hydrolysis [25].

Due to high moisture and temperature during the procedure conducted in the fibers, hydrolysis hypothesis would be the most likely. According to Helmerius et al. [26] this pre-treatment (hot water) is a self-catalytic process with the mechanism of hydrolysis, resulting in a hemicellulose solubilized as a mixture of oligomers and monomers, as seen in Table 3 by the decrease of the hemicelulose amount of the treated fibers. Sugarcane bagasse fibers are structured in organized (crystalline) and disorganized (amorphous) fractions [17]. However, due to the hydrolysis process would be

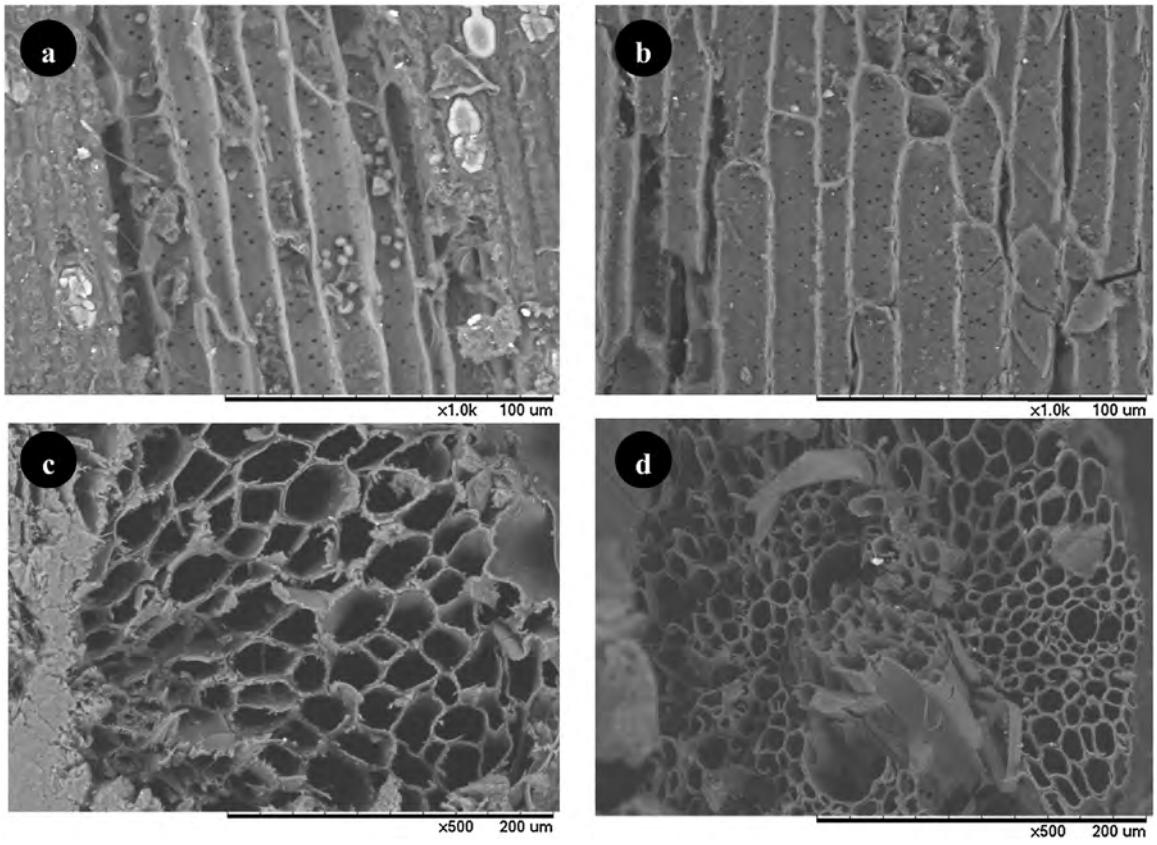

Fig. 5 – SEM analysis applied to sugarcane bagasse: (a) non-treated fiber, longitudinal section; (b) treated fiber, longitudinal section; (c) non-treated fiber, cross section; and (d) treated fiber, cross section.

Table 4 – DCA measurements by for bagasse sugarcane bagasse fibers.

Sugarcane bagasse fiber	Contact angle (°)
Non-treated	61.6[a]
Treated	90.4[b]

Means with same letter in the column do not differ by the Tukey Test $p < 0.05$.

intensified the structural disorganization process. The CI values of sugarcane bagasse fibers were 0.77 (non-treated) and 0.46 (treated) (Table 5). Likewise, regarding minimum reductions in crystallinity after aqueous pre-treatments are also found by Ballesteros et al. [25].

3.5. *Inhibition index test*

Inhibition index of treated bagasse sugarcane bagasse fibers was 5.9% (Table 6). According to Okino et al. [6], the grade of inhibition for this material is low (Table 2). Then, treated sugarcane bagasse fibers will have good compatibility with PC during the composites production. On the other hand, inhibition index of non-treated sugarcane bagasse fibers was 67.3% (Table 6), which is considered high (Table 2) as reported by Okino et al. [6].

According to Yaguang and Kamdem [27], decreasing of PC maximum temperature (T) of sugarcane bagasse fibers may be related to the volume of the mixture, resulting in generation of a smaller amount of heat during the chemical reactions of the PC hydration. When inserted into the mix, the fibers of sugarcane bagasse can decrease a part of the heat generated by PC. Such phenomena may explain the difference in temperature between the control sample (PC) and PC with addition of treated bagasse fibers sample (Fig. 7).

The results for the temperature evolution of PC are directly related with the chemical composition of the sugarcane bagasse fibers (Table 3). The non-treated sugarcane bagasse fibers delayed the PC hydration, more than the treated fibers, as can be seen in Fig. 7. There is a reduction in the PC activation energy of 85 °C in 9 h, to 56 °C in 12 h with the use of the treated sugarcane bagasse fibers, and to 44 °C in 15 h for non-treated sugarcane bagasse fibers, generating a delay in the setting of PC. As reported by Meier et al. [28], this process occurs because the kinetics of pores supersaturating, which is initially too high for the neat PC and will be blocked by vegetables fibers by the calcium intake which leads to imbalance the formation of further PC hydration products.

3.6. *DSC analysis*

Fig. 8 shows DSC results for the 12 and 24 h of hydration of PC (control), PC containing non-treated and treated sugarcane bagasse fibers.

As shown in Fig. 8 for the 12 and 24 h of hydration, three main exothermal peaks are presented. Peak 1 (50–200 °C) is related to

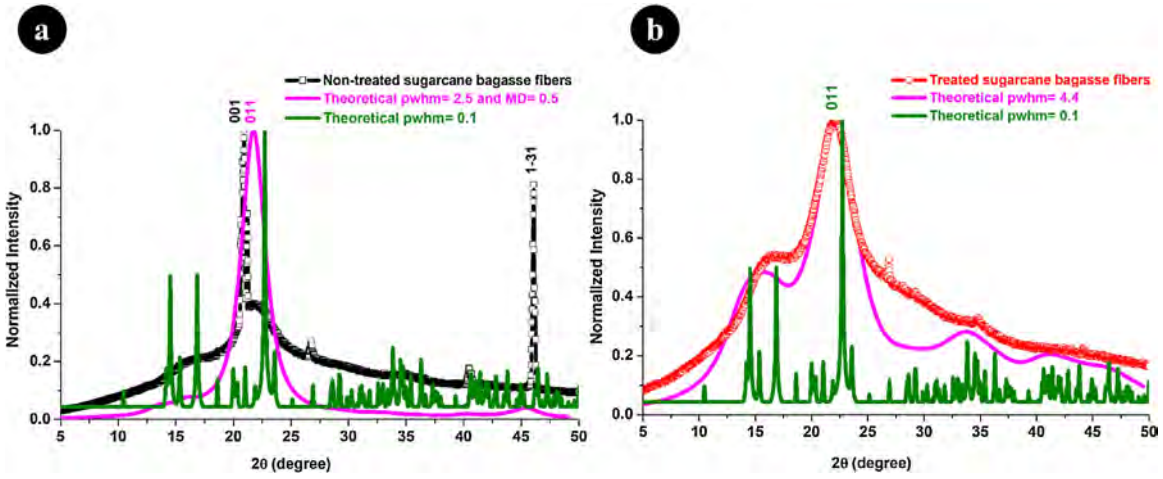

Fig. 6 – X-ray diffraction patterns for cellulose: (a) non-treated; and (b) treated sugarcane bagasse fibers.

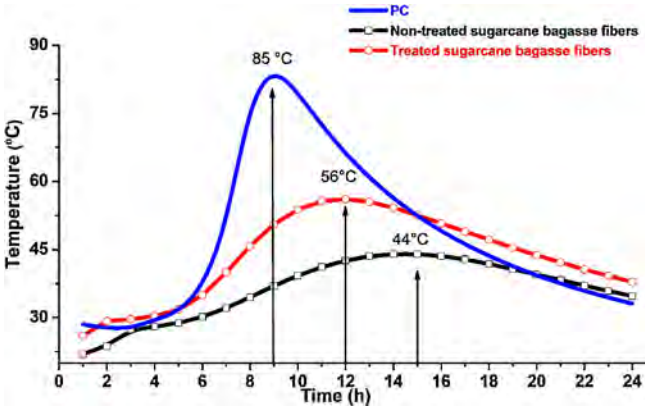

Fig. 7 – Temperature evolution resulted from inhibition index test for samples of Portland cement without and with sugarcane bagasse fibers (treated and non-treated).

Table 5 – Structure of cellulose crystallite.

Sample	Theoretical pwhm	Crystallite size (Å)	CI
Non-Treated sugarcane bagasse fibers	2.5 and MD = 0.5	35.23	0.77
Treated sugarcane bagasse fibers	4.4	23.82	0.46

the exothermal peak monosulfonate phase (AFm), etringite (AFt) or C–S–H. Peak 2 (400–500 °C) represents the exothermal peak of the calcium hydroxide. Peak 3 (650–800 °C) is related to the exothermal peak of calcium carbonate [5].

There is a decrease in the Peak 2 for the non-treated sugarcane bagasse fibers and treated sugarcane bagasse fibers (12 and 24 h). This decrease could be associated to a greater carbonation of the PC due to the vegetable fibers alkaline degradation. Studies conducted by Govin et al. [7] shown that the vegetable fibers alkaline degradation could induce a carbon

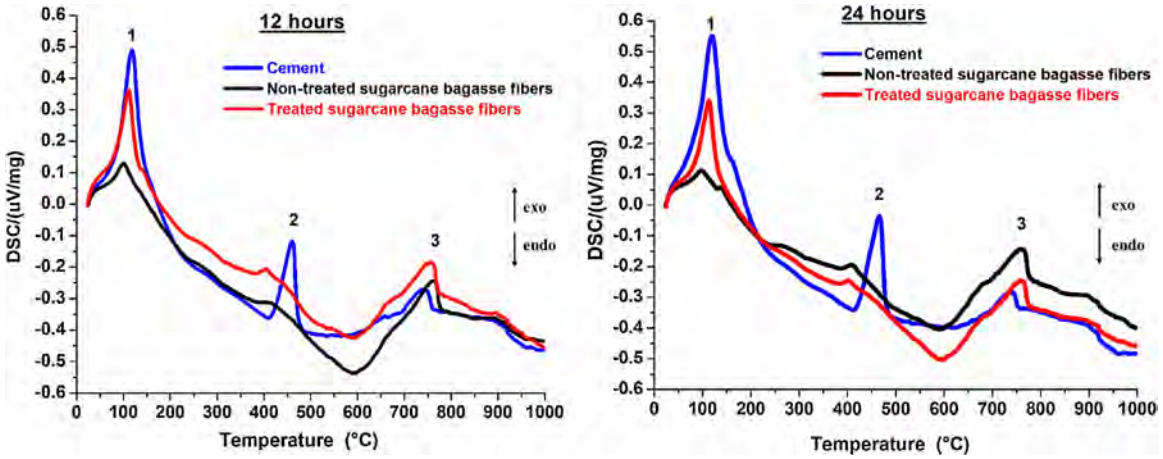

Fig. 8 – DSC for 12 and 24 h of hydration of Portland cement with non-treated and treated fibers, in comparison to the control (pure PC paste).

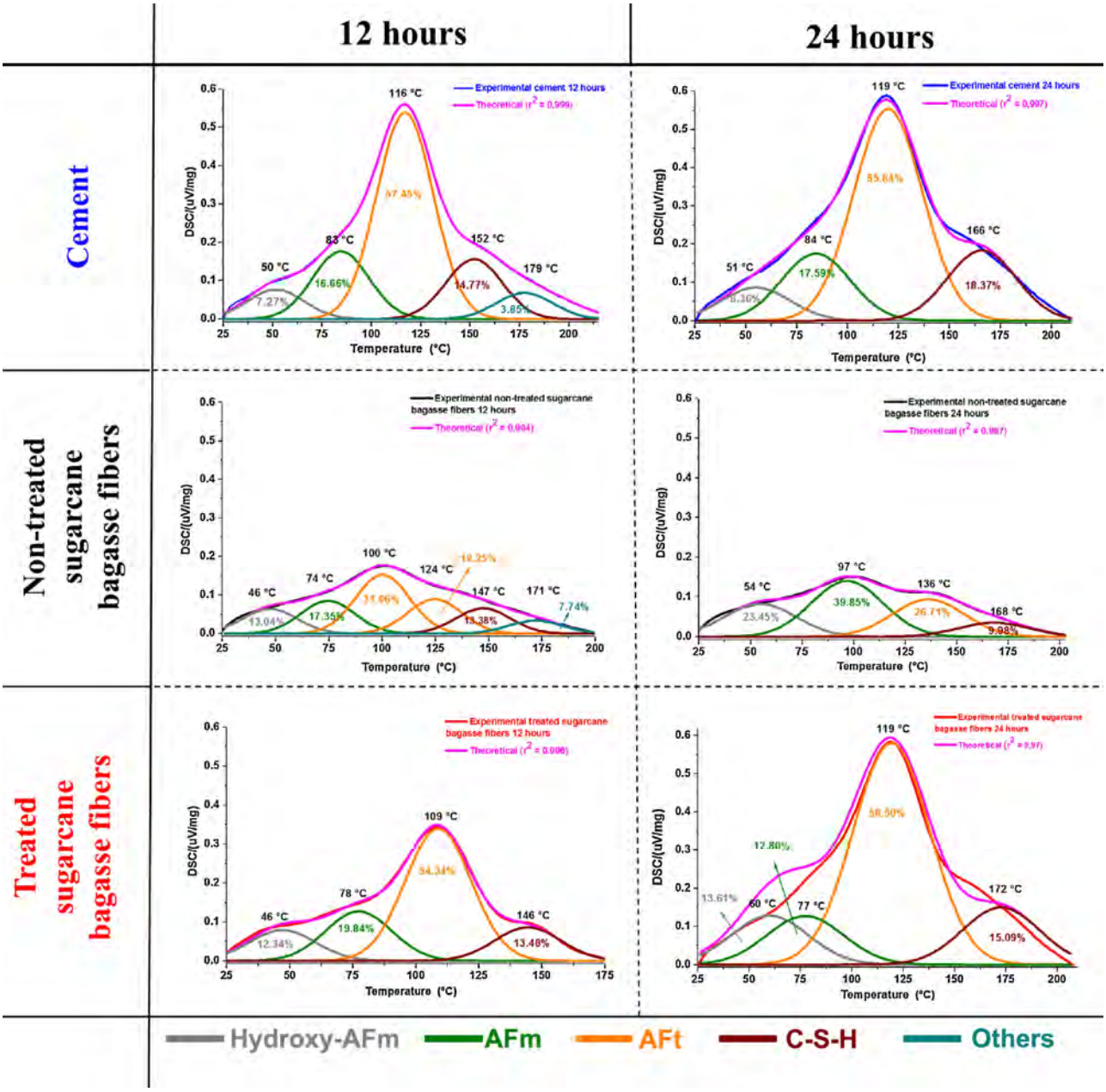

Fig. 9 – DSC deconvolution of hydration products in the early ages (12 and 24 h).

Table 6 – Inhibitory index of sugarcane bagasse fibers used in this study (Standard deviations in parentheses).

Sample	Inhibition index (%)
Non-treated sugarcane bagasse fibers	67.3[a] (1.29)
Treated sugarcane bagasse fibers	5.9[a] (0.08)

[a] Each value represents the mean of three replicates.

dioxide (CO_2) release. This CO_2 release leads to a carbonation of the calcium hydroxide as shown in the increase of the Peak 3 (Fig. 9) when compared with the PC (12 and 24 h). The characteristic AFm, AFt and C–S–H peak (peak 1) is shifted with the addition of non-treated sugarcane bagasse fibers in PC. This shift is not reproduced clearly with the addition of treated sugarcane bagasse fiber in PC.

In order to evaluate the hydrated products of PC by means of the DSC analysis in early ages (12 and 24 h), Peak 1 deconvolution has been carried out, as presented in Fig. 9.

The main hydrated products found in the deconvolution of the peak 1 were: hydroxy-AFm, AFm, Aft and C–S–H (Fig. 9). The exothermal peak of the hydroxy-AFm has started at 25 °C, as reported by Atkins et al. [29]. Hydroxy-AFm presence is due to the water dissolution of the Ca^{2+}, Si^{2+}, SO_4^{2-} e CO_3^{2-} clusters, as observed by Rupasighe et al. [30].

AFm phase is found in the exothermal peak at 50–100 °C as indicated by Taylor [5]. AFt thermal decomposition was found at 120 °C and also at 140 °C if it was hydrated [5], as presented in Fig. 9 just in the deconvolution of the non-treated sugarcane

Table 7 – Average values of physical–mechanical properties of the cementitious materials.

PC composite	Physical properties			Mechanical properties		
	TS 24 h (%)	WA 24 h (%)	BD (kg/m^3)	MOR (MPa)	MOE (MPa)	SE (J/m^2)
Standard (control)	0.38^a	6.00^a	1596^a	2.90^a	5186^a	30^b
With non-treated fiber	4.38^b	28.40^c	1081^b	1.61^b	542^c	825^a
With treated fiber	0.95^a	17.86^b	1051^b	2.97^a	1044^b	871^a

Means with same letter in the column do not differ by the Tukey Test ($p < 0.05$).

bagasse fibers after 12 h of hydration. A greater presence of Aft phases is shown (Fig. 9). According to Scriviner [31], the AFt phases will react with C_3A, and this reaction will consume AFt phases to form hexagonal plates of AFm between 24–72 h. A small amount of C–S–H is seen (Fig. 9), as reported by Taylor [5]. During the early ages, the C_3S reacts to produce initial C–S–H phases on AFt rod network.

Furthermore, the pre-treatment applied in this study removed part of the OH groups (extractives) thus corroborating to mitigate the effects barrier for the formation on the hydration products. Thomas and Birchall [32] have shown that the extractives adsorb the Ca^{2+} ions, and this process has inhibited the PC hydration. Consequently, extractives act as free calcium sequestration during the hydration of the PC, which alters the process of formation of the hydration products and generates materials with lower mechanical performance.

3.7. *Cement composites properties*

WA and TS values of PC composites with non-treated sugarcane bagasse fibers were statistically higher ($p < 0.05$) compared with the values obtained for control composites and PC composites with treated sugarcane bagasse fibers. MOR values of the PC composites with treated sugarcane bagasse fibers were statistically the same ($p > 0.05$) of the standard (control) samples (Table 7).

For MOE values, a performance difference is seen, reference (control) samples present superior values compared to the rest of the samples. As reported by Mármol et al. [4], this high rigidity values of composites manufactured with pure PC can be related to the lower porosity and higher BD (Table 7) than the PC composites reinforced by vegetable fibers.

Regarding the SE values, it is possible to confirm that the sugarcane bagasse fibers transformed a brittle material into a pseudo ductile one. In addition, it is also possible to confirm that the SE results of PC composites with treated sugarcane bagasse fibers were statistically higher ($p < 0.05$), even with the composition having been produced with an amount of 30% lower content of the cement matrix than the control composites.

4. Conclusions

This paper successfully presents the pre-treatment efficiency on sugarcane bagasse fibers to produce cement composites. Through the experimental study of the sugarcane bagasse fibers and cement composites, the following is found.

- Based on the results of the sugarcane bagasse fibers characterization a decrease of extractives and impurities is indicated by chemical and morphological analysis.
- Physical analysis (Contact angle) showed a reduction of the hydrophilicity of the treated sugarcane bagasse fibers. Contact angle has increased from 60.6° for non-treated sugarcane bagasse fibers to 90.4° for treated sugarcane bagasse fibers.
- Inhibition indexes have been calculated for non-treated and treated sugarcane bagasse fibers, and the indexes were 67.3% (high) and 5.9% (low) respectively.
- The hydration monitoring by DSC analysis reveals a strong modification of hydration products by non-treated sugarcane bagasse fibers. This effect is due to the presence of extractives and impurities of the non-treated fibers. Consequently, the treated sugarcane bagasse fibers effect on the delay of PC hydration process was less.
- PC composites with treated sugarcane bagasse fibers shown lower physical properties than the PC composites with non-treated sugarcane bagasse fibers ($p < 0.05$). Mechanical properties determined by three points bending test (MOR and MOE) of their counterparts with treated sugarcane bagasse fibers showed higher values than the PC composites with non-treated sugarcane bagasse fibers ($p < 0.05$), thus proving the pre-treatment efficiency on sugarcane bagasse fibers for cement composites production.

Ethical statement

Authors state that the research was conducted according to ethical standards.

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