Pereira, C.; Savastano, HJ.; Paya Bernabeu, JJ.; Santos, SF.; Borrachero Rosado, MV.; Monzó Balbuena, JM.; Soriano Martinez, L. (2013). Use of hyghly reactive rice husk ash in the production of cement matrix reinforced with Green coconut fiber. Industrial Crops and Products. 49:88-96. doi:10.1016/j.indcrop.2013.04.038.

Use of highly reactive rice husk ash in the production of cement matrix reinforced with green coconut fiber

Pereira, C. L. [a, 1]; Savastano Jr., H. [a]; Payá, J. [b]; Santos, S. F. [a]; Borrachero, M. V. [b]; Monzó, J. [b]; Soriano, L. [b]

[a] Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo, Caixa Postal 23, 13635-900 Pirassununga, SP, Brazil
[b] Instituto de Ciencia y Tecnología del Hormigón (ICITECH), Universitat Politècnica de València, Camino de Vera s/n 46022 Valencia, Spain

Abstract

This study evaluated the influence of partial replacement of Portland cement by rice husk ash (RHA) to enable the use of green coconut husk fiber as reinforcement for cementitious matrix. The use of highly reactive pozzolanic ash contributes for decreasing the alkaline attack on the vegetable fiber, originated from waste materials. The slurry dewatering technique was used for dispersion of the raw materials in aqueous solution, followed by vacuum drainage of water and pressing for the production of pad composites, as a simplified simulation of the Hatschek process for industrial manufacture. Five formulations were evaluated, two of them without any mineral additions. One of the mixtures served as a reference (without green coconut fibers) and the remaining ones were reinforced with the green coconut fibers (5% by weight of binder) and with the content of Portland cement replacement by RHA equal to 0, 30, 40 and 50%. The composites were analyzed at 28 days of age and after ageing by immersion in warm water (65°C), which lasted for 28 additional days. Physical and mechanical tests were applied for assessment of the performance of composites. Thermogravimetric analysis was used to observe the consumption of portlandite and chemically combined water content in the hydrated products for pastes presenting the same levels of Portland cement replacement by RHA (i.e., 0-50%) and with the water/binder ratio kept constant and equal to 0.5. The mechanical performance

---

[1] Corresponding author. Tel.: +55 19 35654153. E-mail address: camila_usp@yahoo.com.br

evaluated by bending test after 28 days reached the MOR of 15.7 MPa after the accelerate ageing, for the composites reinforced with the green coconut fiber and with high levels of Portland cement replacement by RHA demonstrating that the use of green coconut fiber for reinforcement can be very promising for the production of binary cement based matrix. The thermogravimetry showed that the replacement of Portland cement by the RHA helped in maintaining the mechanical behavior of the green coconut fiber in the composite subjected to the accelerated ageing tests, and resulted in improved mechanical performance, providing a lightweight composite.

Keywords: cement based composite; vegetable fiber; rice husk ash; cellulosic pulp; thermogravimetry.

Introduction

In the coming years, the construction industry has the challenge of incorporating sustainability in their production processes, either by searching for new raw materials and products more environmentally friendly and/or contributing for the reduction of CO_2 into the atmosphere. The possibility of incorporating waste from other industrial activities in their production processes can help with this goal, reducing the generation of CO_2 emissions during the conventional construction. Ramakrishna and Sundararajan (2005) discussed composites based on lignocellulosic fibers used in building construction. Particleboards can be produced from any lignocellulosic materials in principle, which confer high mechanical strength and specific predetermined weight (Ashori et al 2012, Ashori et al. 2011). Vegetable fibers are also widely available in most developing countries, which make them convenient materials for brittle cement matrix reinforcement, even though they present relatively poor durability performance (Agopyan et al., 2005).

The world production of coconut (*Cocos nucifera L.*) was around 60 million tons in 2008 - 85% in Asia, 8.5% in America, 2.9% in Africa and 3.2% in Oceania. Brazil is the fourth largest producer of coconut in the world, with production of about 2.8 million tons per year, accounting for more than 80% of the coconut production in South America. It is estimated that 350 million liters of green coconut water are consumed in Brazil every year (Martins & Jesus Jr., 2011, Pietro et al., 2011). After the consumption of the coconut water, the resulting waste generate significant and increasing volumes of useless material, since 80-85% of the gross weight of the green coconut are nominated as residues. 70% of the waste generated in Brazilian coastal urban centers is green coconut husk (Rosa et al., 2001; Pietro et al., 2011). Although being an organic material, the residue degradation is slow and can take more than eight years to fully degrade (Carrijo et al., 2002). Estimates indicate that the volume of waste generated from the green coconut is equivalent to 6.7 million tons of husks/year, becoming a serious environmental problem (Machado et al., 2009).

The green coconut fibers in cement composites can be used as reinforcement in the early ages. The adhesion between the matrix and the reinforcing component has a strong influence on the characteristics of the composite, contributing to an adequate stress transfer between the fibers and the matrix. These fibers increased the impact resistance by 3-18 times, respectively, compared to plain cement specimens. The main drawback for the use of vegetable fibers is the durability of these fibers in a cementitious matrix and also the compatibility between both phases (Agopyan et al., 2005).

The recycling of various types of cellulose pulps for the production of fiber cement has shown a significant effect on the mechanical properties and absorption. Yadollahi et al. (2013) found that relatively denser, stronger, and stiffer composites were obtained from the boards made with 40% pulp and paper sludge.

To use alternative binders by the inclusion of pozzolanic additions are necessary to reduce the alkalinity of the matrix and the content of calcium hydroxide (portlandite), avoiding the long-term degradation in non-conventional fiber cement material employing vegetable fibers as reinforcement.

The hydration process depends on the type and the fineness of the cement, the water/cement ratio, curing temperature and the presence of chemical admixtures and mineral additions. When mineral additions with high pozzolanic activity are incorporated into the cement matrix, can chemically react with calcium hydroxide, resulting from cement hydration to form an additional amount of hydration product in cement matrix. Results showed that RHA can be applied as a pozzolanic material to cement and also can improved resistance to water absorption (Hamzeh et al., 2013). The amount of this hydration product can reduce the porosity of the matrix and the porosity of the fiber-matrix transition zone and the permeability of binder materials, contributing to an increase in durability.

The ash production is generated by the burning process of rice husk as sources of energy and cogeneration for power. If adequately processed, the ash becomes a pozzolan predominantly amorphous, which is soluble in an alkaline medium and reacts in an aqueous solution with Ca^{2+} and OH^- ions. The final result of the reaction is the calcium silicate hydrate (CSH), the main product of hydration of the ordinary Portland cement.

The rice husk ash and active silica are highly reactive pozzolan, as they are essentially composed of pure silica in non-crystalline form. The non-crystalline rice husk ash (RHA) is obtained by burning at temperatures below 700°C, and consists of a disordered structure of silicon (Si) and oxygen (O) resulting from the decomposition and sintering without fusion of the amorphous silica (Payá et al., 2001).

The techniques of differential thermal analysis (DTA) and thermogravimetry (TG and DTG) have been frequently used by different researchers, to determine the amount of chemically combined water proportional to the hydrates (Dweck et al., 2000; Marsh and Day, 1998; Vedalakshmi et al., 2003). Using thermogravimetry it can be observed that the hydration products in the matrix release the chemically combined water in characteristic peaks that may occur in specific temperature ranges, as follows: calcium silicate hydrate (CSH), ettringite and calcium aluminate hydrate - 100 and 300ºC and calcium hydroxide - 425 and 550°C (Taylor, 1997). Studies carried out by Roszczynialski (2002) and Giergiczny (2006), using thermal analysis (DTA / DTG), showed the influence of the fly ash in the chemically combined water content of hydrates in the cementitious matrix. Payá et al (2003) used TG techniques for monitoring the pozzolanic reaction of spent FCC catalyst. Rodríguez (2012) determined by TG the consumed portlandite by different types of silica fume.

The use of supplementary materials in non-conventional fiber cement can provide increments in performance, both in fresh and hardened state, improving its mechanical properties and durability. The use of pozzolan like rice husk ash as a partial substitute to ordinary Portland cement allows enabling the production of non-conventional fiber cement reinforced with natural fibers, once it acts to reduce the alkalinity of the matrix and in the preservation of vegetable fibers, if compared to a matrix composed exclusively of cement Portland (Bezerra et al., 2006).

The present study evaluated the use of cementitious matrix modified by partial replacement of the ordinary Portland cement by rice husk ash for the production of non-conventional fiber cement reinforced with cellulose pulp generated from the cement Kraft bags and fiber extracted from the green coconut fruit shell.

Materials and Methods

Characterization of the green coconut fiber

The green coconut fibers were mechanically extracted from the husks with an initial length of 14.8 cm and passed through the cutting process in a knife mill, brand JFS®, JF5 model, with a 4 mm screening separation. The characterization of the fibers included the determination of the aspect (length/diameter) ratio, the real density and water absorption. To evaluate the water absorption, the fibers were initially dried at 65 ± 5°C and stood in a climatic chamber (Thermotron, model SM-3.5s) at 25 ± 2°C, with the relative humidity varying in the range of 30, 50, 70 and 90%. The different samples were weighed every 12 h until constant mass for each humidity level assessed. Table 1 depicts the dimensional and physical characteristics of the green coconut fibers. Figure 1 shows that the cutting process in a knife mill promoted a distribution of length of green coconut fibers.

Table 1. Dimensional and physical characteristics of the green coconut fibers.

Fig 1. Distribution of length for green coconut fiber.

Characterization of the cellulosic pulp

The use of cellulosic pulp in cement based composites is important because of the retention of cement particles in the slurry dewatering technique and some reinforcement effect in the early ages. It was decided to use a residual cellulose pulp obtained from the disintegration of cement bags produced with unbleached Kraft paper. The chopped cement bags remained immersed in water for three days. For the preparation of the pulp a blender was used adjusted (with blunt knives) with the addition of 1 L of water to 12 g of the previously chopped bags. In the following step, the materials passed through the process of disintegration for 1 min at maximum speed and the excess water was removed by filtration. The produced pulp was then kept under refrigeration in sealed plastic bags. The morphological characteristics of fiber length and diameter, fiber deformation (curl and kink) and fines content (length under 0.2 mm) of the cement bag pulp were analyzed using the equipment TM Pulptec MFA-500 Fiber Morphology and Shive Analyser - MorFiTrac.

Characterization of the rice husk ash

The binder used was the ordinary Portland cement CEM I 52.5 R, CEMEX brand (Spain), with specific surface area (BET) of 1.74 m^2/g. Rice husk ash (RHA) was provided by Maicerías Españolas DACSA S.A. They were obtained in a high temperature furnace (T > 1000ºC), in which the husks remained only for few seconds at this temperature. In these conditions, some unburned carbon was produced in the ash and no crystallization of amorphous silica was reached. Before being used it was milled for 20 minutes in a Gabrielli-2 jar mill with 18mm diameter-alumina balls, to increase its reactivity. For the granulometric studies, a laser diffraction granulometer (LDG) was used, it was the Mastersizer 2000 produced by Malvern Instruments. This equipment allows the measurement of particles of a size between 0.02 and 2000 micrometers, defining for this case a refraction index of 1.54 and an absorption index of 1. Mean particle diameter of ground RHA was 10μm.

Preparation and characterization of the composites

The content of both green coconut fiber and cellulose pulp was up to 5% of the total weight of the binder (ordinary Portland cement – OPC – and rice husk ash – RHA) as shown in Table 2. The mixture of raw materials formed with approximately 20% of solids in a mixer was stirred at 1,000 rpm for 15 min. The slurry was transferred to the evacuable casting box and the vacuum was applied until a solid surface formed. The pads of each formulation were pressed at 6.4 MPa for 10 min and wet curing of the pads for 28 days, as described below.

Table 2. Proportions between binder materials (OPC x RHA) and between reinforcing fiber / binder materials.

For the production and characterization of the composites, flat pads were molded with dimensions of 200 x 200 mm and 5 mm thick. The test pads were submitted to the wet curing for two days in sealed plastic bags and then kept in a climatic chamber at 20 °C and 90% relative humidity until they completed the 28 day period. The pads were then cut into the test specimens (200 x 40 mm) using a diamond disk cooled by water in order to be prepared to the physical and mechanical tests. Half of the specimens passed the physical-mechanical tests after the initial curing period (28 days) and the other half remained in thermal bath at 65°C (ageing process) for another 28 days before the tests, totaling 56 days of curing + degradation.

Eight specimens (test repetitions) were used to determine the physical and mechanical properties for each of the mixtures or curing conditions under evaluation. The physical properties were bulk density, water absorption, apparent porosity and permeability (ASTM, 1981). The four-point bending tests (equidistant distances between the supports) were carried out in the universal testing Instron model 3382 using a 5 kN cell machine Instron model 2714-010®, with the cross-head speed of 1.5 mm/min, for the calculation of the following mechanical properties: modulus of rupture (MOR) and specific energy (SE). The completion of the tests was achieved after to be observed a 70% reduction in relation to the maximum load (Savastano Jr., 2000).

The analysis of variance (ANOVA) followed by Tukey test were applied to compare the mean results between groups at a significance level of 5%.

For the thermogravimetric analysis (TG), it was used a simultaneous thermal analyzer Mettler Toledo brand, model 850 TGA, to determine the reactivity of the RHA and the amount of calcium hydroxide fixed by pozzolanic reaction in the cementitious pastes produced. Cement pastes were prepared according to the levels of replacement of ordinary Portland cement by the RHA, and the water/binder ratio was constant and equal to 0.5. The evaluation ages were chosen at 7 and 28 days for wet curing, and after different periods of ageing in warm water bath at 65°C for 28 and 90 days. The samples to be analyzed by TG were previously prepared from small fragments of the pastes which have been ground in acetone at the age of analysis. The powder obtained was separated through a sieve nº 120 (125 μm) and the residual moisture of the sample was removed using acetone followed by filtration and drying at 65ºC. The TG analyses were performed under an atmosphere of dry air with gas flow equal to 75 mL/min, heating rate of 10°C/min and a temperature range between 35°C and 600°C. Aluminium crucibles with 100 μL capacity having a sealable lid with a pin hole to obtain water vapour self-generated atmosphere were used.

Results and Discussion

Characterization of the green coconut fibers

The determination of the humidity absorption in a climatic chamber was adopted to be considered more appropriate for evaluating the fiber behavior under storage before the composite preparation (Fig. 2). However, the experimental test adopting water immersion resulted in 93.8% absorption, due to the high incidence of permeable pores, including the central gap and lumens of the individual cells that are commonly present in the structure of the green coconut fiber (Fig. 3).

Fig 2. Evolution of the average water absorption of the green coconut fiber for different relative humidity set at 30, 50, 70 and 90% and temperature set at 25°C.

When increasing the relative humidity, the absorption also increases. With this behavior, cement composite bulk density may decrease when the amount of vegetable fiber is higher. Another important aspect directly connected to the moisture absorption of the fibers is the ability to absorb water rich in hydration products of the cement at high pH and highly aggressive solution to the fibers over the time exposition.

Fig 3. Cross sectional (A) and longitudinal surface (B) of the virgin green coconut fiber, by scanning electron microscopy (SEM).

The green coconut fibers have an approximately cylindrical shape and surface with roughness and protuberances, which can assist in anchoring the fibers in the cementitious matrix. Figure 3A depicts the various unitary cells that compose the fiber and which are agglomerated by intercellular lamellae (middle lamella) and also the lumens (cavities) of the unitary cells. Figure 3B shows an outer layer that involves and protects the unitary cells of the green coconut fiber, improving the protection against the alkaline attack caused by the cement matrix.

The effectiveness of fibers in enhancing the mechanical performance of the brittle matrix is dependent to a large extent on the fiber–matrix interactions. Three types of interactions are particularly important: physical and chemical adhesion; friction; mechanical anchorage induced by deformations on the fiber surface or by overall complex geometry. The efficiency of fiber reinforcement can be judged on the basis of two criteria: the enhancement in strength and the enhancement in toughness of the composite, compared with the brittle matrix. These effects depend upon the fiber length, the orientation of the fibers and the fiber–matrix shear bond strength. A critical length parameter can be defined as the minimum fiber length required for the build-up of a stress in the fiber which is equal to its strength (Bentur, Mindess, 2007).

Characterization of the cellulose pulp

The use of short fibers allowed higher fiber density by mass or volume in relation to the long fibers, which reduces the magnitude of spaces without reinforcement in the matrix. Figure 4 shows the distributions of length and width of the cellulosic pulp from cement Kraft bags.

Fig 4. Distribution of the length (A) and width (B) of the cellulosic fibers obtained from the recycling of the cement Kraft bag.

The shortening of the cellulosic fibers originating from the cement bag through the recycling process of the cellulose pulp generated an expressive amount of small particles (length smaller than 200 μm), known as fines. Table 3 describes the morphological parameters of the cellulose pulp obtained from the recycling of the cement bag. Broken ends increase the surface area of fibers, which turns them more reactive with the cement particles. Curls (curvature of the fiber) and kinks (sudden change in direction of the axis of the fiber) are deformations that occur during the pulping process and affect the resistance and energy to break the fiber. The use of curly fibers can lead to low tensile index, but may also lead to high shear-index (Wathén, 2006).

Table 3. Morphological parameters of the cellulose pulp generated from the cement Kraft bags.

The disintegration process adopted for recycling the cellulose pulp probably contributed to the mechanical damage suffered by the fibers. Those damages can be associated to the incidence of continuous and gradual deformation of the fiber (curl) and the twisted curvature of the fiber (kink), influencing the length of fiber and creating weak points that can be favorable to the rupture of the fiber (Tonoli et al, 2010; Tonoli et al., 2012).

Characterization of the rice husk ash (RHA)

The rice husk ash is a material with two completely distinct phases, the outer layer formed of a denser structure (external epidermis, Figure 5A) and the internal layer, that is formed by an extremely porous structure (parenchyma and sclerenchyma, Fig

5B). Ground particles do not show internal porosity and are irregular in shape (Figures 5C and 5D).

Fig 5. SEM micrographs: the external (A) and internal (B) structures of the RHA before the milling process; ground RHA particles (C) and (D).

Because of this internal structure the RHA should preferably be ground before being used as a pozzolanic material, which increases the fineness and consequently the specific surface area of the material (Payá, 2012) (Fig. 6).

Fig 6. Particle size distribution curves of rice husk ash before (- - -) and after (—) the milling process.

The loss on ignition (LOI) of the RHA was significant (11.67%) and it was attributed to the incomplete combustion of organic compounds in the flash combustion process of the husks. The organic matter decomposed being transformed into carbon. The most relevant inorganic compound was SiO_2 (81.1%), having a high importance because it is one of the reactants in the pozzolanic reaction (Eq. 1). This silica reacts with calcium hydroxide in aqueous environment, yielding calcium silicate hydrates in gel form $((CaO)_x.(SiO_2)_y\ (H_2O)_n$, abbreviated as C-S-H) (Ordóñez et al., 2002), according to the following reaction:

$$y\ SiO_2 + x\ Ca(OH)_2 + (n-x)\ H_2O = ((CaO)_x.(SiO_2)_y\ (H_2O)_n \qquad \text{(Eq. 1)}$$

Where CSH has a stoichiometry similar to jennite $(CaO)_9.(SiO_2)_6.(H_2O)_{11}$ (Taylor, 1986).

C-S-H produced in the pozzolanic reaction is a very poor crystalline product, similar to those found from hydration of calcium silicates from OPC and presents stability, insolubility and cementing properties (Qijun et al., 1999; James et at., 1986). Al_2O_3 and Fe_2O_3 contents in RHA were very low, and consequently, no noticeable contribution on pozzolanic reaction may be taken into account.

Physical and mechanical properties of the composites

Table 4 shows the mean values of the physical properties of fiber reinforced matrices produced with ordinary Portland cement (OPC) and with the blended binder (OPC and RHA) at two different ages, after 28 days of wet curing and after the same period of ageing in heated thermal bath at 65°C.

Table 4. Mean values and their respective standard errors of the physical properties of the composites in two different ages.

With the exception of the composite without green coconut fiber, all the remaining ones showed higher values for the water absorption, apparent porosity and lower values for the bulk density, indicating that the inclusion of green coconut fiber and the increase in the total fiber content resulted in a composite with greater capillary porosity by incorporation of air in the matrix. Another factor that explains the high values of the apparent porosity of the blended binder composite reinforced with the green coconut fiber was the observed values of the w/b (water/binder) ratio, being binder the sum of OPC and RHA (see Table 2). This parameter increased from 0.4 for the matrix with 100% OPC to 0.57-0.63 for the different composites prepared by replacement of cement by RHA. This fact was attributed to the water absorption, the high fineness and morphology of RHA particles.

Fig. 7 presents the typical stress-specific deformation curves obtained from four-point bending tests. In Fig 7A mechanical behavior of the formulation 1 without macrofiber (green coconut fiber) before thermal curing can be observed, showing an abrupt drop of stress after rupture. The improved mechanical performance of the formulations 2 to 5 as compared to composite without macrofiber indicates the effect of green coconut fibers on the toughness of the composite and its capacity of crack control (Bentur, Mindess, 2007). Different mechanical behavior was found in the ageing composites, after the thermal bath (Fig. 7B). A clear difference was observed in the area under curves between composites before and after the thermal bath, especially for those reinforced with green coconut fibers. The highest values for stress and specific energy of the formulation 5, if compared to other formulations after the thermal bath, suggests a decrease of degradation mechanisms of the fibers with less alkaline matrix promoted by RHA.

Fig 7. Typical stress-specific deformation curves at different ages ((A) 28 days and (B) 28 days in thermal bath) for specific composites.

Fig 8. Correlation between modulus of rupture (MOR) and specific energy (SE) of the composites.

In Figure 8, the average values of MOR at 28 days show that the formulation 5 (15.7 MPa) has significantly higher strength than the composite without green coconut fibers (12.5 MPa), as well as specific energy. In general, the MOR and specific energy were partially maintained in the formulation 5 after the thermal bath, which may be associated with the fiber-matrix interfacial bond. The substitution of 50% of OPC by RHA provided the refinement of the pores and did not prejudice the mechanical resistance of the composite. It may also have assisted the preservation of the green coconut fiber due to the reduction of alkalinity in comparison with the OPC matrix. The results also show that the ageing period of 28 days in a water bath at 65°C was important to complement the curing process. The pozzolanic reaction between silica from RHA and portlandite from hydration of OPC produced an appropriate environment for the chemical stabilization of green coconut fibers.

The specific energy is related to the toughening mechanisms provided by de-bonding, pull out, bridging and fracture of the fibers, playing a role in the process of cracking of the composites. Even after the period of ageing in thermal bath, the composite with 50% RHA (formulation 5) presented a average specific energy significantly higher than the others, which support the statement that the high amount of RHA was very effective in preserving the green coconut fibers in the cementitious matrix. The fibers positively work in the post-stage cracking of the composite, dissipating the energy applied during the mechanical test. This high absorption of energy can be explained by the variation of the fiber diameter along its length, surface roughness and good adhesion regions distributed along the porous transition zone, which behave as anchoring points of the fiber.

Savastano Jr. (2000) evaluated the influence of the microstructure on the mechanical properties of cement based composites, concluding that the mechanism of fiber pullout is more important than the fracture of the fiber in order to improve toughness. It is possible to attest an improvement in the performance of the fiber-matrix transition zone through the incorporation of the RHA, causing the two phases to be better connected to each other, given the results in the Figure 8.

Thermogravimetry of the cement pastes

Table 5 shows the values of calcium hydroxide (CH) fixation corresponding to the different amounts of RHA replacement. The CH fixation was calculated according to Payá et al. (2003). This method takes into account the amount of portlandite formed from OPC in RHA/OPC mixtures for calculating the percentage of calcium hydroxide reacted. For calculating the values of CH fixation, the mass loss corresponding to the thermal decomposition of calcium hydroxide was evaluated (Eq. 2):

$$Ca(OH)_2 \Rightarrow CaO + H_2O \qquad \text{(Eq. 2)}$$

The decomposition process took place in the 520-600ºC temperature range, according to the thermal analysis parameters (sealed aluminum crucible, with a pinholed lid).

Table 5. Fixation of calcium hydroxide (CH) and combined water according to the amount of cement replacement by rice husk ash and the age of the pastes.

One should notice the influence of the amount of cement replaced by RHA on the fixation of portlandite (CH). The greater the amount of RHA, the higher the fixation of calcium hydroxide (CH), confirming the pozzolanic behavior of this material. Higher amounts of water combined to RHA in the cement pastes are directly connected to the additional formation of hydration products (mainly CSH).

The DTG curves related to the pastes produced in accordance with the different levels of Portland cement replacement by RHA provide information about the weight loss as a function of heating temperature. The mass losses related to the different ages are always obtained at the same temperature, only varying the quantity of water lost. The smaller the peak the lower content of portlandite, and consequently the higher fixed portlandite by RHA. The counting numbers (1, 2 and 3) next to the curves of the graphs are intended to facilitate the discussion (Fig 9).

Fig 9. DTG curves for the different formulations with partial replacement of ordinary Portland cement by the RHA at different ages and different conditions.

From the DTG curves corresponding to the cementitious pastes in both ages evaluated, it is possible to visualize the peaks as follows: the first peak 1 is the dehydration of ettringite (100-180°C) with an overlap with the dehydration of the phase CSH (calcium silicate hydrate), the second peak corresponds to the dehydration of calcium aluminosilicate hydrate (180-240°C). Finally, the peak 3 shows the dehydroxylation of portlandite (CH) (520-600°C).

By comparing the curves of the reference paste with the paste with the addition of 50% RHA, after the thermal bath treatment, it is observed the total reaction of portlandite during the pozzolanic process: the peak 3 in pastes cured in thermal bath for 28 and 90 days was not identified or was extremely small, for OPC/RHA pastes of 60/40 and 50/50. The pozzolanic reaction did not exhaust the total amount of portlandite in OPC/RHA paste of 70/30, probably because the amount of RHA was not enough for reacting completely with the portlandite generated in the hydration of OPC. The peak 3 on the curves corresponding to control paste (100% OPC) did not change significantly with the thermal treatment. It should be noticed the influence of the amount of cement replaced by RHA on the consumption of portlandite. The increased level of substitution resulted in a higher fixation of calcium hydroxide (CH), confirming the pozzolanic character of the mineral addition. The test results obtained by thermogravimetric analysis show that the replacement of Portland cement by RHA helped with the conservation of green coconut fiber in the matrix and therefore resulted in the improved mechanical performance, providing a lighter composite.

Conclusions

The mechanical performance after 28 days, with MOR of 15.7 MPa, for the composites reinforced with the green coconut fiber and with high levels of Portland cement replacement by RHA (50%) demonstrates that the use of the fiber as reinforcement can be very promising for the production of fiber cement with blended binder.

All composites showed higher values for the water absorption and apparent porosity and lower values for the bulk density, with the exception of the composite without green coconut fiber, indicating that the inclusion of green coconut fiber and the increase in the total fiber content resulted in a composite with greater capillary porosity by incorporation of air in the matrix.

Thermogravimetry allowed identifying the larger portlandite consumption in the RHA formulations. The obtained results show that highly reactive rice husk ash presents suitable characteristics for their use as pozzolanic material in Portland cement products, with very high portlandite consumption, finding 93.4% of portlandite fixation at 28 days when the replacement of ordinary Portland cement by RHA was 50% and 100% of fixation after thermal treatment. These results demonstrate the low alkalinity medium which was reached using high proportion of RHA.

The presence of RHA generates benefits related with the reduction in clinker consumption as through the decrease of matrix alkalinity and consequently reducing vegetable fibers degradation.

The results are promising for the potential use of composites in applications with higher risk of degradation, such as outdoor panels exposed to weathering.

Acknowledgments

To the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support and ICITECH Universitat Politècnica de València for facilitating the research development. To the Federal Agency CNPq, Brazil for grants provided to the USP team.

References

AGOPYAN, V., SAVASTANO Jr, H., JOHN, V. M., CINCOTTO, M. A. Developments on vegetable fibre–cement based materials in São Paulo, Brazil: an overview. Cement and Concrete Composites v. 27, p. 527–536, 2005.

ASHORI, A., TABARSA, T., SEPAHVAND, S. Cement-bonded composite boards made from poplar strands. Construction and Building Materials v. 26, n. 1, p. 131-134, 2012.

ASHORI, A., TABARSA T., AZIZI, K., MIRZABEYGI, R. Wood-wool cement board using mixture of eucalypt and poplar. Industrial Crops and Products, v. 34, n. 1, p. 1146-1149, 2011.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. Dry and wet bulk density, water absorption, and apparent porosity of thin sections of glass-fiber reinforced concrete - ASTM C 948. Philadelphia, 1981.

BENTUR, A., MINDESS, S. Fibre reinforced cementitious composites, 2nd edition, published in the USA and Canada by Taylor & Francis, 2007 603 p.

BEZERRA, E. M.; JOAQUIM, A. P.; SAVASTANO JR, H.; JOHN V. M.; AGOPYAN, V. The effect of different mineral additions and synthetic fiber contents on properties of cement based composites. Cement & Concrete Composites, v. 28, p. 555-563, 2006.

CARRIJO, O. A; LIZ, R. S.; MAKISHIMA, N. Fibra da casca do coco verde como substrato agrícola. Horticultura Brasileira, v. 20, n. 4, p. 533-535, 2002.

DWECK, J.; BUCHLER, P. M.; COELHO, A. C. V.; CARTLEDGE, F. K. Hydration of a Portland cement blended with calcium carbonate. Thermochimica Acta, n.346, p.105-113, 2000.

GIERGICZNY, Z. The hydraulic activity of high calcium fly ash. Journal of Thermal Analysis and Calorimetry, v. 83, p. 227-232, 2006.

HAMZEH, Y., ZIABARI, K. P., JAVAD TORKAMAN, ASHORI, A., JAFARI, M. Study on the effects of white rice husk ash and fibrous materials additions on some properties of fiber-cement composites. Journal of Environmental Management, v. 117, p. 263-267, 2013.

JAMES, J; SUBBA RAO, M. Reaction product of lime and silica from Rice husk ash. Cement and Concrete Research, v. 16, 67-73, 1986.

MACHADO, K. C.; DAMM, D. D.; FORNARI, C. C. M. J. Reaproveitamento tecnológico de resíduo orgânico: casca de coco verde na produção de gabinetes ecológicos de computadores. In: Fórum Internacional de Resíduos Sólidos, 2., 2009, Ilhéus. Anais ... Ilhéus, 2009.

MARTINS, C. R.; JESUS Jr., L. A. Evolução da produção de coco no Brasil e o comércio internacional: panorama 2010. Aracaju: Embrapa Tabuleiros Costeiros, 2011.

MARSH, B. K.; DAY, R. L. Pozzolanic and cementitious reactions of fly ash and blended cement pastes. Cement and Concrete Research, v. 18, p. 301-310, 1998.

ORDÓÑEZ L.M., PAYÁ J., COATS A.M., GLASSER F.P. Reaction of rice husk ash with OPC and Portlandite. Advances in Cement Research v. 14, p. 113-119, 2002.

PAYÁ J. La “transmutación” sostenible de los residuos para nuevas materias primas en el ámbito del concreto. Dyna v. 79, p. 38-47, 2012.

PAYÁ, J.; MONZÓ, J.; BORRACHERO, M. V.; VELÁZQUEZ, S. Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R- Portland cement pastes. Cement and Concrete Research, v. 33, p.603-609, 2003.

PAYÁ, J. MONZÓ, J., BORRACHERO, M. V., MELLADO, A., ORDOÑEZ, L. M. Determination of amorphous silica in rice husk ash by a rapid analytical method. Cement and Concrete Research, v. 31, p. 227-231, 2001.

PRIETO W. H., IGUTI A. M., NITZ M. Drying evaluation of green coconut pulp for obtaining a snack-like product Procedia Food Science v. 1, p. 1618-1627, 2011.

QIJUN Y., SAWAYAMA K., SUGITA S., SHOYA M., ISOJIMA Y. “The reaction between rice husk ash and $Ca(OH)_2$ solution and the nature of its product”. Cement and Concrete Research. v. 29. p. 37-43. 1999.

RAMAKRISHNA, G., SUNDARARAJAN, T. ‘Impact strength of a few natural fibre reinforced cement mortar slabs: a comparative study,’ Cement and Concrete Composites, v. 27, p. 547 – 553, 2005.

RODRÍGUEZ, E. D.; BERNAL, S. A.; PROVIS, J. L.; PAYÁ, J.; MONZÓ, J. M.; BORRACHERO, M. V. Structure of Portland Cement Pastes Blended with Sonicated Silica Fume. Journal of Materials in Civil Engineering, v. 24, 1295-1304, 2012.

ROSA, M. F., SANTOS, F. J. S., MONTENEGRO, A. A. T., ABREU, F. A. P., CORREIA, D., ARAÚJO, F. B. S., NORÕES, E. R. V. Caracterização do pó da casca de coco verde usado como substrato agrícola. Fortaleza: Embrapa Agroindústria Tropical, p. 6 (Comunicado Técnico, 54), 2001.

ROSZCZYNIALSKI, W. Determination of pozzolanic activity of materials by thermal analysis. Journal of Thermal Analysis and Calorimetry, v. 70, p. 387-392, 2002.

SAVASTANO JR, H.; PIMENTEL, L. L. Viabilidade do aproveitamento de resíduos de fibra vegetal para fins de obtenção de material de construção. Revista Brasileira de Engenharia Agrícola e Ambiental, v. 4, n. 1, p. 103-110, 2000.

TAYLOR, H. F. W. Cement Chemistry. Academic Press Ltd, London. 1997.

TAYLOR H. F. Proposed structure for calcium silicate hydrate gel. Journal of the American Ceramic Society, v. 69, n. 6, p. 464-467, 1986.

TONOLI, G. H. D.; BELGACEM, M. N.; BRAS, J.; PEREIRA-DA-SILVA, M. A.; LAHR, F. R.; SAVASTANO JR, H. Impact of bleaching pine fibre on the fibre/cement interface. Journal of Materials Science, v. 47, p. 4167-4177, 2012.

TONOLI G.H.D., SAVASTANO JR H.., FUENTE E., NEGRO C., BLANCO A., ROCCO LAHR F.A. Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. Industrial Crops and Products v. 31 p. 225–232, 2010.

VEDALAKSHMI, R.; SUNDARA RAJ, A.; SRINIVASAN, S.; GANESH BABU, K. Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique. Thermochimica Acta, n. 407, p. 49-60, 2003.

WATHÉN R. Studies on fiber strength and its effect on paper properties. Thesis, Helsinki University of Technology, p. 97, 2006.

YADOLLAHI, R.; HAMZEH, Y.; ASHORI, A.; POURMOUSA, S.; JAFARI, M.; RASHEDI, K. Reuse of waste sludge from papermaking process in cement composites. Polymer Engineering and Science, p. 1-8, 2013.