TITLE

# Portland cement, gypsum and fly ash binder systems characterization for lignocellulosic fiber-cement.

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ABSTRACT

The present work aims to obtain an optimal Portland cement, gypsum and fly ash (OPC-G-FA) ternary binder matrix and assess both the addition of paper pulp -by means of mechanical dispersion in aqueous suspension- for cementitious composites reinforcement and the fiber properties over time. To evaluate microfibers preservation from pulp in low-alkaline environments, ternary binder matrices OPC-G-FA are optimized to achieve lower pH values. For that purpose, pH and electrical conductivity over time were analyzed. Only samples with the lowest content in Portland cement (15-20%) offered low alkalinity for short-term. The use of ternary binder systems enhances microfibers conservation compared with control samples (matrices 100% Ordinary Portland Cement) by using FA that, as expected, reduces the presence of $Ca(OH)_2$ in the matrix. Mechanical results prove that obtained matrices yield to a mechanical properties maintenance unlike samples with OPC matrices where toughness is reduced by 95%.

HIGHLIGHTS

- pH and electrical conductivity assessment of Portland cement, gypsum and fly ash binders.
- TG and DTA analysis of ternary blended systems and their components.
- SEM for lignocellulosic fiber durability evaluation under low-alkaline environments.
- Fibers preservation within low-alkaline matrices by specific energy conservation in flexural tests.

KEYWORDS

Fiber-cement, Lignocellulosic fibers endurance, Ternary Portland cement, Pozzolan and Gypsum systems.

## 1. Introduction

Recent efforts to produce vegetable fiber reinforced composites for construction purposes have been intensified in order to enable these products from a technical and economical point of view. Lignocellulosic fibers present a potential use as reinforcement due to their optimal mechanical performance, availability and reduced cost if compared with synthetic fibers usually applied in air-cured fiber-cement. However, vegetable fibers durability as reinforcement for fiber-cement is one of the most important shortcomings [1–6]. Although this problem has been widely addressed, up to now this degradation mechanism is still one of the biggest concerns related to a loss of mechanical properties within the cementitious matrices. Between the most recent studies, different hypotheses are exposed to explain this phenomenon:

a. an aging process due to fiber mineralization, resulting in a reduction of the tensile strength of the fibers and a decrease of the fiber pull-out ligament after fracture. This mineralization process is a result of migration of hydration products (mainly calcium hydroxide [$Ca(OH)_2$]) to the fiber structure [7];

b. deterioration due to the alkaline hydrolysis because the low corrosion resistance of lignin and hemicelluloses that exist in the middle lamellae of the fibers and cellulose molecules in high alkalinity environment [8];

c. secondary ettringite precipitation into pulp fiber within cement matrix [4,9].

A definitive solution to permit vegetable fibers to be used as reinforcement in the conventional fiber-cement is far from being offered. Also, many publications have broached natural fibers durability in cementitious environments with alternative approaches. A possible solution is fiber treatment to preserve thereof from a chemically aggressive environment [10–12]. Another option to avoid fibers degradation is to limit matrix alkalinity, by reducing pH of the pore solution in cementitious matrices. This alternative has also been tested by different studies achieving remarkable results by means of diverse techniques: cement matrix carbonation [13–15] and using pozzolanic materials [16]

Nevertheless, in all these cases alkalinity reduction is based on calcium hydroxide [$Ca(OH)_2$] reduction which is generated during cement hydration. These techniques require a certain reactivity time [17–19], before decreasing alkaline environment in early stages [14,15]. Therefore, calcium hydroxide reduction from the matrix by using pozzolanic materials may not be considered a fully effective method.

There are binder matrices with lower cement content with possible application in civil construction and acceptable mechanical performance, like cement, gypsum, pozzolan blends. According to Roldán [20], it is possible to use FA to enhance the compatibility between cement and gypsum and at the same time achieve a satisfactory mechanical performance. Thus it is possible to obtain new economic and environmental low cost materials with a considerable reduction of cement content. These binder materials, besides reducing calcium hydroxide content, might also help to preserve fibers, surrounding them with gypsum particles. In this way, more chemically compatible matrices can be obtained without the prejudice of mechanical performance degradation.

In order to get lower alkalinity matrices this ternary system were be assessed in different stages;

- Firstly pH and electrical conductivity of different paste mixes are studied over time;
- Once the mix with a lower pH at early ages is obtained, it is employed in the production of fiber-cement elements to evaluate their flexural performance and their ability to preserve the fibers after being aged.

## 2. Materials and methods

### 2.1 Materials and preparations

The cement used for this research is Portland CEM I-52.5R according to BS EN 197-4:2004 [21], with a mean particle size value of 14 µm. The gypsum used, with no hardening regulator additives, meets the BS EN 13279-1 [22] standards. This gypsum has a purity index over 75%, retained fraction on the 200 mesh below 50%, maximum combined water value of 6%, minimum pH value of 6 and flexural strength higher than 2.0 MPa at 28 days.

Fly Ash used is F class, from silica or silicoaluminte rich fly ashes, with a specific gravity of 2.52 g/cm$^3$. Chemical composition by means of X-rays fluorescence of the Fly Ash is shown in Table 1. The original Fly Ash (FA) has a mean particle size of 29.9 µm and 10.4 µm for milled Fly Ash (FAm). Particle size distribution was determined by laser diffraction spectroscopy.

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | SrO | $TiO_2$ | $P_2O_5$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|
| % by mass | | | | | | | | | | | |
| 38,34 | 22,98 | 20,14 | 13,25 | 0,95 | 0,35 | 1,06 | 0,25 | 0,07 | 0,94 | 0,35 | 1,32 |

Table 1. Fly Ash composition

The water used for specimen's preparation and pulp extraction is characterized in Table 2. For paste molding and fiber observation at optical microscopy deionized water is used.

| Chloride | $Ca^{+2}$ y $Mg^{+2}$ | Sulfates | pH | Conductivity |
|---|---|---|---|---|
| 93mg/l | 480mg/l | 298mg/l | 7.88 | 939µS/cm |

Table 2. Water characterization

Cellulosic pulp fibers used in this work (pine fibers) are obtained from cement packaging kraft pulp. The process to get this cellulosic pulp is mechanical dispersion in water solution. For this purpose, cement packaging kraft is previously torn in smaller pieces and immersed in water for

24 h. After water immersion the kraft pieces are mechanically dispersed in water suspension for 20 min at 2000 rpm. The excess of water from the suspension is removed by filtration and humid pulp is kept refrigerated at 5 $^{o}$C until its use. Table 3 presents the main physical properties for this recycled pulp.

| Characteristics of the unbleached and unrefined softwood pulp (Pinus) | |
|---|---|
| Ashes (%) | 3,36 ± 0,62 |
| Fibers ($10^6$/g) | 1,32 ± 0,07 |
| Length arithm. (mm) | 2,19 ± 0,16 |
| Length weighted in length (mm) | 3,325 ± 0,12 |
| Width (μm) | 24,17 ± 0,91 |
| Coarseness (mg/m) | 134,25 ± 20,76 |
| Kink angle (◦) | 38,05 ± 0,02 |
| Kinked fibers (%) | 11,08 ± 0,21 |
| Curl. (%) | 0,82 ± 0,06 |
| Rate in length of macrofibrills (%) | 47,23 ± 1,76 |
| Broken ends (%) | 36,17 ± 3,53 |
| Fine elements (% by length) | 3,51 ± 0,34 |
| Fine elements (% by area) | 4,55 ± 0,64 |

Table 3. Fibers characterization

By using the pulp from the kraft paper the ratio of fine elements is reduced when compared to other pulp sources as hemp [1] or eucalyptus [2]. Also pine kraft pulps present longer fibers which could difficult their dispersion in the matrix. [1]. However, the high arithmetic length, length weighted in length, average width and coarseness values of the pine pulp used in this work offers the possibility of promoting high pull-out bonding with lower porosity. This factor may help to see the efficiency of lower alkalinity matrices to keep high adherence between long pine fibers and matrix after ageing.

## 2.2 Test methods

The different tasks carried out during this study have been structured according to the next diagram (Fig. 1):

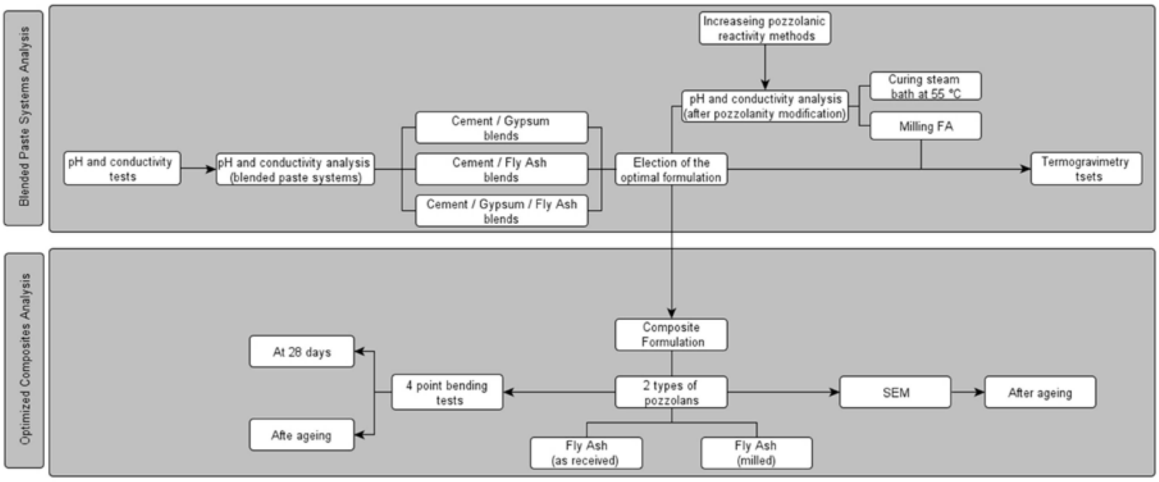


Figure 1- Schematic diagram with the work structure.

## 2.2.1 Blended paste system analysis

### 2.2.1.1 pH and electrical conductivity analysis of the blended paste systems

According to the ternary systems to study, three groups of blends may be observed, as shown in Figure 2. This pH and electrical conductivity analysis is conducted to observe the alkalinity and hydration evolution of the paste systems over time (at 1, 4 7, 14, 21, 45, 60 and 90 days for blended paste systems and 1, 2, 3, 4, 5, 10, 15, 21, 28 and 60 for samples with modified pozzolanicity) and determine which mixes achieve a lower in shorter time.

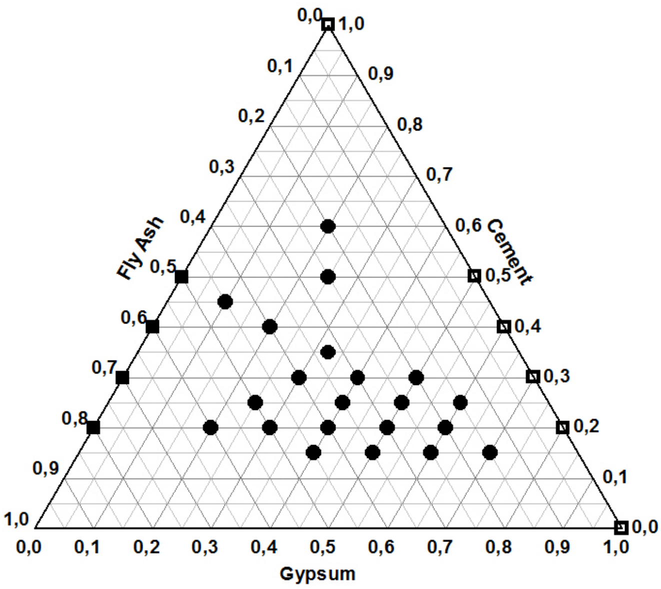

Figure 2. Ternary system blends (Hollow square series correspond to cement, gypsum and their blends; Solid square series correspond to cement-fly ash blends; Solid circle series correspond to C-G-FA blends (inner points in the diagram)).

After the initial test with all the previous mixes analyzed (corresponding to 31 dots in the ternary diagram), different methods to improve pozzolan reactivity, e.g., Fly Ash milling and steam bath curing was used to achieve lower alkalinity in shorter times.

For pastes samples, 50 g of cement-gypsum-fly ash blend are mixed with 30 g of deionized water (water/binder = 0.6) for a mixing time of 30 s, until paste homogenization. Curing is carried out in a plastic bottle. In the first stage curing bottles are kept in a humidity chamber with a relative humidity of 95% and a temperature of 20$^{o}$C and for the next evaluation stage curing are stored in a steam curing chamber at 55$^{o}$C.

For each test age, a hardened paste specimen is crushed and milled and two aliquots of 1 g each are obtained. Both aliquots are dispersed in 100 mL of deionized water and mixed for 5 min at 700 rpm. Then pH and electrical conductivity are measured using a pHmeter (Crison micropH 2001) and conductivimeter (Crison micro cm 2201) at 20 ± 5 $^{o}$C. Each measurement is repeated after 5 min. In case of a significant difference (pH value diverging ± 0.1 from the previous measurement), the process is also repeated after 5min until stable non-significant difference.

#### 2.2.1.2 TG & DTG analysis of the blended paste systems

For thermogravimetric analysis, hardened pastes at different ages (3, 7, 14 and 28 days) were grinded into powder (until particle size under 75 microns). TG 850 model, Mettler-Toledo® equipment is used. 50-70 mg samples are placed in sealed aluminum crucible, in air atmosphere, heated from 35 to 635$^{o}$C with a heating rate of 10$^{o}$C/min. Thermogravimetric tests are performed on the different mixes selected for the fiber-cement production. Termogravimetric tests are also performed for samples with milled Fly Ash.

### 2.2.2 Optimized composite analysis

#### 2.2.2.1 Microscopy (SEM)

JEOL JSM6300® is used. Images are obtained from secondary generated electrons applying a 20 kV voltage, from a work distance of 15 mm. Samples for SEM were cut off from fiber-cement elements and used to observe fibers state after their ageing process.

#### 2.2.2.2 Flexural tests

Since reinforcing fibers are used to improve the composites flexural performance, 4 points bending configuration was used to assess fibers effectiveness, at 28 days and after ageing. Mechanical tests are performed using Instron® 3382 equipment. By means of a 1 kN cell load, 4 points bending tests are carried out, with a load speed of 1.5 mm/min and a finishing load of 50% from maximum load. 100% Portland cement samples are used as reference alkaline matrices samples. Specimens are reinforced with 5% of pulp by mass according to Bezerra et al. [23] since in this study the compositions that suffered the most perceptible flexural degradation were those with a 5% by mass of reinforcing elements. After pH and electrical conductivity evaluation the two matrices mixes are tested. Table 4 shows these mixes.

| Mix | Cement (%) | Gypsum (%) | Fly Ash (%) |
|---|---|---|---|
| F1 | 15 | 50 | 35 |
| F2 | 20 | 50 | 30 |
| 100%C | 100 | 0 | 0 |

Table 4. Matrices mixes for mechanical tests

The cement-based composites were molded in plates measuring 200mm×200mm. They were prepared using a slurry vacuum dewatering device followed by pressing as described in detail by Savastano et al [24].

Bending tests are performed at 28 days after molding and after ageing treatments. For samples with milled Fly Ash (AFm) the ageing treatment applied was 10 months (F1 mFA and F2 mFA) in a climatic chamber at 25 $^{o}$C and 95% HR. For samples with Fly Ash (F1 and F2) the ageing treatment applied was of 28 days in a thermal curing bath.

## 3. Results

### 3.1 pH and electrical conductivity

3.1.1. Pastes of cement and gypsum

During the first stage, in order to determine the optimal binder matrix blend for composites reinforced with cellulosic fibers, pH and electrical conductivity trend were measured along time for both sort of binders separately used in the matrix: cement and gypsum.

As shown in Figure 3a, pH keeps reasonably stable along time for each binder for the studied period. For gypsum, a slight oscillation occurs, but values in the early stages are between 8.16 and 9.58. For Portland cement a similar phenomenon happens. In this case pH oscillation is even more gradual, with results always between 12.71 and 12.99. This difference in the pH values for each paste (3-3.5) reveals a differential alkalinity and, therefore, a different potential application as a binder. Given the time constraints of the study were 90 days, and assuming as can be expected that these be maintained stable at longer times, the study would reveal a difference of alkalinity and, therefore, a different potential application as a binder. These differences in pH values are due to the presence of alkaline and alkaline earth products from cement hydration, mainly, calcium hydroxide [$Ca(OH)_2$] [24].

Electrical conductivity results show a close tendency to pH evolution since electrical conductivity and pH are related. For 100% cement pastes values vary between 8.40 and 9.90 mS/cm, meanwhile for gypsum pastes the variation goes from 2.09 up to 2.31 mS/cm. The only difference observed from pH tendency is that cement pastes electrical conductivity presents a minor increase when gypsum values stay constant. The increase in electrical conductivity for cement pastes may be associated with the development of crystalline structures in the matrix.

3.1.2. Cement/gypsum blended pastes

From results in Figure 3b it may be pointed out how Portland cement has an important influence in pH values. Regardless of the blend proportions, pH values diverge from 12.50 and 12.89. These values are neatly adjusted to the registered values for cement based pastes. Again, electrical conductivity results meet the pH behavior and with cement high influence. Values slightly differ from values for 100% cement and a trivial increase with time is reproduced as happen for cement pastes. Despite of replacing up to 80% of cement by gypsum, gypsum influence in alkalinity is rather limited.

### 3.1.3 Cementfly ash blended pastes

In order to analyze how the presence of a pozzolan material affects the matrix alkalinity, pastes made out of cement and fly ash were studied. Firstly, gypsum was not considered because the initial pozzolan reaction comes from calcium hydroxide. Dosing of the blends and their pH and electrical conductivity values are also shown in Figure 3c. From the pH values it can be deduced that pozzolanic reaction begins to progress approximately at day 60. Until that age pH is around 12.70, which suggests high concentration of portlandite in the paste. It also may be seen that when replacing between 50-60% of cement (high cement samples), pozzolanic reaction is still insignificant. However, for higher substitutions of cement (70-80%) an appreciable reduction takes place (pH value down to 11.21 after 90 days).

Over again, according to electrical conductivity results, pH tendency may be extrapolated as well. Electrical conductivity values stay similar to early age values until day 60 and from there an anticipated decrease might be monitored for pastes with a cement replacement of 70-80% (low cement pastes). An important decrease from 60 to 90 days was observed for this blend (from 6 to 3 mS/cm): this behavior is attributed to the pozzolanic reaction, which decrease the amount of available portlandite after 60 days.

The difference between pH and electrical conductivity results is that for conductivity results a disparity in values from the beginning is produced according to the amount of cement. The higher quantity of cement reveals the higher conductivity results. This distinction may be explained by the high pH values related to the presence of $Ca(OH)_2$ that in the early ages occurs in the matrix. Consequently, even though facilitating pozzolanic reactions and reducing the portlandite present within the matrix, an important reduction in the quantity of cement must be achieved to reduce high alkaline levels and assure a less harmful environment for vegetable fibers during early stages [17].

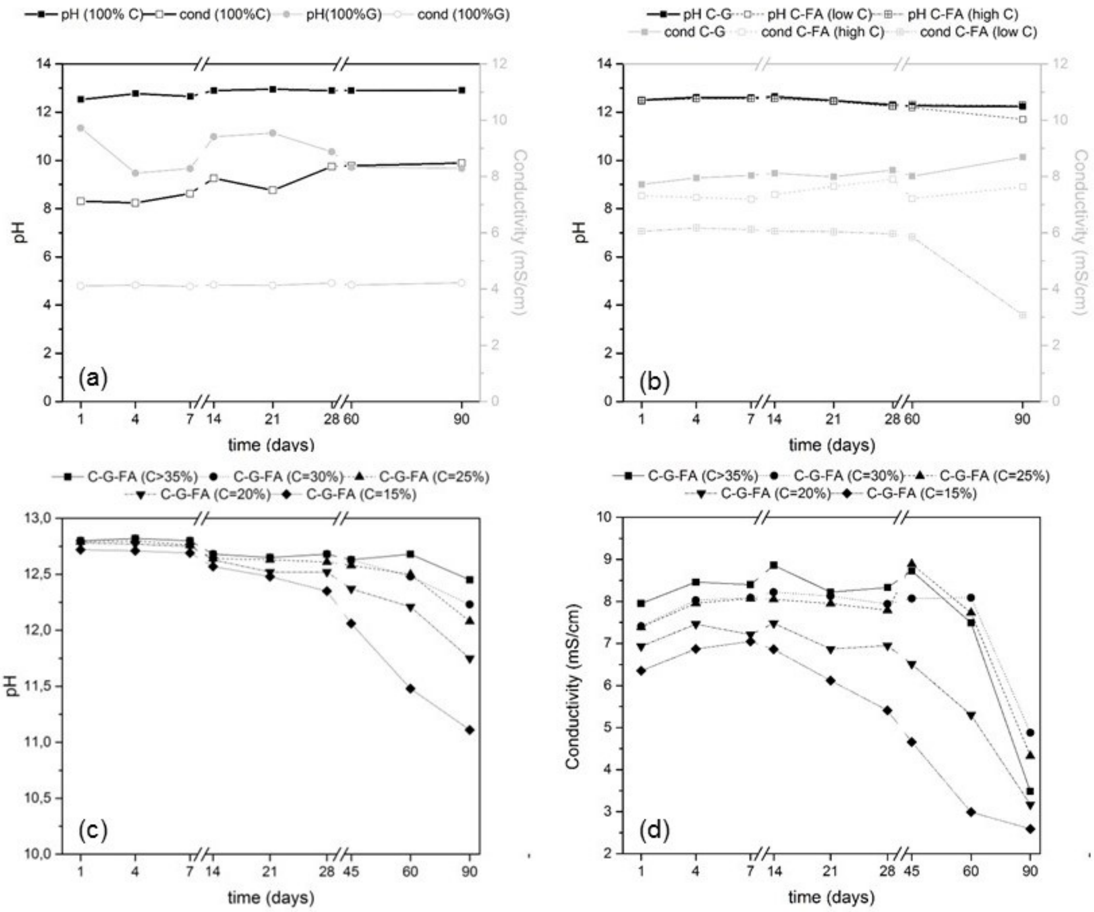


**Figure 3 (a**) pH and electrical conductivity trend for 100% portland cement and gypsum samples. (**b**) pH and electrical conductivity trend for cement-gypsum blend samples (average blends) and cement-fly ash blend samples (high and low cement content). **(c)** pH values for cement-gypsum-fly ash blends for different concentrations. (**d**) Electrical conductivity values for cement-gypsum-fly ash blends for different concentrations

3.1.4. Cement/gypsum/fly ash blended pastes

When gypsum is added to cement and fly ash (Figures 3c and 3d), changes in the trends produced by pozzolanic reaction have been observed. At 60 days, for cement-fly ash blends reductions in pH and electrical conductivity values were observed for low cement content blend. Now, in the gypsum containing mixes, these reductions were observed for earlier ages. Thus it can be assumed that gypsum has certain effect in the paste reactions, at least until day 90. Certain differences may be considered. Lowest cement content blends show pH values close to 12.50 at 21 days: however, after 45 days a significant decrease of pH was observed, and reached values were lower than 12.25 for mix with 20% of cement as can be seen in Figure 3c. The most important pH regression happens after 60 days, although most of the samples keep values over 12 even at 90 days.

From 45 days, samples with 15% content in cement begin to register a pronounced pH descent. For these samples the descent is significant, reaching values close to 11 after 90 days. For the rest of the samples pH value descent takes place at 45 days though alkalinity remains high (around 12) even at 90 days.

Regarding electrical conductivity, an intense decline appears, in some cases in more than 4.5 mS/cm. Thus, at 45 and 60 days, an intense decrease was observed for pastes containing 20 and 15% of Portland cement. This decreasing was produced earlier than that observed for cement/fly ash mixes, suggesting that there is an important role of gypsum in the reduction of available portlandite. This phenomenon may be explained because, even though portlandite crystals remain in the matrix, after a certain age, part of portlandite particles reacts with fly ash to form silicate gels or hydrated calcium silica-aluminates, reducing the amount of free ions from portlandite in solution; additionally, the reaction of alumina phases from fly ash with portlandite and sulphate ions produces more cementing phases [25]. Contrarily, while the conductivity within the paste is reduced, [$Ca(OH)_2$] still has a high alkaline power, so as long as calcium hydroxide is not completely removed pH keeps high.

The two ages where electrical conductivity for most of the mixes decreases are 45 and 60 days. It may also be pointed out that for samples with higher content in cement, conductivity reduction starts at 60 days whilst for samples with less cement content conductivity reduction starts earlier.

For samples with 15% of cement pH values decrease much earlier than for the rest of the samples. From the beginning these samples show a lower electrical conductivity than the rest, around 6.30 mS/cm, and a drop takes place to values around 2.20-2.47 mS/cm at 90 days. It is remarkable that these values are in the range of values achieved by the samples made of 100% gypsum.

3.1.5. Election of cement-gypsum-fly ash pastes composition to develop low alkalinity matrices for composites reinforced with vegetable fibers

For the election of the paste as a matrix for composites three factors are studied:

- pH evolution of the pastes along time;
- mechanical properties of the pastes;
- optimization of waste reuse for composite elaboration.

First and third criteria converge with identical conclusions, because for both aims it is needed to reduce the cement amount for the matrix. As it has been proved, the lowest pH values are obtained when pastes are dosed with 15% of cement. Besides, from an environmental point of view, the maximum optimization of waste reuse is achieved when the amount of cement is also reduced [26].

Nevertheless, mechanical properties [20] are higher when the content in cement is high. Definitely the optimization of mechanical properties in combination with economic cost leads to establish a "mechanical properties/cost" ratio. It is proved [20] that the best ratio is that for pastes with 20/50/30 (cement/gypsum/pozzolan). Taking into account that diminishing pozzolan content increases notoriously pH of the samples, the mix 15%C/50%G/35%FA is also chosen.

In order to fulfill all the requirements, the mixes considered to develop the low alkalinity composites are (Table 4):

- 20%C-50%G-30%FA
- 15%C-50%G-35%FA

3.1.6. Next evaluation

The next evaluation tries to analyze pH and electrical conductivity and evolution with time of the chosen mixes, but trying to modify the pozzolanic reactivity. The pozzolanic reactivity modification intends to reduce the time to achieve low pH values.

The pozzolanic reactivities modification techniques used are:

- Fly ash milling
- Steam bath curing at 55 °C

Evidently, the expected aim is achieved with the introduction of new pozzolanic reactivities (Figures 4a and 4b). At 2 days, all the blends show pH values between 11.5 and 12.5. Samples with milled FA show values around 11.5. In this way it is proved that both steam curing at 55°C and fly ash milling are effective, since to achieve these values of pH with fly ash without milling it took more than 60 days and in this experimental stage now are achieved at 2 and 21.

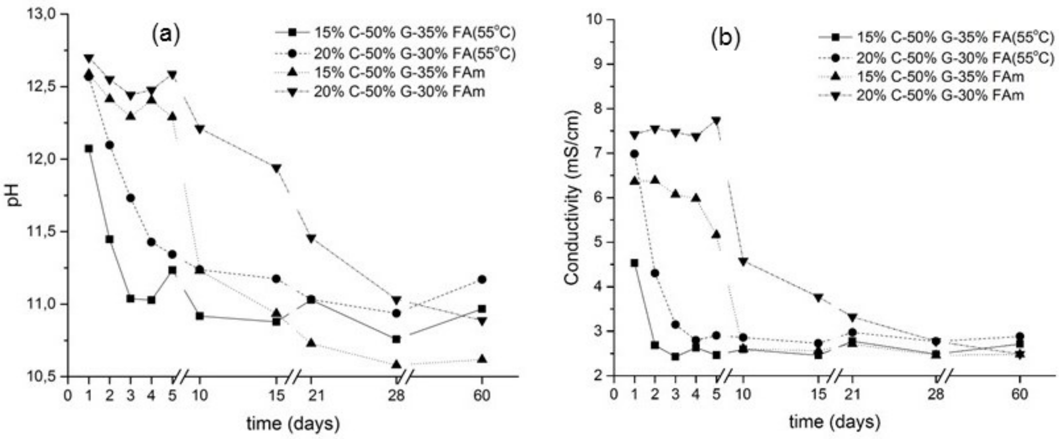


Figure 4. (a) pH and (b) electrical conductivity trend of the selected matrices respectively.

This considerable reduction of pH means a lack of portlandite initially released during cement hydration. Besides, after 21 days it is seen that all but one mix confirm values below 11 that stay low until 60 days.

Concerning conductivity, for samples with milled FA after 4 days values are below 3. Once again the values achieved by these samples are in the range of those made of 100% gypsum. Consequently in 4 days all the soluble crystalline elements produced during cement hydration disappeared.

## 3.2. TG and DTG analysis

Figure 5 shows the results of the TG analysis with the mass loss curves for the different samples produced with blended matrices at different ages (3, 7, 14 and 28 days). From this TG analysis, for all the samples, it may be concluded that the longer curing time is associated to the more hydration gels present in the samples. This can be deduced because for each sample, mass loss increases between 3 and 28 days (20% higher) and this increase is larger for samples containing higher percentages of Fly Ash and milled Fly Ash [20].

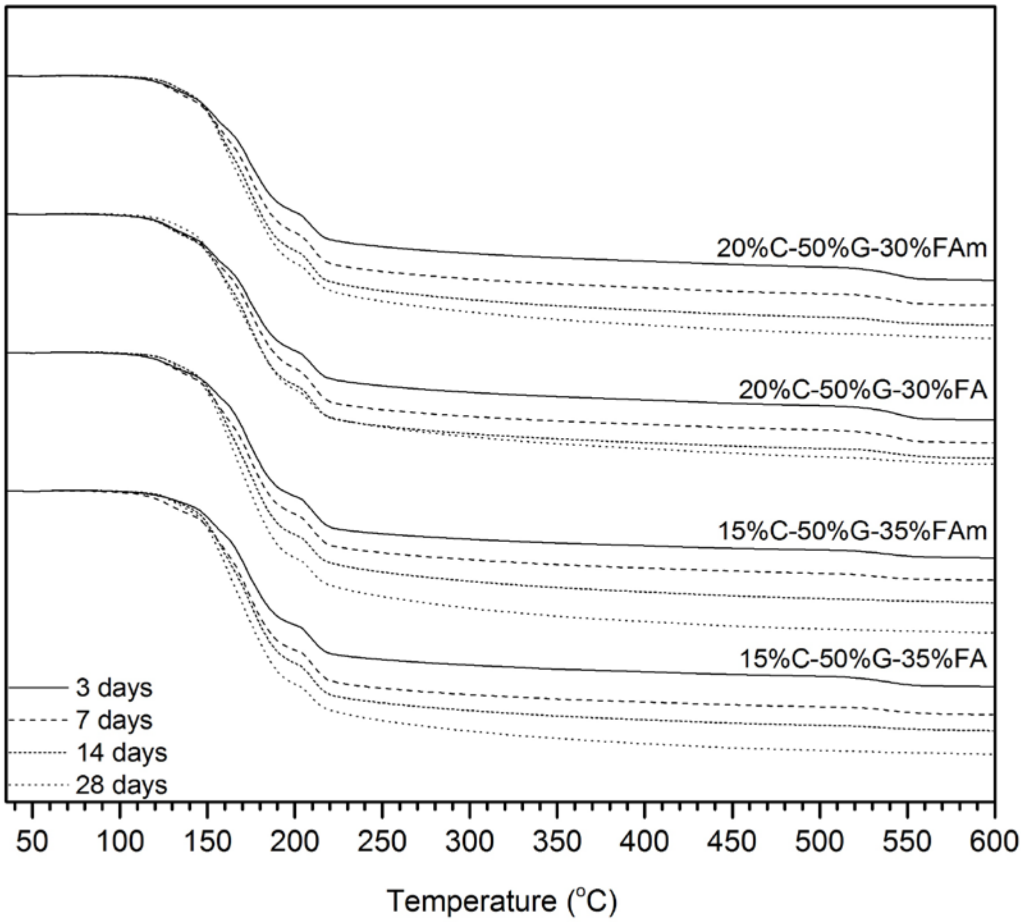


Figure 5. TG analysis showing the mass loss curves for the different samples made with blended matrices at different ages (3, 7, 14 and 28 days)

It can also be seen that in particular, mass losses are greater in the region up to 235°C, where approximately 80% of mass loss occurs. Within this range mass loss may be associated to dehydration of different phases in the pastes. For hydrated gypsum two different dehydration processes take place: $CaSO_4 \cdot 2H_2O$ at 100-140°C and $CaSO_4.1/2H_2O$ at around 150-180°C. Also for Portland cement- pozzolans blends diverse dehydration developments come about: CSH at 120-125 °C; ettringite at 136-143 °C and for CAH-CASH between 200-205°C. The rest of mass loss happens at higher temperatures (520-580°C) and it is assigned to the presence of $Ca(OH)_2$ [20].

According to DTG results (Figure 6), two different trends may be remarked comparing samples with different Fly Ash particle size and content. The first observable fact is that $Ca(OH)_2$ content is lower for samples with higher content in Fly Ash. For the same Fly Ash percentage, samples containing milled Fly Ash present lower $Ca(OH)_2$ content. This can be explained due to a higher reactivity of the pozzolan. Thus Fly Ash reacts with $Ca(OH)_2$ explaining the reduced alkalinity of this pastes [17].

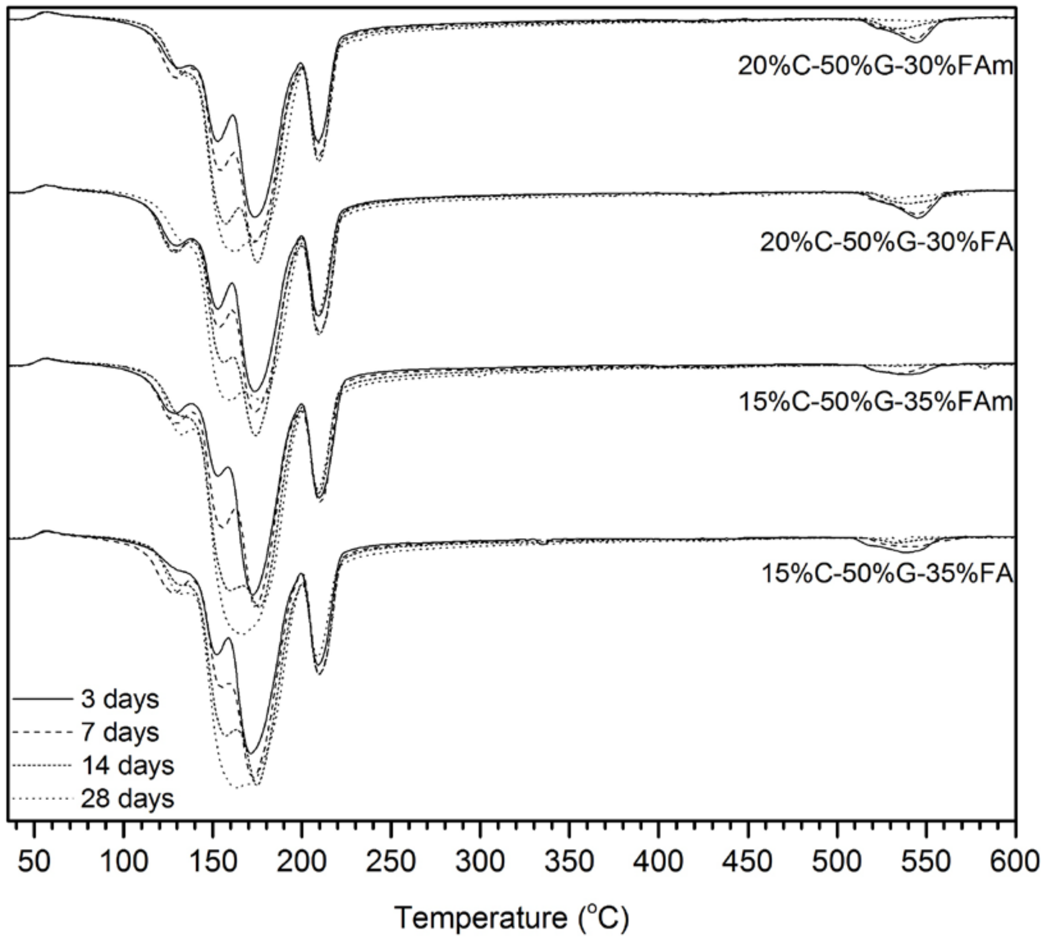


Figure 6. DTG curves for the different samples made with blended matrices at different ages (3, 7, 14 and 28 days)

The second remarkable pattern occurs between 140 and 170°C, where it can be observed for each sample a higher mass loss for longer ages. This mass loss increase can be mainly related to the dehydration of CSH gels which implies a development of these phases over time. From DTG analysis it can also be deduced that for higher content in pozzolan higher amount of CSH gels is dehydrated merging this mass loss with the one associated to the dehydration of ettringite. Even CSH gel formation seems to be more rapidly form for higher content in Fly Ash, probably due to a reduction of the $Ca(OH)_2$ from pozzolanic reaction[17].

**3.3. Flexural analysis after 28 days and after ageing treatment.**

3.3.1. 28 days results

According to Table 5 results, samples with 100% cement matrices show higher modulus of rupture (MOR), elastic limit (EL) and modulus of elasticity (MOE) values in the bending test. Nevertheless these samples have lower specific energy (SE) and deformation values. Taking into account that the first group of properties is strongly influenced by matrix features, it seems reasonable that samples with matrices totally based on cement show better MOR, EL and MOE (10 MPa, 5.5 MPa and 15 GPa respectively). This trend is due to the rest of the samples are constituted by 50% of gypsum, material with lower mechanical performance than cement. Another explanation may be that pozzolan materials that compound the matrix have not completely reacted at that age [18].

For MOR and EL results, a linear relation may be observed. The EL/MOR ratio for most of the samples is 0.55-0.7. After approximately of 60% of flexural load is reached, first crack occurrence, the further increasing in stress carrying capacity is due to the adherence with the matrix which transfers the flexural loads to the reinforcing elements

For MOE results, an important performance difference is seen. Samples with matrices made of 100% cement present superior values compared to the rest of the samples, approximately 4 times higher than samples with Fly Ash and nearly 2 times higher than samples with milled Fly Ash. This differential rigidity may be explained by the fact that hydrated cement presents a lower porosity and, therefore, less possibilities of appearing defects in the matrix.

| Mix | MOR (MPa) | Elastic Limit (MPa) | Specific Energy 50% MOR (J/m²) | Elastic Modulus (MPa) | Specific deformation at MOR (mm/mm) | Specific deformation at 50% MOR (mm/mm) |
|---|---|---|---|---|---|---|
| | | | 28 days | | | |
| F1 | **2,67**±0,74 | **1,57**±0,50 | **1642**±1053 | **3870**±901 | **0,039**±0,029 | **0,066**±0,027 |
| F2 | **2,91**±0,40 | **1,64**±0,46 | **1692**±585 | **3389**±801 | **0,026**±0,005 | **0,071**±0,023 |
| F1_mFA | **6,14**±0,87 | **3,77**±0,82 | **1757**±479 | **8120**±946 | **0,016**±0,003 | **0,040**±0,007 |
| F2_mFA | **5,92**±0,90 | **4,26**±0,84 | **2166**±479 | **8665**±1016 | **0,023**±0,002 | **0,045**±0,006 |
| 100%C | **9,99**±1,33 | **5,49**±1,70 | **928**±211 | **15325**±699 | **0,010**±0,001 | **0,016**±0,003 |
| | | | After ageing | | | |
| F1 ($55^{o}$C) | **5,88**±0,83 | **3,55**±0,81 | **2401**±755 | **8156**±1366 | **0,026**±0,009 | **0,052**±0,014 |

| | | | | | | |
|---|---|---|---|---|---|---|
| F2 (55°C) | **7,42**±1,27 | **4,49**±1,14 | **1565**±467 | **8506**±1427 | **0,017**±0,006 | **0,029**±0,010 |
| F1_mFA | **10,13**±1,09 | **5,68**±2,01 | **2052**±526 | **9269**±1228 | **0,020**±0,005 | **0,031**±0,008 |
| F2_mFA | **12,05**±1,97 | **4,32**±0,91 | **1352**±517 | **9637**±585 | **0,012**±0,004 | **0,020**±0,003 |
| 100%C | **5,51**±0,82 | **4,33**±0,82 | **53**±19 | **13317**±888 | **0,001**±0,000 | **0,001**±0,000 |

Table 5. Mechanical results of the different mixes

Regarding properties influenced by reinforcement elements, higher SE values are achieved by mixes where milled Fly Ash is used as a pozzolanic material (2.2 kJ/m$^2$). It also may be detected that when milled Fly Ash is used SE values are higher than Fly Ash. This might be explained because of Fly Ash reactivity increases with finer particle sizes [27], generating consequently materials with higher SE in shorter time.

Specific deformation values show, in contradiction to SE values, that the bigger deformations are achieved by samples where non-milled Fly Ash is used. This is due to fibers work as a reinforcement of low mechanical performance matrices. Lower tension values are required to begin to transfer all the loads to the reinforcement elements. If fibers start to resist all the stress by their own at low values, they will reach their tensile strength with higher deformation. Thus when fibers start to be under stress conditions, over EL, low tension values have to be resisted (around 1.7 MPa) and hence low energy is dissipated by then. This low tension values range allows the fibers absorb enormous amounts of energy, reaching higher deformations values than the other samples that present a stronger matrix.

3.3.2. After ageing results

After samples ageing, contrarily to what happened at 28 days, samples with matrices made of 100% cement do not preserve any elevated mechanical performance. After ageing, whilst the rest of the samples have improved or hardly preserved their properties, composites with 100% cement matrices have suffered a significant extent. The decrease of flexural strength may be associated to complete degradation of the fibers by alkaline matrix environment. Thus the composite loses its reinforcement to resist the loads over the EL. Additionally, the diminution of the EL (around 20%) may also be associated to fibers degradation that generates imperfections in the matrix yielding to plastic deformation. Analyzing specific energy (SE) results, the complete fibers degradation becomes obvious due to

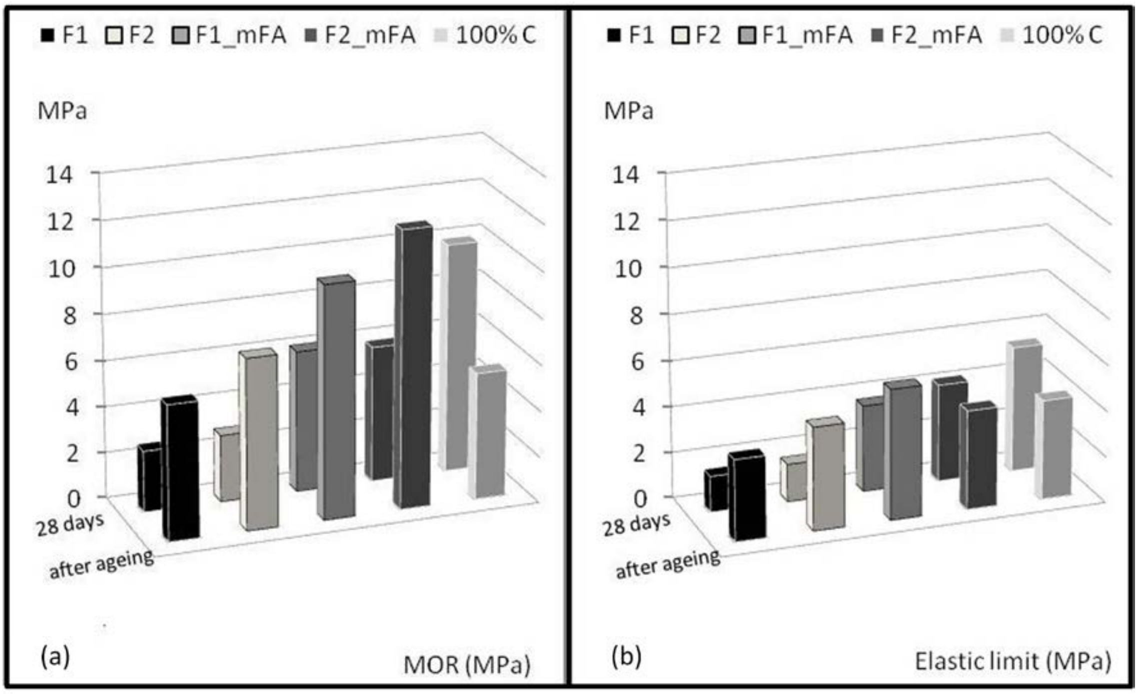


Figure 7. Modulus of rupture (a) and Elastic Limit (b) results respectively for every studied mix at 28 days curing time and after 10 months ageing time.

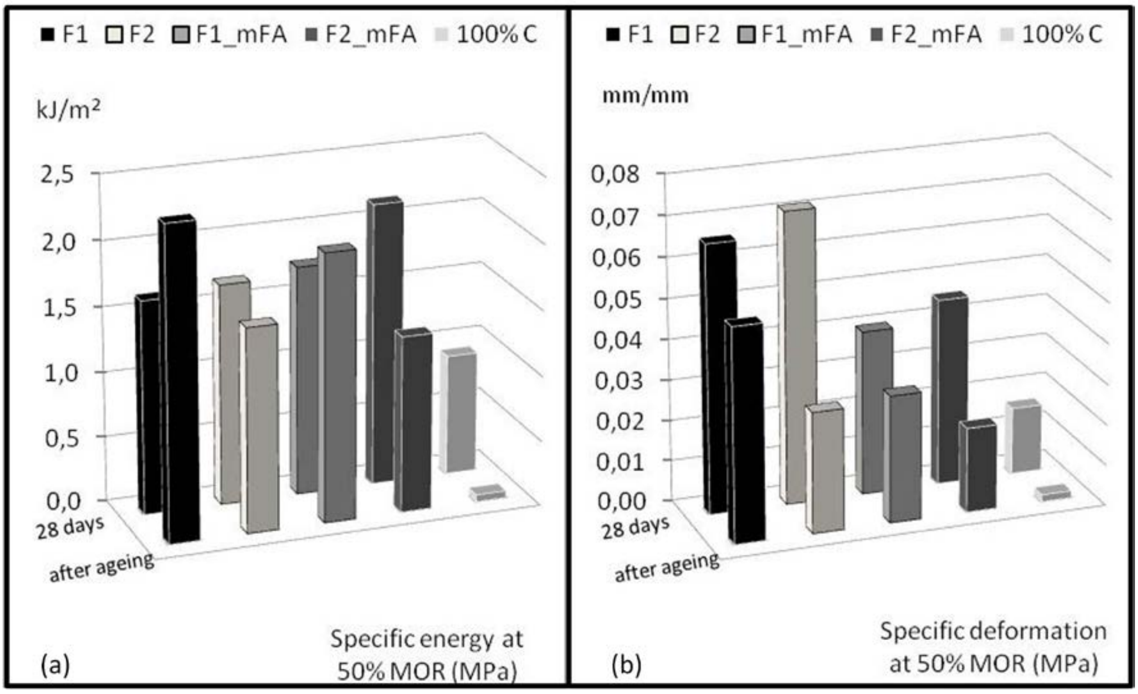


Figure. Specific energy (a) and deformation (b) for every studied mix at 28 days curing time and after 10 months ageing time respectively.

the disappearance of 100% cement samples values. In this case, values go down from 928 $J/m^2$ to 53 $J/m^2$.

As seen in Figure 7a, the highest flexural strength is achieved by mix with milled Fly Ash, in both cases with flexural strength over 10 MPa (10.13 and 12.05 MPa). In addition, composites with non-milled Fly Ash in their matrices have increased their values at 28 days. This improvement is due to the evolution of pozzolanic reactions that, with enough time, make $Ca(OH)_2$ released from cement hydration react with pozzolans, generating matrices with higher mechanical performance [17].

Besides, assuring the maximum humidity conditions (95%) during the whole ageing process, expansive reactions occur within the matrix [28] which closes inner pores improving adherence in the interface fiber-matrix. For these blended pastes expansion does not become an issue because the porosity of these systems, so expansive compounds will help to refill the pores instead of generating internal stress. One evidence of lower porosity and, hence, the occurrence of expansive reactions is the improvement of MOE after ageing. Another phenomenon that displays the better adherence fiber-matrix is the decrease of EL/MOR after ageing for F2 with milled Fly Ash. In this particular case, fibers resist up to 65% of the flexural load. Once the material is cracked, flexural strength can only go higher due to the material that behaves as a rigid body, which in this case is the reinforcement element. Otherwise, after cracking tensile stress would drastically go down.

Higher tenacity values after ageing are achieved by F1 with milled Fly Ash (2 $kJ/m^2$). For F2 samples with milled Fly Ash a slight descent of SE occurs, probably due to minor degradation of the fibers. However, all the specimens show a superior SE than samples with pure cement matrices at 28 days (928 $J/m^2$). Therefore, in spite of a partial deterioration of the fibers, the pulp does not suffer a complete lose of effectiveness as reinforcement. For specific deformation, identical trends are observed for F1 and F2 with milled Fly Ash.

Steam bath cured samples (at $65^oC$) present lower SE values when dosed with higher content in cement matrices. Samples with 15% of cement content SE values are 2.7 $kJ/m^2$, whereas for samples with 20% of cement content values descent down to 1.7 $kJ/m^2$ (approximately 35% less). This fact can be associated to high temperatures that accelerate fibers degradation by alkaline attack [7]. Thus, though high temperatures enhances pozzolan reaction, before all calcium hydroxide liberated during Portland cement hydration reacts, fiber degradation may occur, declining its efficiency as reinforcement.

The same occurrence is reflected for specific deformation, where samples cured at 65$^{o}$C show significant descent of values when they were formulated with higher contents of cement. For specific deformation at 50% MOR, values for F2 samples after ageing decreased by 60% compared to 28 days values. This descent of values after ageing also takes places for F1 values, although it is not that significant (20%) compared to the F2 results.

### 3.4. SEM microscopy

From composites with 30% and 35% Fly Ash cured in humid chamber it may be seen that fibers are well preserved and with incrustations of hydrated products on the surface (Fig 9a). This phenomenon helps to manifest an adhesion and good chemical compatibility between fiber and matrix. Since fibers were pulled out, those incrustations on the fiber surface indicate higher energy consumption for the pull-out to take place due to shear stress. There also are evidences that the layer of matrix bonded to the surface has passed through a portlandite carbonatation process, since there are signs of rhomboidal crystals that suggest the presence of $CaCO_3$. Formation of a hydrated cementitious layer on fiber surface may be appreciated in Fig 9b.

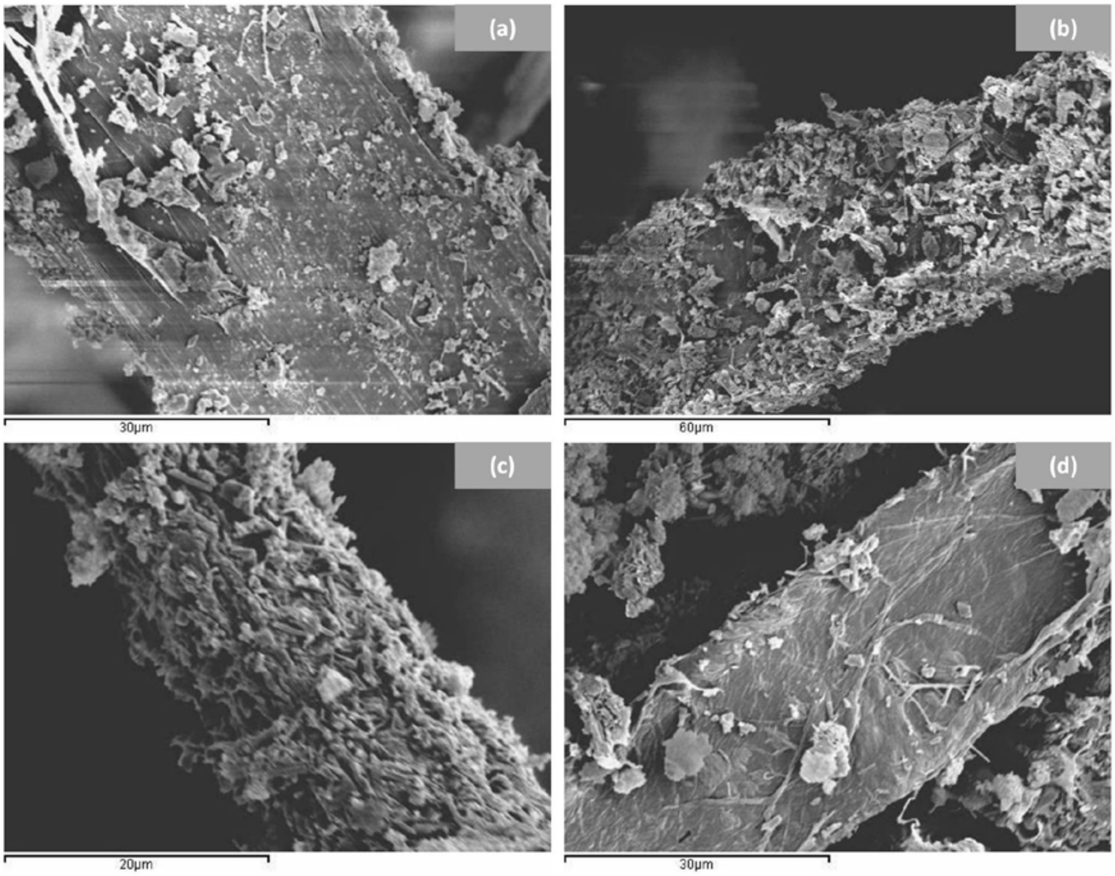


Figure 9. SEM micrographs of unaged samples: (a) (F2 mFA), (b) (F1 mFA), (c) and (d) (F2) showing the different stages of fiber degradation.

When these samples are cured in thermal bath, as shown in Fig 9c, signals of degradation of the fiber are identified. Images show microfibrils exposed on the fiber surface which may involve an outer layer removal of the fiber surface due to an extremely alkaline environment exposition (Fig 9d), however without fiber degradation as such. It also may be seen an impregnation of the surface of several fibers to cement matrix hydrated products. From Fig 10a, it is noted that microfibrils of cellulose are exposed with a preserved surface structure. $CaCO_3$ crystals from calcium hydroxide carbonation deposited on the surface of the fibers (Fig 10b).

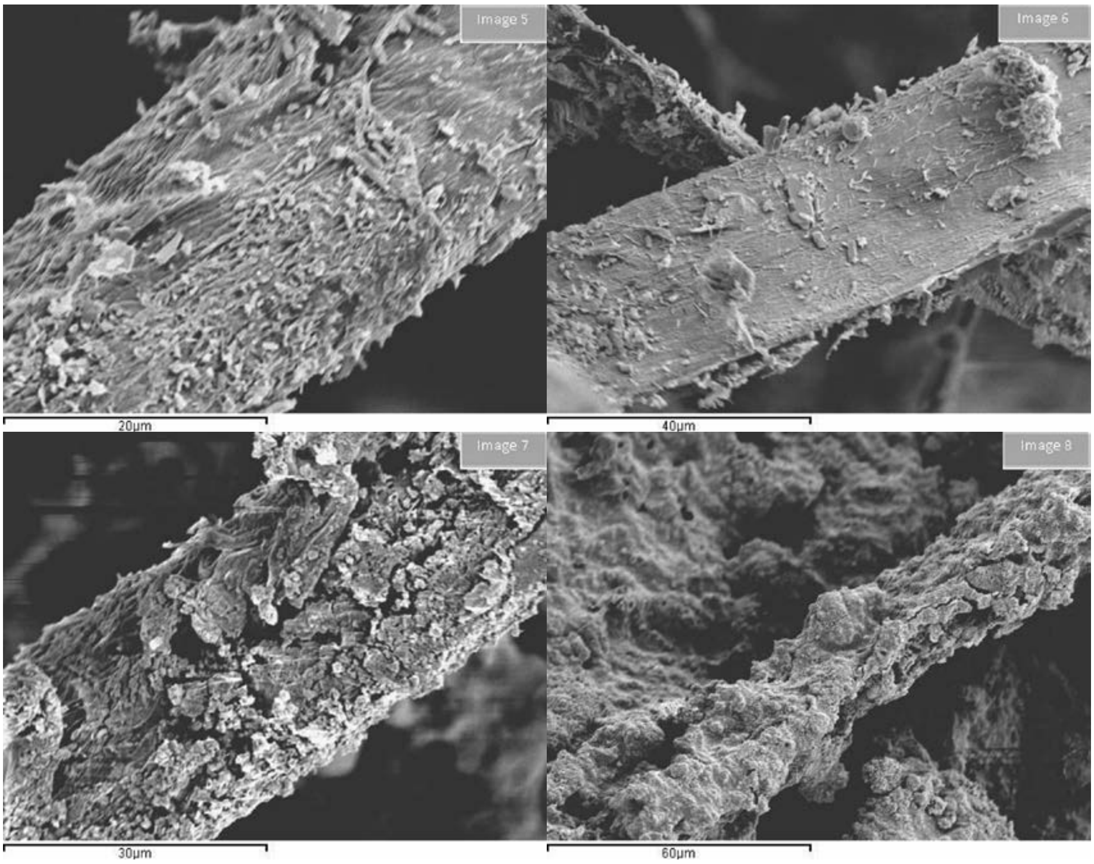


Figure 10. SEM micrographs of aged samples (a) and (b) F2 samples, (c) and (d) control samples, 100% Portland cement, showing the different stages of fiber degradation.

In contrast, different results are obtained when composites are made with 100% cement matrices regardless the type of curing. Fibers appear in a very advanced state of degradation (Fig 10c) and mineralization (Fig 10d).

## 4. Conclusions

The pH and electrical conductivity analysis shows that cement content for cement-gypsum-fly ash blends strongly affects the trend for all the samples. When not milled fly ash is used until 45 days no significant difference is observed for both pH and electrical conductivity regardless the mix.

Reducing Portland cement content, fly ash milling and higher temperatures curing enhances earlier pH and electrical conductivity reduction, making feasible the use of vegetable fibers as mechanical composite reinforcement, even with the presence of gypsum. Besides no deleterious expansion effects are shown. On the contrary, expansion phenomena would only help to enhance the fiber-matrix interface.

From TG and DTA analysis is deduced that $Ca(OH)_2$ reduction is associated to CSH gel formation, which induces better mechanical performances.

Better mechanical performance after ageing is associated to the use of low alkalinity matrices, preserving most of the mechanical properties whereas samples with 100% cement content present strongly reduced features. This suggests that this type material preserves in an efficient manner cellulosic fibers and could be used as constructive elements exposed to low humidity environments.

SEM images also confirm how matrices with low cement content preserve cellulosic fibers from degradation.

## 5. Acknowlegments

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