DURABILITY OF NATURAL FIBERS REINFORCED CALCIUM ALUMINATE CEMENT MATRICES

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Abstract

In this paper we describe a study of the durability of calcium aluminate cement (CAC) reinforced with nano- and micro- cellulose fibers. The nanocelluloses were in the form of nanofibrillated cellulose -obtained from sisal pulp by the application of a high intensity refining process- or as nanocrystals –obtained from acid hydrolysis of pure microcellulose. The setting time (Vicat), strength development (flexural strength), and durability to aging (wet/dry cycles and scanning electron microscopy analysis) were studied. The results have show that the presence of fibers in the matrices modifies the setting times towards reducing them; the mechanical behavior was found better in the fiber CAC matrices compared with CAC mortars. Regarding the durability tests, CAC cementitious systems keep intact the mechanical properties of the fibers. SEM photographs of fracture section show the surface of the fibers with very little state of degradation. These results would indicate that the absence of calcium hydroxide prevents the chemical degradation of cellulose.

Keywords:

Calcium aluminate cement; vegetable fibers, durability

1 INTRODUCTION

Portland mortar or concrete is a composite material in which the cementitious material bounds with aggregates by hydration chemical reactions. Anhydrous Portland cement (PC) consists of four major mineral phases: alite (C_3S), belite (C_2S), C_3A, and C_4AF. The hydration products of this cement are basically ettringite, C-S-H gel and portlandite ($Ca(OH)_2$) [Taylor 1990].

The use of fiber reinforcements in PC matrices has been used in order to improve toughness, ductility, flexural capacity and crack resistance and also to prevent the formation of deformation cracks due to the normal shrinkage of the material [Onuaguluchi 2016]. Traditionally metallic, ceramic (mainly glass) and polymeric fibers in different sizes and forms and different loading contents have been used as reinforcement for the construction sector [Wang 1990]

The interest in using natural vegetable fibers as an alternative to the aforementioned man-made fibers has been growing during the last years mainly because due to environmental concerns. In this sense, the main advantages of using these natural fibers are the renewable resource materials and it use do not represent an increase in global energy consumption neither increases the emission of polluting gases into the environment. There are many studies on mechanical properties of vegetable fiber reinforced cement (VFRC) such as sisal and bagasse fiber that have been reported [Aggawal 1995– Tian 2016].

However, one of the main drawbacks of VFRC is the low durability of the vegetable fibers in the PC mixtures due to the high alkalinity induced by the presence of portlandite [Tonoli 2016]. One major reason for the deterioration of vegetable fibers in cement composites is the dissolution of lignin and hemicellulose linking individual fiber cells by alkaline pore solution [Toledo 2000]. Degradation is further exacerbated by alkaline hydrolysis induced de-polymerization of fibers, whereby linked glucose molecules are disrupted and molecular chain length shortened [Marmol 2013].

Nowadays, research groups working on this topic are pain attention to solve this problem of durability. Some studies have focus in the incorporation of supplementary cementitious materials (SCMs) as fly ash, blast furnance slag, metakaolin, etc. [Toledo 2003-Ferreira 2014]. Other researchers are focusing on some treatments to the fibers as the hornification, whereby fibers are alternately dried and rewetted to irreversibly decrease its water retention value. This treatment has been shown to enhance fiber-cement bond [Claramunt 2010] and fiber durability in cement

matrix [Claramunt 2011]. An early carbonation process of this PC fiber composites have been also explored as an alternative methodology [Tonoli 2016].
However, the use of other cements different than PC has been less analyzed. Calcium aluminate cements were developed as an alternative to PC for its better properties in sulfate ambient. The monocalcium aluminate (CA) is the major phase and hydration products are depending on the temperature. At ambient temperature the hexagonal calcium aluminates (CAH_{10}) are formed; and at higher temperatures the hexagonal calcium aluminates (C_2AH_8) join with aluminum hydroxide are the products of the chemical reactions. The absence of portlandite - that responsible of the low durability of the vegetable natural fibers- make this cement suitable for better durable cement fiber composites.

This paper focuses on the manufacturing and analysis of properties of calcium aluminate cement reinforced with vegetable fibers (CACVFR) as an alternative to the PC reinforced ones in order to achieve better durability to wet/dry aging of these composite materials.

2 MATERIALS AND METHODOLOGY

2.1 Materials

The materials used in this study were:

A Calcium Aluminate Cement ("Electroland" supplied by Cements Molins, Barcelona, Spain).

Five different fibers: Polypropylene fibers (FP) composed of a cross linked monofilaments ("SikaFiber M-12", from Sika S.A.U., Madrid, Spain). Two types of nanocellulose: Nanofibrillated cellulose (NF) prepared by the application of a refining proces in a Valley Beater machine following ISO 5264/1-1979 standard. The refining procedure was applied for 6 hours; and Cellulose Nanowhiskers (NC) obtained from microfiber cellulose by acid hydrolysis using 96% solution of sulfuric acid, washed by centrifugation and dialysis bags filtration, and conserved in powder form after freeze-drying process. And two types of microcellulose: Unbleached softwood kraft pulp (Pinus insignis) (MP) with a 7.8% of lignin (Smurfit Kappa Nervión, S.A. (Spain)) and Cotton linters (ML) (Celsur (Cotton South, S.L., Spain)).

The cement matrices were prepared by mixing the cement, the fibers and the water with the dosage depicted in the Table 1.

Table 13. Dosage of matrices (W=Water) used for Vicat, Flexural and Aging Tests

		Dosage (g)							
Type test	Sample	CAC	W	a/c ratio	FP	NF	NC	MP	ML
Setting time (Vicat) test	CAC	500	150	0.3	-	-	-	-	-
	CAC+FP	500	150	0.3	1.5	-	-	-	-
	CAC+NF	500	150	0.3	-	1.5	-	-	-
	CAC+MP	500	150	0.3	-	-	-	1.5	-
Flexural and Aging test	CAC	400	160	0.4	-	-	-	-	-
	CAC+NF	400	160	0.4	-	0.8	-	-	-
	CAC+NC	400	160	0.4	-	-	0.8	-	-
	CAC+MP	400	160	0.4	-	-	-	20	-
	CAC+ML	400	160	0.4	-	-	-	-	20

2.2 Performed test

Initial and final setting time

The setting parameters of the fiber composites were measured using the Vicat test. The setting test was carried out at room temperature (20 °C). For testing, cement pastes of a normal consistency with a relation of 0.30 water-cement were elaborated. Recording the time of mixture and using the mixer to prepare the paste, performing movements in a slow cycle of 60 seconds, then stir it up manually for 15 seconds by a big spoon to mix particles or dissolve the possible lumps and clots in the paste, then once again we mix it by mixer for 60 seconds in a fast cycle which is the last cycle was. In the case of the mixtures with nanocelluloses, less water was added due to their water content.

Flexural Test

4x1x16 cm specimens were manufactured with the five compositions of the twice nanocelluloses and microfiber, and a non fiber composition as reference mixture, respectively CAC+NF, CAC+NC, CAC+MP, CAC+ML and CAC. Six specimens where produced for each test. The samples were performed following the next steps:
1.The molds were covered in a stainless steel tray and were pressed manually by a machine in order to remove and collect the excess water and to be able of compacting very well the panels. 2. It was applied to the samples by a hydraulic press around 10 tons of force, afterward it was left for 24 hours of rest under the pressure of the steel piece on top of each cell to cover the paste, then the day after was demolded, afterward placed the samples in a humid camera for 7 days at 20 ºC. To perform this test an Incotecnic model MUTC-300 equipped with a 3 kN load cell was used, at a 1 mm/min of cross head speed.

Aging process

After the curing time, ten wet/dry cycles were performed on specimens in order to observe the durability of each mixture. The wet/dry cycle used for this study was 3 days drying in an oven with air circulation at 60º C and 4 days soaking in water at 20º C, to complete one week per cycle. To avoid thermal shock, each stage begins with the same temperature as the previous cycle.

Microstructure of fibers

The fracture section of specimens where studied by using a Jeol JSM 6400 scanning electron microscope (SEM). The surface of a dried section composite was made conductive by sputtering deposition of a thin layer carbon.

3 RESULTS AND DISCUSSION

3.1 Initial and final setting time

The initial setting time is defined as the point when the hydration of the cement components generates an increased concentration of soluble material in the water that will end up precipitating in form of gel or hydrates, and forming rigid and denser compounds. In this case study the nucleation is occurred by the effect of the fibers in the matrix. The surface of the fibers provides an initial starting point where the precipitation begins. In this case, the more efficient is the nano vegetable fiber for its ability to exchange the water; afterward, micro vegetable fiber, for the same reason and then polypropylene and CAC matrix. The Table 2 shows the obtained time results from the Vicat test.

Table 14. Results of Vicat test (min)

Sample	Initial time	Final time	Time process
CAC	303	558	255
CAC+FP	215	470	255
CAC+NF	181	416	235
CAC+MP	198	452	254

The fact that the vegetable fibers modify the hardening process could be due to the dissolution of organic compounds from virgin fibers that modify the hydration reactions [25]. Overall, compared with CAC serial, all fiber-composite mixtures reduce both, the initial and the final setting times. Comparing the different fiber mixtures, the CAC with nanocelluloses presents the shorter initial and final setting times and the CAC plus polypropylene fibers presents the larger ones. Although, more research needs to be done in this area, one reason explaining this behavior could be the nucleation points due to the presence of nanocelluloses which also would justify the accelerating hydration process. Moreover, the vegetable fibers would absorb some water available for the hydration of cement phases inducing a modification of the availability of water for the hydration process. The Figure 1 shows a comparative of these results.

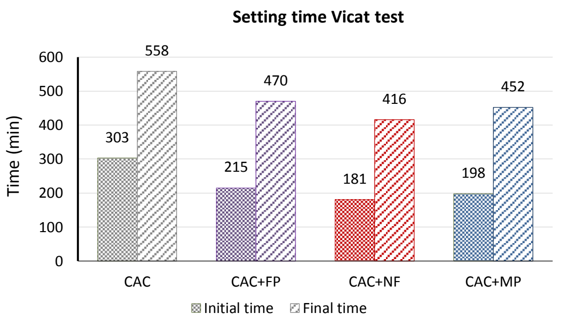

Fig. 54 Setting times for Vicat test

3.2 Flexural test and durability

In the Figure 2 are depicted the representative curves for the bending tests of the specimens at 7 curing days and after the ageing process.

The Figures 3, 4 and 5 presents the average values of the mechanical parameters obtained from the bending curves: the modulus of rupture (MOR); the modulus of elasticity in the area relative to the 80% of the MOR (MOE 0.8) and the toughness, defined area under the curve force versus displacement from the beginning to the limit of 40%of the MOR.

The obtained curves show two different behaviors respecting to the fiber type used. On the one hand, for the composites prepared with the cellulose nanocrystals and nanofibrillated cellulose the behavior is close to a “brittle” material.

In these composites it was found an increase of the MOR values of 5.5% and 9.9% respectively for the NC and NF with respect to the CAC matrix. No significant differences were found for the MOE values of toughness, as it was expected for the brittle behavior of these composites.
On the other hand, the micro fibers reinforcement led to high tenacity values of the composites, although reaching lower values of MOR and MOE 0.8.

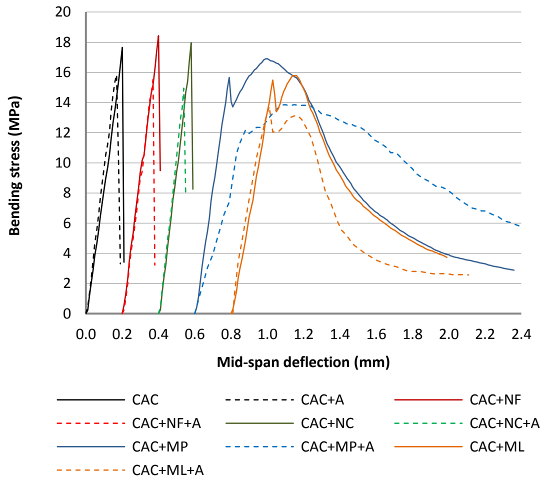

Fig. 55 Representative curves obtained from the bending test. The curves were displaced 0.2 mm respectively to avoid the results overlapping.

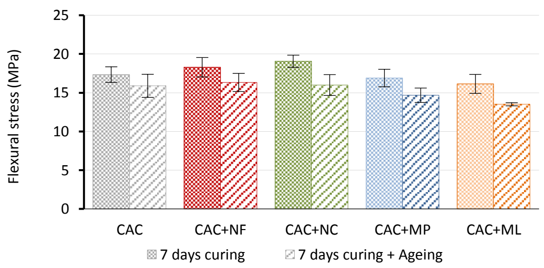

Fig. 56 Average values and standard deviation of MOR obtained from bending tests.

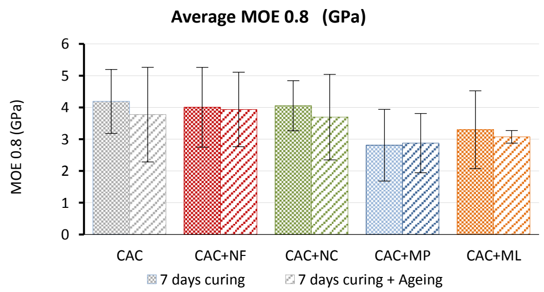

Fig. 57 Average values and standard deviation of MOE 0.8 obtained from bending tests

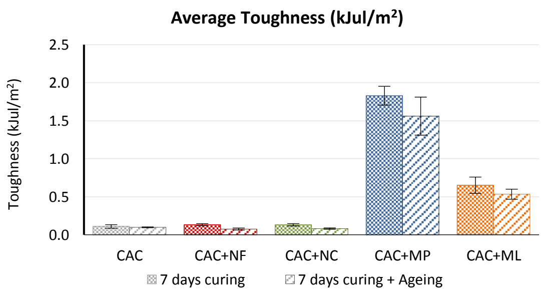

Fig. 58 Average values and standard deviation of toughness obtained from bending tests

Comparing the behavior of the kraft pulp with respect to the cotton linters, as can be seen, the higher values of toughness and MOE were found for the kfraft pulp meanwhile cotton linters led to higher MOE 0.8 values. The fact of the superior slenderness joint to a minor elasticity modulus of the kraft pulp than cotton linters could explain the less reduction of the MOR and the major decrease of the MOE 0.8 respectively. Spite this strength and elasticity modulus decrease compared to the CAC reference matrix, it is remarkable the increase of the toughness of the composites by the effect of both microfibers reinforcement.

Respecting durability test, a general decrease in mechanical strength behavior was found after subjecting the composites to an accelerated aging. The major reduction of the MOR values was found for the composites reinforced with the CN and the cotton linters with reductions of 16.1 and 16.3%, respectively. All these results can be related with the nature of the fiber, both are pure cellulose with major water absorption capacity.

The less decrease was found, on the contrary, for the nanofibrilated cellulose and Kraft pulp, with 10.7% and 13.1% decrease, respectively. Both used fiber types are containing lignin which is the responsible for the reduction of water absorption. In reference to the MOE, the differences between values were found less than the result dispersion values, and that the reason why we attempt that there are not significant differences.

In relation to the toughness values, there were not significant differences and the values are very close to that of materials microfiber reinforced. The decrease was found minor in the kraft pulp, with a decrease of a 14.7%; the cotton linter presented a decrease of 18.1%. Taken in consideration than Spanish Normative allows variations of fibrocement of 25% for fiber cements plates of maximum durability category, the obtained results are acceptable.

3.3 Fibers microstructure

Figure 6 shows several Kraft pulp fibers used in previous researches. The image shows the natural surface of fiber without contact with the cementitious matrix. The surface is clean and a few superficial microfibers can be observed.

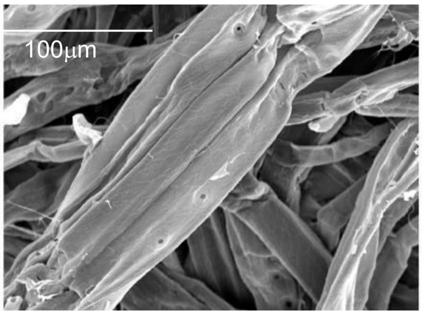

Fig. 59 SEM picture of Kraft pulp fibers.

The Figure 7 presents a detail of fiber surface obtained from a slurry of hydrated PC paste [Claramunt 2013] submitted to 4 wet/dry cycles. The cement paste was slurried during 7 days and regularly during 21 days more in order to separate the fiber from the paste. As can be seen in the picture, the fiber was cracked and with the surface wrinkled. On the other hand, calcium hydroxide particles deposits were observed and originated from the slurry of PC, both on the surface and inside the fiber.

The Figures 8, 9 and 10 show the microstructure of the surface of fibers in matrices CAC+MP and submitted to 10 wet/dry cycles. The general overview of the matrix can be seen in the Fig. 8 there were gaps in the matrix from stripped fibers, but it was not possible to observe any fiber flush at the surface.

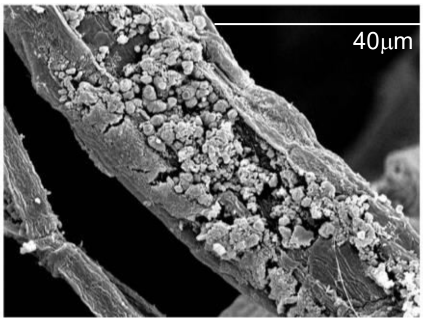

Fig. 60 SEM picture of kraft pulp in PC submitted to 4 wet/dry cycle.

Fig. 61 SEM image of CAC+MP matrix after wet/dry cycles.

A bunch of fibers appears in the Figure 9. Apart from the remaining cement in the surface there were no other surface marks indicating a low durability. The Figure 10 presents a detail of these fibers.

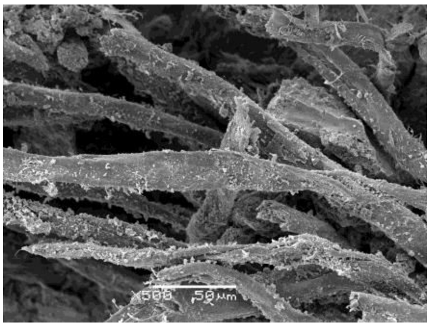

Fig. 62 Microstruture of fiber surfaces of CAC+MP matrix after wet/dry cycles.

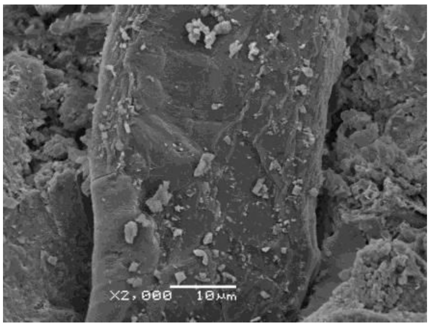

Fig. 63 Microstructure detail of fibers in sample CAC+MP after the wet/dry cycles.

These results are in concordance with the absence of portlandite in the CAC hydrated binders, chemical compound associated with the degradation process of the cellulose fibers in these composite materials.

4 CONCLUSIONS

The following conclusions can be drawn from the present research:

1 The mechanical behavior of fiber cement with CAC matrix reinforced with cellulose fibers was found slightly superior to that of reference samples (CAC).
2 Matrices manufactured with reinforcements of nanometric size fibers have a better strength behavior and a modulus of elasticity to those of microfibers and to the matrix itself, but still maintain the brittleness of the material.
3 Microfiber reinforcements exhibit a small reduction of strength and modulus of elasticity with respect to the fiberless matrix but considerably increase the ductility of the material.

As a general conclusion, these results indicate that the absence of calcium hydroxide of the matrix prevents the chemical degradation of cellulose and make CAC an interesting matrix to be explored in the feel of natural fiber durability.

5 ACKNOWLEDGMENTS

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