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Effect of cellulose microcrystalline particles on properties of cement based composites

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ABSTRACT

The hydrophilic character and water retention capability of cellulose microcrystalline particles (MCC), are useful properties to achieve new developments in cement based materials. This work evaluates the influence of interactions between MCC, cement particles, hydration products and water; on rheology, hydration kinetic, microstructure and mechanical properties of cement based materials. The effect of MCC on mechanical properties of cement mortars with 0 wt.% and 3 wt.% of MCC, were evaluated by flexural and compression tests within two curing procedures (i) *regular curing*: specimens were cured 28 days into lime stone solution (pH 13) at room temperature, (ii) *accelerated curing*: specimens were cured into a lime stone saturated solution for 7 days at room temperature followed by 7 days at 50 °C. Finally they were kept in a dry oven at 60 °C for 48 h. Thermogravimetric analysis was used to characterize the effect of curing procedure and MCC addition on hydration degree of cement materials with 0 wt.% and 3 wt.% of MCC. Results showed that interactions between MCC, cement particles, hydration products and water, decreased the workability and delayed the hydration reaction. Additionally, results from thermogravimetric analysis showed that, both accelerated curing and MCC addition increased the hydration degree of cement materials because of increases in temperature during the curing process and because of MCC releases its water content, contributing to hydration process. From results discussion it was found, that MCC could be added to increases the hydration degree of based composites; additionally it was concluded that cement based composites with MCC could be used to elaborate precast pieces.

1. Introduction

Natural fibers are constituted by several cellulose microfibrils, where cellulose chains are arranged in two types of conformations: an amorphous conformation, characterized by its flexibility; and a crystalline conformation in which the cellulose chains are disposed in organized and repetitive arrays to form crystals [1–4]. Microcrystals of cellulose microfibrils are highly hydrophilic, have high water retention capability and excellent mechanical properties: an elastic modulus of about 150 GPa, superior to glass fibers (85 GPa) and aramide fibers (65 GPa) modulus [4,5].

Hydrolyzing the cellulose chains, MCC can be extracted from vegetable matter by means of a diluted mineral acid at its boiling temperature. The hydrolysis process removes most of the amorphous fraction and destroys the fibrillar morphology of cellulose as follows: first vegetable mater is selected and cuted, then is hydrolyzed converting insoluble hydroxides, oxides and sulfates of vegetable mater in soluble compound that are removed by a filtration process. Finally the filter cake is suspended in water and subjected to a spray drying process, yielding the MCC with a size distribution and moisture content according to the conditions of the last two stages [6].

The MCC have been widely utilized in the food, cosmetics and medicine industries; as stabilizers for aqueous suspensions, flow controllers and as reinforcement of final product [4,5,7]. However, until now there are not known publication that investigate the use of cellulose microcrystalline particles in cement based materials. Developments in cement based materials have shown great progress for humanity, because their usefulness in infrastructure, housing and transport [8]. Portland cement is a combination of minerals specially formulated and processed to react with water by several physical and chemical processes, known as hydration. Water is a substance strongly involved in elaboration of cement based materials, therefore the hydrophilic character and the water retention capability of MCC, are interesting properties to consider exploring potential applications of MCC in cement material.

This work studies interactions between MCC, products of cement hydration and water. In addition, it was analyzed how those interactions modify rheology, hydration reaction and hydration

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Table 1
Mineralogical composition of Portland cement of low alkali 40.

Mineral	Composition (%)
MgO	0.7
SiO_2	20.6
CaO	63.5
Al_2O_3	3.9
Fe_2O_3	4.6
Na_2O	0.5
K_2O	0.6

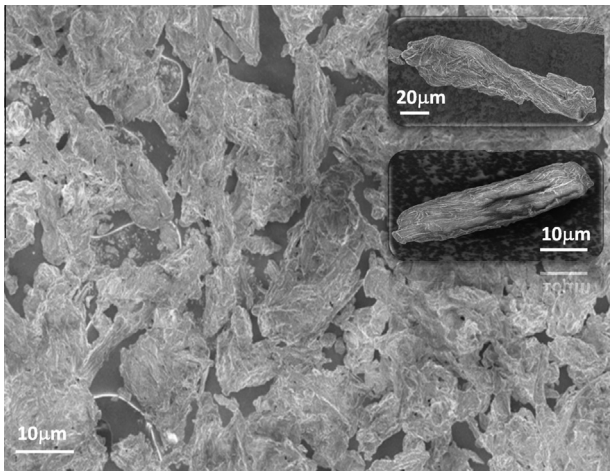

Fig. 1. FE-SEM images of cellulose microcrystalline particles used to elaborate cement materials.

degree. Until now are known few investigations on the subject of cement based materials with micro and cellulose nanofibers; their results usually are focused on the mechanical properties of cement based materials without study the interactions between micro and nanocellulose fibers and cement particles and without determine how those interactions changes the properties of cement based composites. Mohamed et al. [9] studied the effect of microcellulose addition to a self-compacting concrete mix. They found that microcellulose fibers addition (21 wt/v.%) increased compression and flexural resistance after 7 of curing. Moreover, Peters [10] determined that adding 3 wt.% of a mixture of micro and cellulose nanofibers to a reactive powder concrete with high compressive strength, increased their impact strength by 53%. Additionally, Claramunt et al. [11] elaborated cement mortars with nanofibrillar cellulose to studied its mechanical properties; they concluded that addition of 3 wt.% of nanofibrilar cellulose increased significantly flexural properties after 28 days of curing. The work of Nilsson and Sargenius [12], is the most recent publication on this filed; they developed Portland cement mortars with 0.11, 0.22 and 0.33 wt.% of recycled cellulose microfibers from the paper industry; in order to characterize changes in workability of fresh mixture, and changes in mechanical properties, autogeneous shrinkage by drying and capillary absorption properties of cement mortars in hardened state. They concluded that, cellulose microfibers addition modifies the rheology; decreases the mechanical properties and has no effect on drying shrinkage properties. However they found that cellulose microfibers addition had a positive effect on the water absorption: increases strongly absorption resistance because cellulose microfibers modify the pore structure of cement mortars.

The aim of this work is investigate the effects of MCC on properties of cement based materials in fresh and hardened state, to evaluate the possibility of use MCC to develop new cement based composites. Techniques used in this work are not commonly used to characterize cement based materials. However its information resulted useful to characterize cement based materials with MCC and to develop applications for cement based composites with MCC as a building material.

2. Materials

2.1. Portland cement

Cement Portland Low Alkali CP40, following Argentinean standard IRAM 50.000 from Cemento Loma Negra Argentina, with 391 m^2/kg of blaine surface was used as received. The general composition of this cement is presented in Table 1; this cement was used to achieve a lower pH on cement materials and reduce the possibility of cellulose degradation by the alkaline environmental.

2.2. Sand

Cement mortars with 0 wt.% and 3 wt.% of MCC were elaborated using standardized sand supplied by MPA Stuttgart University in accordance with EN standard 196-7 [13].

2.3. Cellulose microcrystalline particles (MCC)

The cellulose microcrystalline particles provided by Sigma Aldrich were saturated for 2 days in water. Fig. 1 shows the field emission scanning electronic microscopy images of MCC used in this work. Sigma Aldrich reported that MCC have the size distribution shown in Table 2.

The following methodology was applied to estimate the amount of water absorbed by MCC and replace it to elaborate the fresh cement mix: a proportion of 0.5 g of MCC were mixed with 3 ml of water and left standing for 3 days at 25 °C, to promote saturation. After 3 days the saturated solution, was separated into two phases by centrifugation at 3000 rpm during 25 min. Following several tests, it was found that 0.5 g of MCC absorbed about 1.05 ml of water, which corresponds to 100% of its own volume and 230% of its own mass. The MCC bulk density was calculated by a volumetric method. It occurs that 0.5 g of MCC occupied a volume of 1.09 ml, therefore MCC have a bulk density of 0.459 g/ml.

3. Methods

3.1. Cement pastes elaboration

The composition of cements pastes with 0 wt.% and 3 wt.% of MCC are presented in Table 3; cement pastes were named by its MCC content. A Hobart planetary mixer (Model N-50) was used to mix both cement pastes, following a procedure very similar to described in the EN standard 196-7 [13]. In case of cement paste with 3 wt.% of MCC, first saturated MCC mixture was added to Portland cement, and then the remaining water was added. The mixer was set at the low speed setting for 30 s and then paused for 90 s. A paddle was used to scrape the sides of the mixing bowl during the first 30 s of pause. After the pause, the mixer was set at the high speed setting for 60 s.

Cement pastes were prepared using 3 wt.% of MCC, based on results reported by Peters et al. [14]. They found that 3 wt.% of microcellulose provided the greatest increment in mechanical properties. Higher additions of microcellulose decreased the workability of the fresh material increasing the super-plasticizer requirements.

Table 2
Mass proportions used to elaborate cements pastes.

Material	0 wt.%	3 wt.%
Cement BA	1	1
Water	0.45	0.45
MCC (wt.%) by weight of cement BA	None	0.03

Table 3
Mass proportions used to elaborate cements mortars.

Material	*M* 0 wt.%	*M* 3 wt.%
Cement BA	1	1
Sand/cement	2.7	2.7
Water/cement	0.45	0.45
CMF (wt.%) by weight of cement BA	None	0.03

3.2. Cement mortars elaboration

The composition of Portland cement mortars with 0 wt.% and 3 wt.% of *MCC* are presented in Table 3; cement mortars were named by the letter *M* followed by the *MCC* content. A Hobart planetary mixer (Model N-50) was used to mix both cement mortars in a procedure very similar to described in the EN 196 standard. In case of cement paste with 3 wt.% of MCC, first saturated MCC mixture was added to Portland cement, and then the remaining water was added. The mixer was set at the low speed setting for 30 s. After 30 s of mixing, the sand was added steadily during the next 30 s, after that the mixer was set at high speed for 30 s; then the mixer was paused for 90 s. A paddle was used to scrape the sides of the mixing bowl during the first 30 s of pause. After the pause, the mixer was set at the high speed setting for 60 s. In order to compare mechanical properties prismatic specimens were manufactured (40 mm × 40 mm × 160 mm).

Two different curing procedures were evaluated in both cement mortars and cement pastes [14]:

3.2.1. Regular curing

After 24 h specimens were unmolded and just placed into a lime stone saturated solution for 28 days at room temperature.

3.2.2. Accelerated curing

After 24 h specimens were unmolded and placed into a lime stone saturated solution for 7 days. Then the specimens were maintained for 7 days more into a lime stone saturated solution at 50 °C. Finally they were kept in a dry oven at 60 °C for 48 h.

3.3. Slump test for cement pastes

Stoppage tests like slump test are commonly used in civil engineering because are cheaper and could be developed on-site construction work. They consist in measuring the shape of a fresh material deposit after flow occurred. This kind of tests are based on the fact that if shear stress in tested sample is smaller than yield stress, flow does not occurs [15–19].

The slump test was developed using a mini-cone test. It is a smaller version of the Abrams cone for concrete; its dimensions are shown in Fig. 2a and b shows the final shape of a cement paste tested. Mini slump test was conducted on cement pastes with 0 wt.% and 3 wt.% of MCC. This test was realized following the ASTM: C-143. The mini-cone was supported on a flat glass; once its entire volume was filled the mini-cone was lifted to allow the cement paste to flow. When the fresh cement past reached the equilibrium the slump was measured.

3.4. Density determination for cement pastes (PUV)

The test of mass per unit weight or density determination was carried out on cement pastes with 0 wt.% and 3 wt.% of MCC in fresh state; results were used in calculus of yield critical stress values. This test was performed following ASTM: C-138.

3.5. Monitoring early hydration reaction for cement pastes, from adiabatic temperature data over time

In order to study the hydration kinetics on cement pastes with 0 wt.% and 3 wt.% of MCC, a semi adiabatic box of 150 mm × 150 mm × 150 mm was fabricated using Styrofoam sheets of 15 mm thick and expanded polyurethane foam to fill the voids between the box and the specimen. The fresh cement paste specimen was placed at the middle of the box. The scheme of the semi-adiabatic box and the measure system used are shown in Fig. 3. The semi adiabatic box was placed in a temperature controlled room at 25 °C and the temperature was measured with a *Test Electrical Electronic Corp* data-logging using a *K* thermocouple. The temperature of the system increases as the hydration reaction proceeds, therefore the rate of hydration reaction can be represented as the slope of the curve temperature vs. hydration time [22]. However, this system is not completely adiabatic and is necessary an energy balance to calculate the global heat transference coefficient (U), and correct the adiabatic temperature. Eq. (1) shows the energy balance on the semi adiabatic box:

$$\rho \cdot C_p \frac{dT_{\exp}}{dt} = (-\Delta H) \cdot \rho \frac{d\alpha}{dt} - U(T_{\exp} - T_0) \tag{1}$$

With U is the global transfer heat coefficient per unit mass, $T_{\exp}$ is measured temperature, T_0 is room temperature, C_p is specific heat, t is time and α is hydration degree, ΔH is hydration heat and ρ is the density.

Integrating Eq. (1) when $\frac{d\alpha}{dt} \to 0$, leads to:

$$\ln(T_{\exp} - T_0) = \ln(T_{\exp 1} - T_0) - U'(t - t_1) \tag{2}$$

where $(T_{\exp 1}, t_1)$ are the particular set of values at the beginning of the integration and $U' = \frac{U}{\rho C_p}$ is assumed to be constant.

Eq. (3) shows the relationship between experimental and adiabatic temperatures:

$$\frac{dT_{\text{ad}}}{dt} = \frac{dT_{\exp}}{dt} + U'(T_{\exp} - T_0) \tag{3}$$

where $T_{\exp}$ is the experimental temperature and T_{ad} is the adiabatic temperature.

Finally integrating Eq. (3), leads to expression used to calculate the adiabatic temperature:

$$T_{\text{ad}} = T_{\exp} + \int_0^t U'(T_{\exp} - T_0)dt \tag{4}$$

3.6. Thermogravimetric analysis (TGA)

With the aim of study the effect of MCC addition and curing procedure on hydration degree, cement pastes with 0 wt.% and 3 wt.% of MCC were subjected to a thermogravimetric analysis between 25 and 800 °C at 10 °C/min under N_2; in a thermogravimetrical analyzer (Shimadzu TGA-50).

3.7. Mechanical test for cement mortars

Three point and compression tests were performed in a Baldwin universal machine for cement mortars with 0 wt.% and 3 wt.% of MCC. Those tests were carried out in accordance to EN standard 196-1 [20].

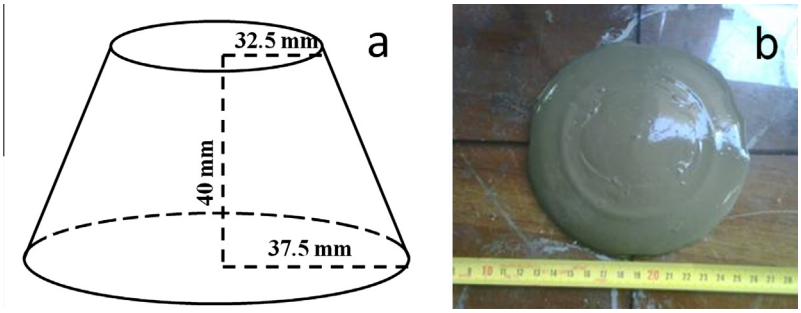

Fig. 2. Images form mini-slump test for cement paste. (a) Sketch of the cone used in mini-slump test. (b) Images of the slump test for cement paste with 3 wt.% of MCC.

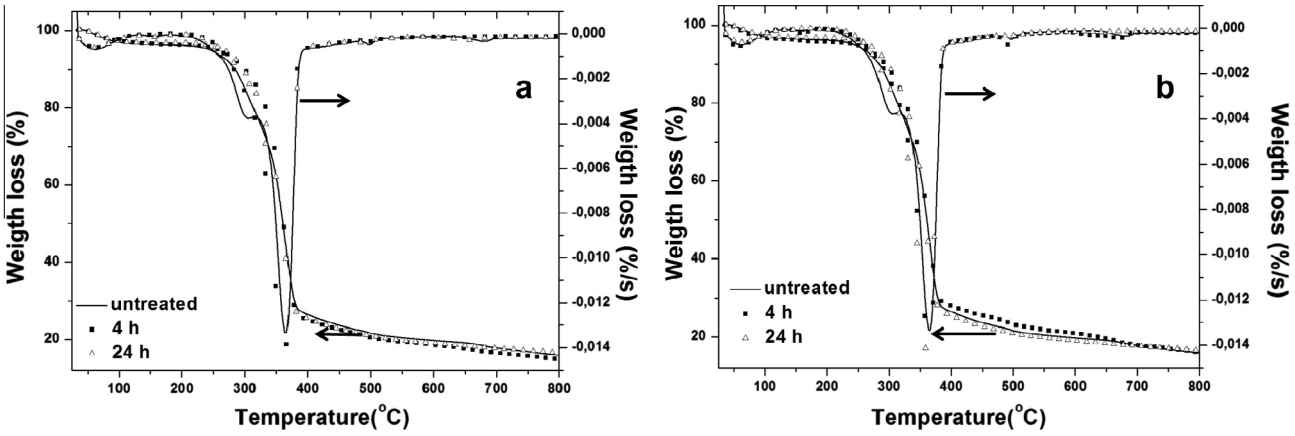

Fig. 3. Scheme of semiadiabatic box developed to measure the adiabatic temperature of cement pastes during the early hydration reaction.

3.8. Microstructure analysis

The microstructure of all cement materials was analyzed using a Zeiss Supra 40 Field emission scanning electron microscope (FE-SEM) operated at 3 kV.

3.9. Energy dispersive X-ray spectrometer (EDX)

Energy dispersive X-ray spectrometer (EDX) attached to the FE-SEM operated at 20 kV was used for identifying the MCC in cement materials.

4. Results and discussions

4.1. Microstructure analysis of cement bases materials with MCC

To understand the results of this research, first it is necessary understand the interactions between MCC, hydration products, cement particles and water. Fig. 4a–c shows the FE-SEM images of three different MCC surrounded by calcium silicates hydrated crystals (CSH). The MCC have highly hydrophilic character and highly water retention capacity, therefore they could link closely with the CSH as can be observed in Fig. 4b and c. The ability of interaction between the MCC and the hydration products as the CSH or calcium hydroxide (CH) is because MCC are constituted by several bonded chains of cellulose with three hydroxyl groups per anhydroglucose unit [1]. Those free –OH groups gives to MCC the ability to interact through hydrogen bonds with other compounds containing hydrogen atoms in its structure like CSH and CH [1]. Agglomeration of MCC in cement materials was not observed in microstructure analysis because affinity between MCC and hydration products favored the dispersion of MCC in cement matrix.

Additionally, the MCC are saturated with water and therefore, products of cement hydration growing close to them and use some of its water content for its formation. The size of CSH crystals and porosity of cement materials depends on cement composition and especially on water cement ratio (w/c) [8,21]. If the proper w/c is used, the CSH crystals reaches lengths between 6 and 8 μm, like the CSH crystals observed Fig. 4a and b. As mentioned in materials and method section, MCC used in this work have the size distribution shown in Table 2. Therefore the MCC are around 4 times bigger than the CSH crystals, with size distribution near to air voids size. The air voids, are voids intentionally incorporated into freshly mixed cement to protect the cement material from freezing and thaw processes [8,21].

Size distribution and composition are the most important difference between MCC and cellulose pulp commonly used to elaborate cement based composites [22–24]. Fibers of cellulose pulp have lengths between 0.8 and 1.5 mm [25,23], additionally hemicellulose and lignin in low concentrations are still present in cellulose pulp, making them more susceptible to degradation in alkaline environmental [26]. Micrometrical sizes of MCC make them more reactive than cellulose pulp, therefore MCC interact with hydration products more closely than cellulose pulp.

4.2. Mini-slump test for cement pastes

The method proposed by Roussel et al. [16], was used to calculate the yield stress from slump test. The surface tension effects were neglected because they are smaller than yield stress consequences. Roussel et al. [16], proposed this model for a finite volume of fluid that is released on a horizontal plate, following the next three assumptions: (i) the initial shape of the fluid is conical; (ii) there is not angular velocity and (iii) the characteristic length of

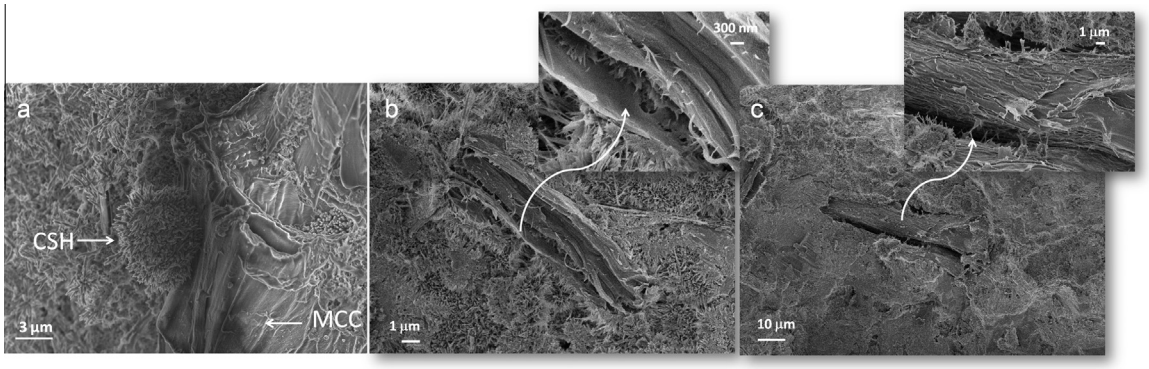

Fig. 4. FE-SEM image of cement based materials with 3 wt.% of MCC. (a) cement mortar with 3 wt.% of MCC. (b) cement paste with 3 wt.% of MCC. (c) FE-SEM image of cement paste with 3 wt.% of MCC.

Table 4
Results from PUV and mini-slump test.

Specimen	ρ (kg/m^3)	Diameter (m)	τ_0 (Pa)
0 wt.%	1805 ± 1.3	0.17 ± 4.8E-4	0.55 ± 0.01
3 wt.%	1766 ± 5.1	0.14 ± 4.9E-4	1.43 ± 0.02

the contact surface is larger than the characteristic length of the fluid depth. They deducted Eq. (5) and we used it to calculate the yield stress of cement pastes.

$$\tau_0 = \frac{225 \cdot \rho g V^2}{128 \cdot \pi^2 R^5} \tag{5}$$

where ρ is the density of the tested sample, g is the gravitational constant, V is the tested sample volume and R is the slump measured.

Results from mini slump test are presented in Table 4. The addition of 3 wt.% of MCC decreased the slump of cement past in 3 cm. Cement paste in fresh state is constituted by a large number of small suspended particles interacting via colloidal forces, like Van der Waals, electrostatic repulsion, steric hindrance and hydrogen bonding, and some bigger particles that interact via direct contact like friction or collisions and the yield stress (τ_0) is the stress necessary to break those interactions and separate the particles [15–19]. As mentioned above the free –OH groups in MCC gives them the ability of interact through hydrogen bonds with hydration products, cement particles and water through hydrogen bonds; increasing τ_0 by 2.6 times respect to cement paste with 0 wt.% of MCC.

The increment in τ_0 generated by MCC addittion, increases the energy costs in construction, because it will be necessary higher compaction energy and higher pump power to transport concrete from one side to another. However cement materials with high τ_0 values are useful to elaborate precast pieces; during processing of these pieces is necessary that material retains the shape of the mold, and does not flow easily outside it to be able to remove the formwork rapidly. Additionally cement materials with high τ_0 values are also useful to elaborate rigid pavements in which is required that mixture keeps its shape in fresh state.

4.3. Monitoring early hydration reaction of cement paste, using data in adiabatic temperature time

Fig. 5a shows the experimental temperature curves of cement paste with 0 wt.% and 3 wt.% of MCC. The U' values presented in Table 5, were calculated for every test using the curve data far apart from the curve plateau because at this time the reaction is governed by diffusion and occurs slowly therefore it could be neglected [21]. After calculate U' for every test, the experimental temperatures were corrected using Eq. (4). Fig. 5b shows the curves of adiabatic temperature vs. time, for cement pastes with 0 wt.% and 3 wt.% of MCC. The addition of 3 wt.% of MCC delayed the hydration reaction; additionally cement paste with 3 wt.% of MCC reached a maximum adiabatic temperature 5 °C lower than cement paste with 0 wt.% of MCC (Table 5). Polysaccharides are admixtures commonly used in construction industry to modify the water retention ability of the cement materials [27], with the secondary effect of delaying the hydration reaction because:

(1) Absorption of polysaccharides in the surface of anhydrous particles of cement and CH crystals, forming a water-resistant film on cement particles that is hydrolyzed with time [28–32].
(2) Formation of complexes between ions of CH solution and the polysaccharides, increasing solubility of CH and decreasing its rate of formation [28–32].
(3) Formation of insoluble derivatives by the interaction between the polysaccharide and the pore water solution or alkaline solution, these derivatives are precipitated around anhydrous cement particles forming a protective layer that prevents water ingress [28–32].

Additionally, Pourchez et al. [29] studied the delay produced by different cellulose ethers in hydration reaction of cement pastes, the molecular structure and specially the degree of substitution of cellulose ether influence significantly the delay of this reaction; because greater number of hydroxyl groups in cellulose molecule, generates a larger number of interactions between cellulose molecules, cement particles and cement hydration products, increasing the delay in hydration reaction.

The heat generated by the hydration of cement increases the temperature of concrete. During normal concrete construction that heat is dissipated into the environment therefore the temperature of structure decrease rapidly. However in massive structures such as dams, mat foundations, or any element more than about a meter or yard thick, the heat cannot be readily released. These temperature rises cause expansion while the concrete is hardening. If the temperature rise is significantly high and the concrete undergoes non uniform or rapid cooling, stresses because of thermal contraction in conjunction with structural restraint can result in cracking [8]. Therefore the reduction in adiabatic temperature generated by MCC addition will be useful where larges masses of concrete are used. Since a reduction of 6 °C in maximal adiabatic temperature implies a significantly reduction in the heat generated by hydration reaction.

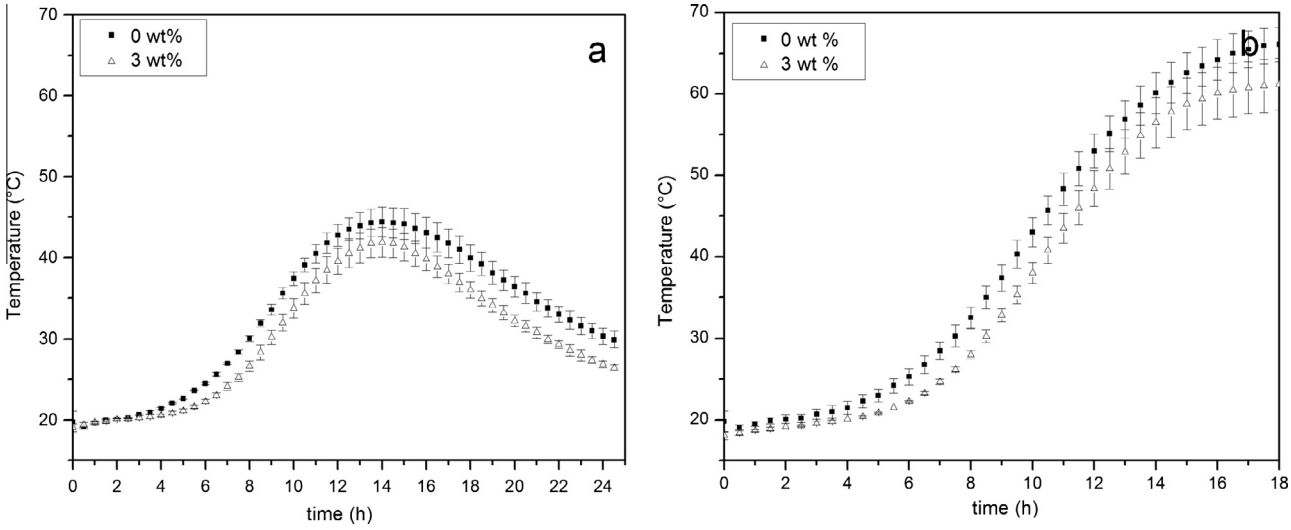

Fig. 5. Temperature curves during the hydration reaction. (a) Experimental temperature. (b) Adiabatic temperature.

Table 5
Global heat transference coefficient and maximal adiabatic temperature.

Sample	$U' = \frac{U}{\rho C_p}$ (min^{-1})	$T_{ad\ max}$ (K)
0 wt.%	0.0025	341
3 wt.%	0.0019	323

4.4. Effect of MCC and curing procedure on hydration degree of cement pastes

The chemical structure of cellulose increases its volume significantly to retain large quantities of water and as its structure releases water, returns to its initial volume. It was necessary use EDX analysis to localize the MCC in cement materials. Fig. 6a–d shows the FE SEM and EDX images of cement mortar, it could be observed that the MCC are constituted by carbon and are surrounded by cement hydration products principally constituted by calcium and silicon. As mentioned above, MCC were saturated before cement material elaboration. When MCC absorbed water they swell; the reverse process of water absorption and swelling is the water removal and shrinkage of MCC [1]. The FE-SEM images presented in Fig. 6a and d show that there are voids between the cement matrix and the MCC because; they shrinkage after release the water retained within their structure.

On the other hand, Fig. 7a and b shows the TGA and DTGA analyses for cement pastes with 3 wt.% of MCC cured by both procedures standard and accelerated; in Fig. 7b are observed three peaks related with three thermodegradation processes: (i) The first peak is observed below 200 °C and is associated with evaporation of free water and water presented on CSH surface [8,21,33]. (ii) The second degradation process associated to the peak at 450 °C is attributed to CH dehydration shown in Reaction (6). (iii) The last

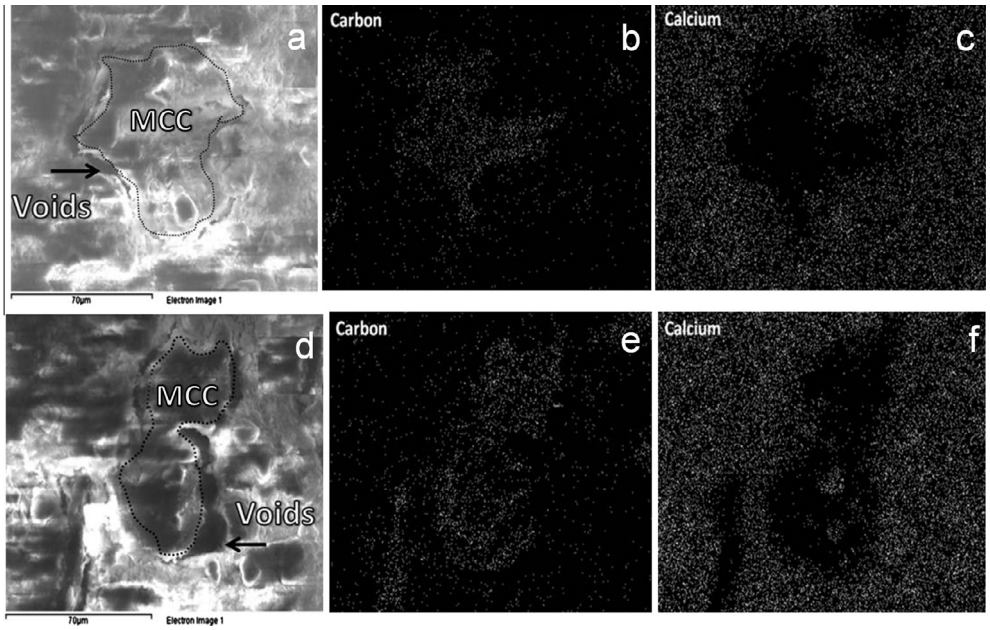

Fig. 6. FE SEM and EDX images for cement materials with 3 wt.% of MCC. (a) FE-SEM imagen of the interface between a MCC and cement paste. (b) Location of the carbon atoms in FE-SEM image. (c) Location of the calcium atoms in FE-SEM image. (d) FE-SEM imagen of the interface between a MCC and cement mostar. (e) Location of the carbon atoms in FE-SEM image. (f) Location of the calcium atoms in FE-SEM image.

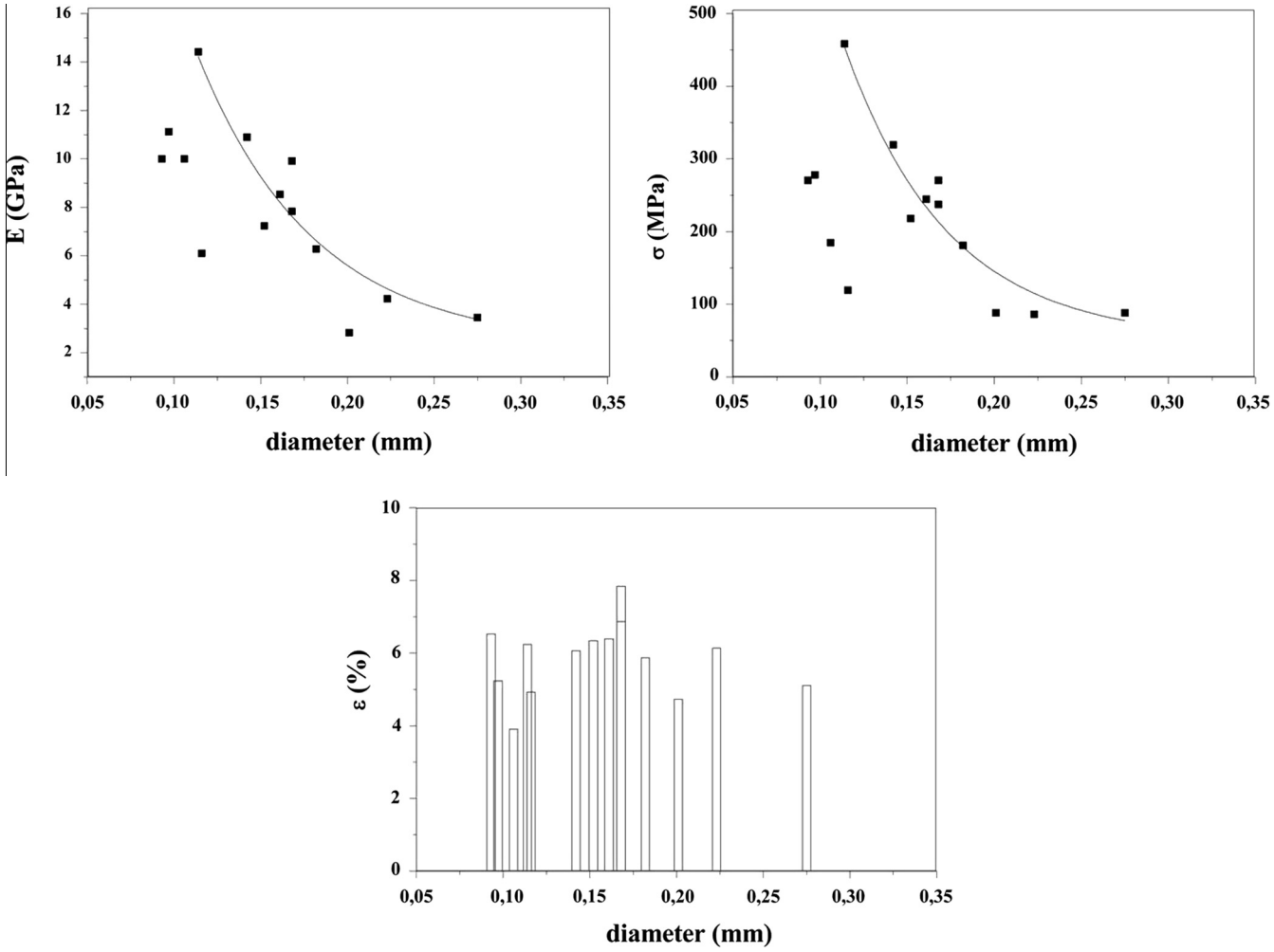

Fig. 7. Effect of curing method on hydration degree of Portland cement pastes. Thermogravimetric analyses of cement paste with 3 wt.% of MCC cured by different curing processes. (a) TGA and (b) differential TGA (DTGA).

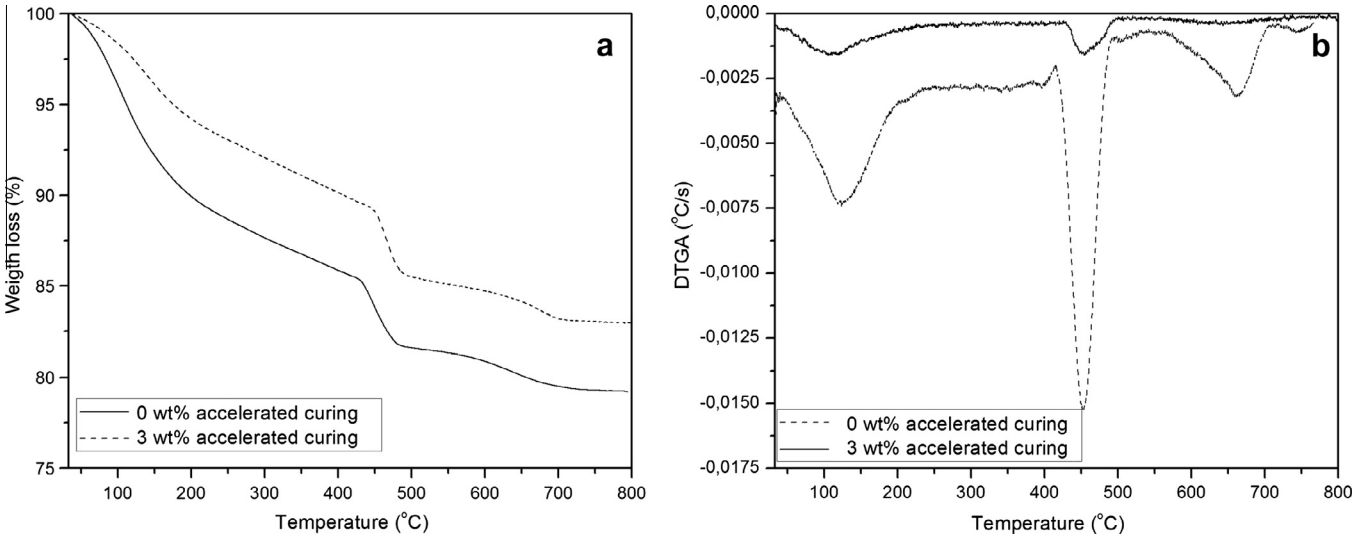

Fig. 8. Effect of MCC content on hydration degree of Portland cement pastes. Thermogravimetric analyses of cement paste with 0 wt.% and 3 wt.% of MCC. (a) TGA and (b) differential TGA (DTGA).

thermodegradation process, occurs around 700 °C is attributed to decomposition of calcium carbonate shown in Reaction (7) [8,21,33]:

$$Ca(OH)_{2(S)} \rightarrow CaO_{(S)} + H_2O_{(g)} \quad (6)$$

$$CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)} \quad (7)$$

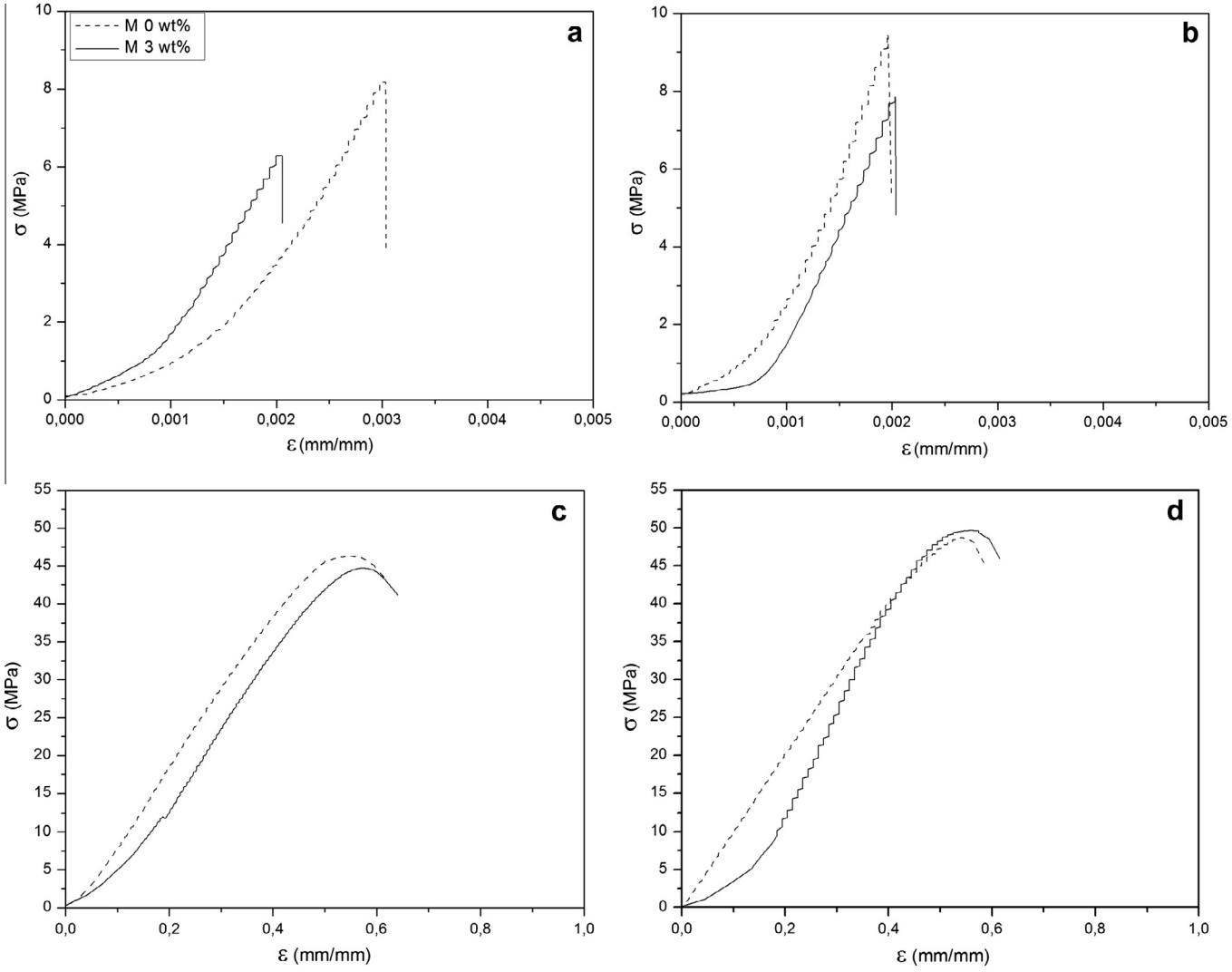

Fig. 9. Stress strain typical curves of mortar from compression test (a) mortar with 0 wt.% of MCC and (b) mortar with 3 wt.% of MCC.

Table 6
Compression modulus (E) and flexural strength (σ) from stress–strain curves for cement mortars.

Specimen	E (GPa) Standard curing	E (GPa) Accelerated curing	σ (MPa) Standard curing	σ (MPa) Accelerated curing
M 0 p/p%	52 ± 1.9	55 ± 3.4	9.5 ± 0.3	11 ± 0.8
M 3 p/p%	45 ± 0.4	51 ± 1.9	7 ± 0.4	10 ± 0.3

The intensity of those three peaks is directly related with the degree of hydration reached by the material [8,21,33]. As can be observed in Fig. 7b peaks corresponding to water evaporation and CH dehydration of cement paste cured by accelerated process increased its intensity respect to cement paste cured by standard process, because of increment in temperature during the curing procedure. Additionally Fig. 8a and b shows the TGA and DTGA analyses for cement pastes with 0 wt.% and 3 wt.% of MCC both cured by accelerated process. It could be observed that peaks corresponding to water evaporation and CH dehydration incremented significantly their intensity in cement paste with 3 wt.% of MCC respect to cement paste with 0 wt.% of MCC. Therefore cement paste with 3 wt.% of MCC cured by accelerated process, reached higher degree of hydration than cement paste with 0 wt.% of MCC cured by accelerated process. This is because as mentioned above, the MCC has a substantial capacity for water retention and as the hydration process progresses; the MCC releases its water to increasing the hydration degree, like was evidenced by the volume change observed in FE-SEM images shown in Fig. 7.

4.5. Mechanical tests for cement mortars

Fig. 9a–d shows the stress strain curves for compression and flexural tests for cement mortars with 0 wt.% and 3 wt.% of MCC. A summarize of results obtained from mechanical tests is presented in Table 6. Flexural strength and compressive modulus were determined according to EN standard 196-1 [20]. Table 6 compares the compression modulus and the flexural strength of cement mortars with 0 wt.% and 3 wt.% of MCC under two conditions of curing. The addition of cellulose microfibrils decreased the modulus and flexural strength for cement mortar cured by standard curing. However cement mortars cured by accelerate curing process increased their

modulus and flexural strength, because of an increment in hydration degree of cement materials, as consequence of water releasing that favored the creation of new hydration products.

The implementation of a thermal curing process increased significantly the hydration degree of cement paste with MCC; and improved the mechanical behavior of cement mortars with MCC. The change in hydration degree and in mechanical properties with curing procedure also represents an advantage in the development of precast pieces. Since processing of precast pieces requires a special curing procedure that allows the piece obtains a determined mechanical properties, related to their degree of cure.

5. Conclusions

This works evaluated the effect of addition 3 wt.% of MCC on properties of cement based materials. The system MCC cement and water is highly compatible because hydrophilic character and water retention capability of MCC; additionally hydroxyl groups of cellulose give to MCC the capacity of interact with hydration products, cement particles and water. It was observed good dispersion of MCC on cement matrix. Additionally because of its micrometrical sizes MCC interact with hydration products more strongly than cellulose pulps commonly used in others investigations.

Results from slump tests showed that because of hydrophilic nature and presence of hydroxyl groups on its surface, the MCC interact with cement particles, hydration products and water; increasing τ_0 of cement paste by 2.6 times respect to cement paste with 0 wt.% of MCC.

Adiabatic temperature measurement in time showed that the ability of interaction between the MCC, hydration products, cement particles and water, promoted solubilization of calcium hydroxide and the formation of a waterproofing barrier on the anhydrous particles of cement. Those interactions delayed the hydration reaction and decreased the maximum adiabatic temperature.

Thermogravimetric analysis showed that both accelerated curing procedure and MCC addition, increased the hydration degree of cement pastes. Accelerated curing increased the hydration degree because of increment in temperature during cure process and MCC addition increased the degree of hydration because MCC released its water content in cement mortar and favored the creation of more hydration products.

Addition of MCC decreased the mechanical properties of cement mortar cured by standard process; however cement mortar with 3 wt.% of MCC cured in accelerated way reached mechanical properties close to mechanical properties of cement mortar without MCC. This is because both accelerated curing and MCC addition increased the hydration degree of cement materials, increasing the presence of hydration products that provide resistance and modulus like CSH.

Increment registered in τ_0 by MCC addition as well as increment registered in hydration degree and improvements reached in mechanical properties by implementation of an accelerated curing procedure and addition of MCC; are important characteristics to consider cement based composites with MCC as a potential material to develop precast pieces. Additionally results from early hydration reaction showed that in case of massive structures MCC could be added to a cement matrix to reduce cracking caused by the stresses because of thermal contraction and the structural restraint.

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