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Control of hydration rate of polymer modified cements by the addition of organically modified montmorillonites



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ABSTRACT

The addition of polyvinyl alcohol (PVA) in concrete causes a delay in the hydration rate of Portland cement paste. Three different montmorillonites (MMTs) (Cloisite Na, 30B, and Nanofil) were previously mixed with PVA in order to control this delay. A comparison between the hydration rate of Portland cement paste and Portland cement paste modified with PVA and the different MMTs was made by means of semi-adiabatic calorimetry, thermal gravimetric analysis and contact angle measurements. Different rates of hydration were obtained with each MMT. The paste with PVA and Nanofil behaves almost the same as the unmodified cement paste. Mechanical properties were also studied. An increase in the flexural strength and a decrease in the compression strength were found, which is expected for a Portland cement paste modified with PVA. The addition of MMT to the cement paste with PVA hardly affects the mechanical properties.

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1. Introduction

The use of polymers combined with classical construction materials generates a synergetic action that can improve their properties and applications [1–12]. Polyvinyl alcohol is a polymer soluble in hot water; during cement hydration, the polymer dehydrates and transforms into a film. This film behaves as an adhesive to aggregates [2,3]. When it is added to concrete it can improve its performance due to its low elastic modulus and high tensile strength (68.5 MPa and 22.5 MPa, respectively [13]). Knapen [4,5] studied the microstructure of the cement paste matrix when PVA was added and found that some mechanical properties, such as flexural and tensile strength, were improved.

The problem with the addition of water soluble polymers to concrete is the delay of the hydration process [9–12]. This can be problematic for field applications. The present work presents a solution to this problem by modifying the polymer to avoid hydration delay, while retaining the advantages of polymer addition.

The recent research in polymer technology involves the addition of nano clay to enhance their properties. Layered silicate clays arranged on the nanometer scale with a large aspect ratio and large specific surface area create a nanocomposite with higher mechan-

ical properties [13–20]. Montmorillonite (MMT) is an aluminum layered silicate with a width of 1 nm and a length of 100–200 nm; silica is its main component. The configuration of the silica sheet is tetrahedral while the octahedral sheet comprises diverse elements such as aluminum, magnesium and iron [16]. Due to the hydrophilic nature of both, unmodified MMT and PVA, MMT can be dispersed into the PVA with an exfoliated configuration [13,14].

Birgisson and Beatty [21] patented a nanomodified concrete with PVA and Cloisite Na. Those authors claim that the addition PVA produced adhesion between the platelets of the clay and cement hydration products. The nanocomposite showed an exfoliated configuration with Cloisite Na+.

In the author's previous work the effect of the addition of natural bentonite to PVA and modified the cement paste with this solution was studied to control the delay in the cement hydration generated by the addition of PVA to the cement paste [22]. PVA delayed cement's hydration, pristine bentonite accelerated it, but no difference was found between the hydration of cement with PVA and cement with PVA and bentonite. This behavior can be explained because the bentonite was agglomerated in the PVA solution due to the fact that its clay had not been previously chemically modified.

The aim of this work is to modify PVA with different types of MMT and use this solution to replace the mixing water for the cement paste. The use of different clays with the PVA produces changes in the hydration kinetic, morphology and mechanical

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properties of the cement paste. The particular aim is to avoid delay of cement hydration, while retaining the benefits of PVA addition.

2. Experimental

2.1. Materials

Portland cement used (CEM) was the so called “CP 50” from Cemento Loma Negra, Argentina, with a Blaine surface area of 442 m²/kg. Its composition is given in Table 1.

The polyvinyl alcohol (PVA) was Celvol 823 with 88% of hydrolysis degree. Fig. 1 shows its chemical structure.

Montmorillonite (MMT) was provided by Southern Clay Products, Inc., United States. MMTs used were: Cloisite Na+ (Na), Nanofil (NF) and Cloisite 30B (30B). They were used as received. Table 2 shows the chemical compounds that modify the clay, the cation exchange capacity and the interplanar distance of each one. Cation exchange capacity (CEC) is expressed in meq/100 g. This is an important characteristic of the clay when it is used for polymer modification [23] and it is related with the capacity to interchange the clay's cations. The interplanar distance of clay layers is calculated by means of Bragg's Law. Alkylammonium compounds are the chemical modifiers. These clays have a different hydrophilic character. Na and NF are the most hydrophilic, while 30B is the less hydrophilic one.

2.2. Methods

A mortar mixer according EN 196-1 was used. Cement was mixed with distilled water or the polymer solution. The ratio of water to dry cement was maintained constant at 0.45. The cement paste was mixed for 3 min at 60 rpm with a stop in between for 30 s to scrape the paste from the inside walls, and for 30 s at 120 rpm. The polymer solution was prepared as follows: PVA was dissolved in water at 80 °C, then it was sonicated for 30 min. It was stored for 24 h at room temperature before use.

For incorporating MMT to the solution the clay was first agitated in water at 40 °C during 1 h and sonicated for 30 min. Then the temperature was raised to 80 °C and PVA was added to the mixture. Again, it was stored for 24 h at room temperature before use. These solutions replaced the mixing water of the paste. PVA was added in 4 wt.% to water. The MMT was added at a dosage of 4 wt.% to PVA, according to the best results obtained by Soundararajah et al. [24].

Table 1
Chemical composition of Portland cement.

(%)	CPN 50
SO ₃	2.87
MgO	0.79
SiO ₂	20.71
CaO	63.53
Al ₂ O ₃	3.81
Fe ₂ O ₃	4.40
Na ₂ O	0.06
K ₂ O	0.92

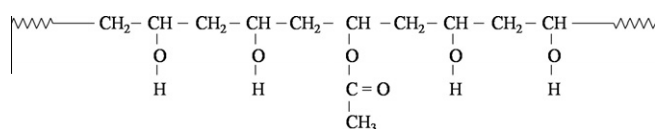


Fig. 1. Chemical structure of polyvinyl alcohol not completely hydrolyzed.

Table 2
Properties of the commercial clay utilized: type of organic modifier, modifier concentration, CEC, and interlayer distance.

Clay	Organic modifier	Modifier concentration (meq/100 g clay)	CEC (meq/100 g clay)	d ₀₀₁ (Å)
Cloisite Na+(NA)	None	None	92	11.7
Nanofil 116 (NF)	None	None	116	12.5
Cloisite 30B (30B)	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{H}_3\text{C}-\text{N}^+-\text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	90	92	18.5

T is Tallow (~65% C18; ~30% C16; ~5% C14).

Table 3
Sample designations.

Designation	Sample
CP	Portland cement paste
CP + PVA	Portland cement paste with PVA
CP + PVA + Na	Portland cement paste with PVA and Na
CP + PVA + NF	Portland cement paste with PVA and NF
CP + PVA + 30B	Portland cement paste with PVA and 30B
CP + Na	Portland cement paste with Na
CP + NF	Portland cement paste with NF
CP + 30B	Portland cement paste with 30B

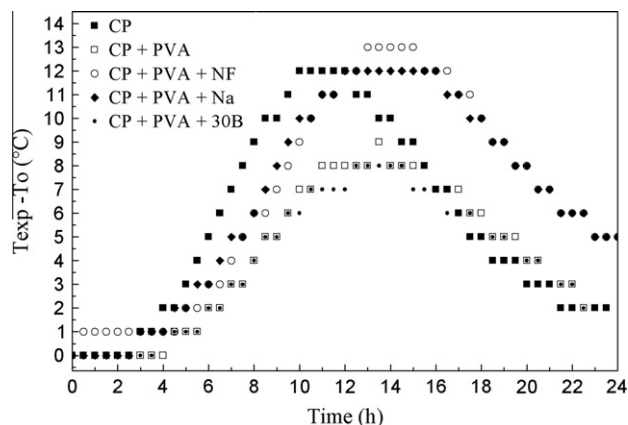


Fig. 2. Experimental temperature versus time for all the samples: ■ CP, □ CP + PVA, ○ CP + PVA + NF, ◆ CP + PVA + Na and ● CP + PVA + 30B.

For measuring hydration temperature of cement paste a semi-adiabatic box of 200 mm × 200 mm × 200 mm was fabricated with 80 mm Styrofoam top, base and wall thickness. The temperature was determined with a thermocouple. The room temperature was measured as well as the temperature in the center of the sample. Zero of hydration time was set when the water or PVA solution was added to the cement. At least, three specimens were measured for each sample and an average value was obtained for the results. The volume of the sample was 0.20 l.

A Shimadzu TGA-51 was used for thermogravimetric analysis (TGA). The samples were heated from room temperature to 1000 °C with a heating rate of 10 °C/min in a N₂ atmosphere. Environmental Scanning Electronic Microscope (ESEM) was studied by means of a Quanta 200 FEI company equipment. The conditions were 9 °C and 133.3 Pa. Portland cement pastes bars (4 cm × 4 cm × 16 cm) were tested for compressive and flexural strength following EN 196 regulations.

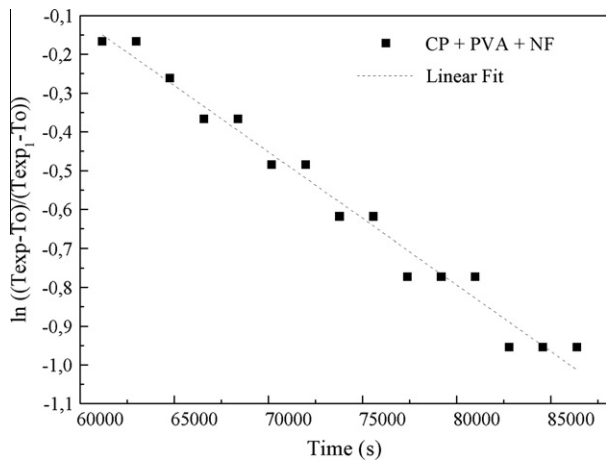


Fig. 3. Determination of the global transference coefficient, $U' = U/C_p$ in a water/cement paste with 2 wt.% PVA and 0.072 wt.% of NF, ratio $w/c = 0, 45$. $U' = \text{slope}$.

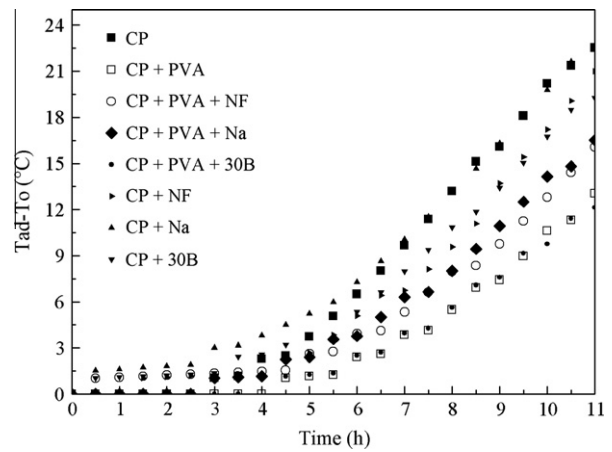


Fig. 4c. Adiabatic temperature rise for all the samples: ■ CP, □ CP + PVA, ○ CP + PVA + NF, ◆ CP + PVA + Na, ● CP + PVA + 30B, ▲ CP + NF, ▲ CP + Na and ▼ CP + 30B.

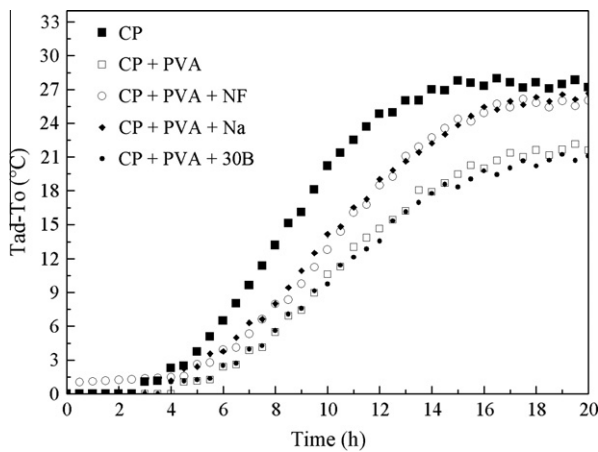


Fig. 4a. Adiabatic temperature versus time for cement paste samples modified with PVA and PVA + MMTs: ■ CP, □ CP + PVA, ○ CP + PVA + NF, ◆ CP + PVA + Na and ● CP + PVA + 30B.

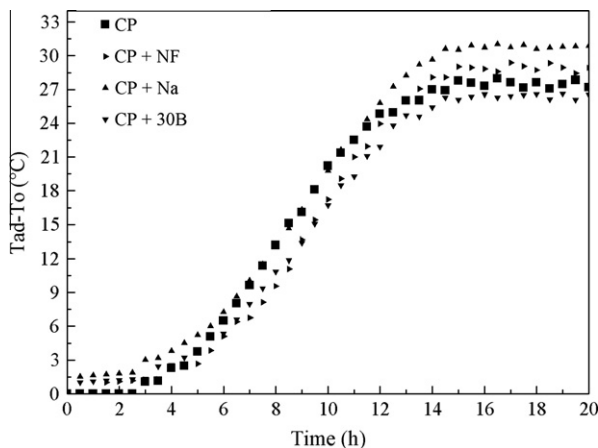


Fig. 4b. Adiabatic temperature versus time for cement paste samples modified different MMTs: ■ CP, ▲ CP + NF, ▲ CP + Na and ▼ CP + 30B.

In order to measure the paste's mechanical strength it was mixed as previously stated. After molding the samples were covered with nylon for 2 days. Then they were stored, after demolding,

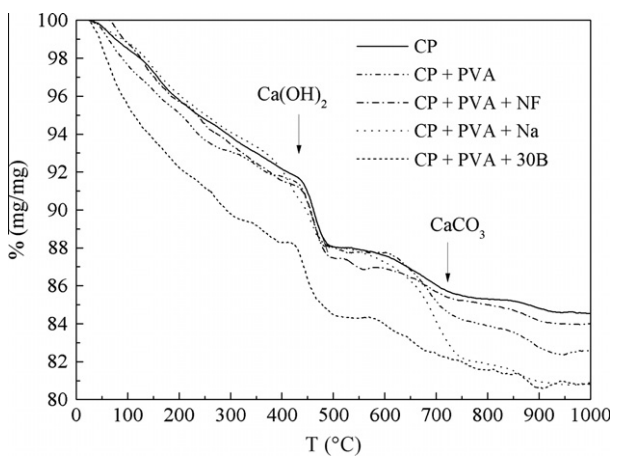


Fig. 5. TGA of different samples of cement paste, cement paste with PVA and cement paste with PVA and clays.

Table 4

Content of $\text{Ca}(\text{OH})_2$ calculated within TGA analysis for the different samples.

Samples	$\text{Ca}(\text{OH})_2$ % mass loss
CP	16.9
CP + PVA + NF	16.8
CP + PVA + Na	16.6
CP + PVA	15.4
CP + PVA + 30B	15.6

in a moist room for 5 days (24 °C, 93% RH) and finally in a dry curing room (24 °C, 50% RH) until the testing day.

A drop of polymer solution placed on a glass surface was photographed in order to measure the contact angle. This was done by image analysis.

Image analysis was also used to determine the air entrapped in the cement paste causing compression strength loss. A 10 mm thick disc of sample was cut and polished under water to obtain a smooth surface. The disc was then dried at 60 °C for 24 h before being impregnated with a black synthetic spray paint. The surface was painted again with wollastonite paste, a white calcium phyllosilicate mineral with water. This paste penetrates the pores creating a contrast between the white, full of wollastonite paste, pores and the solid matrix. The images were then plotted with a high

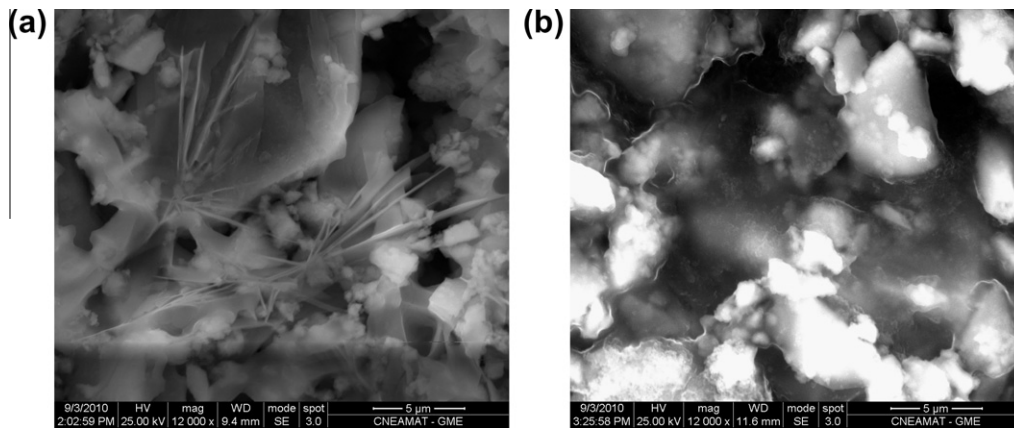


Fig. 6. E-SEM images of (a) cement paste and (b) cement paste with PVA hydrated for 40 min.

Table 5
Contact angle of the different solutions with a pristine glass surface.

Sample	Contact angle
PVA	63° ± 3°
PVA + 30B	57° ± 3°
PVA + NF	51° ± 3°
PVA + Na	44° ± 3°

resolution scanner and analyzed with ImageJ, a public domain, Java-based image processing program [25].

From now on, samples will be referenced by their designations given in Table 3.

2.3. Adiabatic temperature calculation

The reaction rate was followed by a thermocouple immersed in a relatively large volume of adiabatically isolated sample [26]. The adiabatic temperature rise method was applied by taking into account the heat loss correction. The thermal energy balance may be written as:

$$\rho C_p (dT_{\text{exp}}/dt) = (-\Delta H)\rho (d\alpha/dt) - U(T_{\text{exp}} - T_0) \quad (1)$$

where U is a coefficient of global heat transfer per unit mass, T_{exp} is the measured temperature and T_0 is room temperature, C_p is the specific heat, ρ is the mass density, t is the time and α is the cure degree or hydration degree. Integration of Eq. (1), when $d\alpha/dt \rightarrow 0$, leads to:

$$\ln(T_{\text{exp}} - T_0) = \ln(T_{\text{exp1}} - T_0) - U'(t - t_1) \quad (2)$$

where (T_{exp1}, t_1) is the set of values at the beginning of the integration where the effect of hydration and heat transfer through the semi adiabatic box are combined. $U' = U/(\rho C_p)$ is assumed to be constant and $(-\Delta H)/C_p = \Delta T_{ad}$, where ΔT_{ad} is the difference between the maximum adiabatic temperature and the initial temperature.

The relationship between T_{exp} and T_{ad} was obtained as follows:

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

Integrating Eq. (3), leads to:

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

This enables the calculation of the adiabatic temperature from the experimental data.

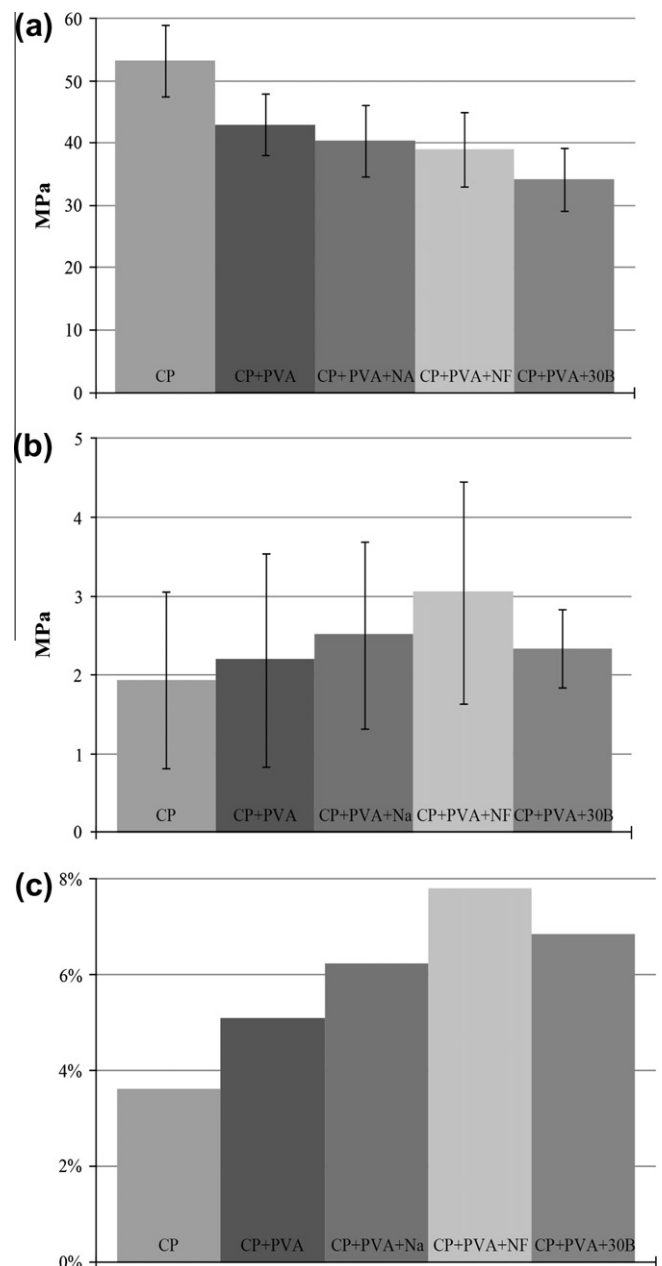


Fig. 7. Mechanical properties of the different samples: (a) compressive strength, (b) flexural strength and (c) flexural/compressive strength ratio.

3. Results and discussion

Temperature was measured in a semi-adiabatic box using cement paste modified with PVA and chemically modified MMT. Fig. 2 shows the experimental temperature measured for each sample. Adiabatic temperature (T_{ad}) was calculated using Eq. (4). The heat flow coefficient (U') was calculated analytically with a high correlation coefficient (>0.90). Fig. 3 shows the determination of U' for one of the samples.

Fig. 4a represents the adiabatic temperature versus time for each sample. It can be appreciated that the addition of PVA to the cement paste delayed the hydration. CP + PVA + 30B showed almost the same delay. CP + PVA + NF and CP + PVA + Na reduced the delay achieving almost the same temperature as CP.

In order to determine the effect of the different MMTs, adiabatic temperature was also calculated for cement paste with the same amount of MMT but without PVA (Fig. 4b). The results indicated little difference with respect to pristine cement paste. In comparison to CP, small delay for CP + 30B and a small step forward for CP + Na and CP + NF appeared. This can be explained by the small amount of MMT compared to cement paste (0.07 wt.%). This amount is sufficient to modify the behavior of PVA, but not enough to significantly modify cement hydration. As a consequence, it can be concluded that MMTs mainly modify the PVA.

Analyzing the first 11 h (Fig. 4c) the hydration rate can be estimated by the slope of each curve. A range of behaviors is observed. The slower rates are those of CP + PVA and CP + PVA + 30B, then CP + PVA + NF and CP + PVA + Na, followed by CP + 30B and CP + NF, and finally CP and CP + Na. This means that the addition of MMT to CP accelerates the beginning of the hydration process;

CP + PVA + Na also accelerates the first stage of the hydration. It can be concluded that Na is the most reactive MMT. CP + 30B accelerates the beginning of the hydration as well as CP + NF, despite their chemical differences. This could mean that particle size is what matters when modifying only CP.

Complementary to the previous results, the degree of hydration of each sample was indirectly determined by means of TGA. This evaluation was done calculating the amount of $\text{Ca}(\text{OH})_2$ [5]. A higher amount of $\text{Ca}(\text{OH})_2$ indicates a higher amount of one of the hydration products, which corresponds to a more hydrated sample. Four-day old samples were grinded and compacted. A small mass loss at $\sim 450^\circ\text{C}$ ($\text{Ca}(\text{OH})_2$) and another one at $\sim 750^\circ\text{C}$ (CaCO_3) were detected through TGA analysis (Fig. 5). The results of $\text{Ca}(\text{OH})_2$ mass loss are presented in Table 4. Similar results were obtained by Knapen and Van Gemert [5] for cement and PVA modified cement. The results agreed with the adiabatic temperature measurements.

It is well known that the delay in the hydration rate and the low adiabatic temperature rise during cement hydration when PVA is added to cement paste occur due to the formation of a gel-like structure of PVA and water [4]. The polymer swells reducing water accessibility to cement, acting like a water controlling release agent.

Fig. 6 shows E-SEM images during the first hour of hydration. Fig. 6a shows the hydration products and formed micropore structure of CP. Fig. 6b shows the film formation around the growing hydration products and their compatibility of the CP + PVA.

The explanation of how the polymer–water solution with clays acts on the hydration rate is based on the hypothesis of the change of the polarity of the PVA solution when different MMTs are added.

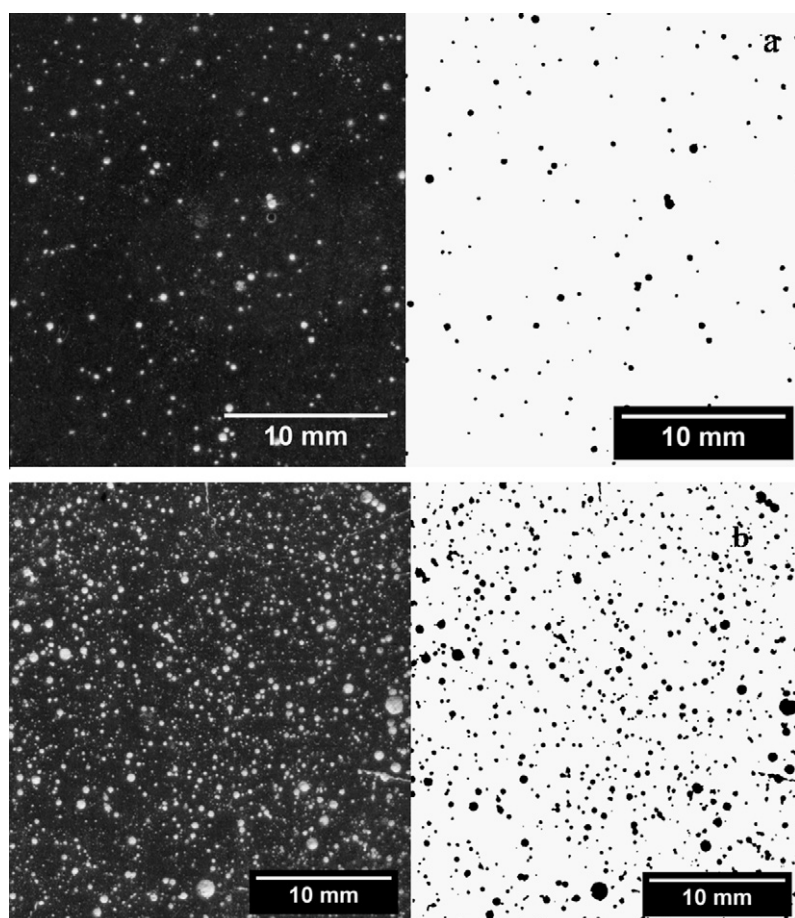


Fig. 8. Pictures of the polished surface and the resulting scanned image, utilized for image analysis of the samples of (a) CP and (b) CP + PVA + 30B.

Table 6
Average porosity of each sample studied within image analysis.

Slice	Average porosity (%)	Standard deviation
CP	1.07	0.40
CP + PVA	2.27	0.50
CP + PVA + NF	2.33	0.67
CP + PVA + Na	2.63	1.24
CP + PVA + 30B	3.10	2.00

This was studied by measuring the contact angle of a 40 μl solution drop at 20 °C on a pristine glass surface.

When the water polymer solution with MMT is used as the mixing water, the polarity of the solution is affected. The polarity will directly affect the release rate of the water to hydrate available cement. This hypothesis is demonstrated with the results given in Table 5. PVA + NF and PVA + Na solutions are more hydrophilic than PVA + 30B and pristine PVA solutions. The solution drops surround anhydrous cement and if the water–polymer solution has Na or NF it has more area in contact with anhydrous cement due to their hydrophilic character. When the contact area is higher, anhydrous cement will be in contact with more water, then more cement is hydrated and the hydration delay will be reduced.

3.1. Mechanical properties and void content

In order to determine how the addition of MMT to PVA modified the mechanical properties, a large number of samples were tested. Compression and flexural strength resistance were tested. Average results are given in Fig. 7.

Tensile strength was calculated from the three-point flexural test results using:

$$\sigma_r = \frac{3P \times l}{2b \times d^2} \quad (5)$$

where P is the peak load, l is the length of the support span, b is width and d is thickness of the specimen.

According to Fig. 7, it can be concluded that the addition of PVA generates a loss in the compressive strength. This can be explained due to the increase of air voids in the paste generated by the air stabilization property of PVA [6]. Image analysis results supported this statement. CP samples had fewer and smaller pores compared to the other samples; CP + PVA + 30B had the most entrapped air (Fig. 8a and b). Table 6 shows the void content of each sample.

An improvement of the flexural strength was obtained for CP + PVA and, despite the large dispersion of strength values, CP + PVA + Na, CP + PVA + NF and CP + PVA + 30B showed better behaviors than CP. Tensile strength increased with the polymer inclusion and even more when the polymer was modified with MMTs. The highest tensile strength was obtained for CP + PVA + NF. NF is the montmorillonite that appears to be most compatible with cement. This result suggests that the addition of PVA with NF to the cement paste generates a better microstructure. Future work is currently being done on this subject.

4. Conclusions

Properties of a cement paste (CP) modified with polyvinyl alcohol (PVA) and chemically modified montmorillonites (MMT) were studied. Based on the rise of adiabatic temperature of modified cement pastes samples and by means of TGA, it was established that when PVA is added to CP the hydration process is delayed in comparison to that of pristine CP. It was also demonstrated that when chemically modified MMT is added to PVA this delay can be controlled. When Na and NF are previously added to PVA this delay

was reduced. This does not happen when 30B is added to PVA; the delay is almost the same as if no MMT were previously added to PVA.

This behavior was explained taking into account the polarity of the PVA solution added to the Portland cement paste. When Na or NF are added to this solution, its contact angle is reduced relative to that of the unmodified PVA solution. Use of the modified solution therefore facilitates the hydration of the cement grains, which then hastens the hydration process relative to that obtained with the pristine PVA solution. When 30B is added to PVA, the solution has almost the same contact angle as the pristine PVA solution; as a consequence, the rate of hydration is similar to that obtained with the pristine PVA solution.

When added to PVA, MMTs do not significantly change the mechanical properties of the hardened cement paste. Film formation of PVA, observed using the ESEM technique, explains why flexural strength of cement paste with PVA was higher than that of the pristine cement paste. The addition of MMTs to PVA improved mechanical properties of the PVA film enhancing the properties of the cement composite. The loss of compression strength was a consequence of increased void content. The highest porosity was found in CP + PVA + 30B, which had the lowest compressive strength. Future work will involve the reduction of the void content.

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