



Synergies on rheology and structural build-up of fresh cement pastes with nanoclays, nanosilica and viscosity modifying admixtures

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ABSTRACT

Nanoclays, nanosilica and viscosity modifying admixtures can be used to tune rheological properties of cement pastes, in order to fulfill the requirements for non-conventional cast-in-place techniques. An experimental study on cement paste rheology was carried out to evaluate their combined effects on fluid cement pastes' properties. A reference paste with cement blended with limestone filler and a low water to binder ratio was designed. A high range water reducing admixture (HRWRA), three types of viscosity modifying admixtures (VMA), and five nanocomponents (nanosilica and four different nanoclays) were added. Flowability, initial rheological properties and structural build-up of cement pastes were assessed with mini-cone slump test and dynamic shear rheometer test (DSR). The synergies between nanoclays, nanosilica and VMAs were evaluated. It was observed that an adequate combination of admixtures and nanoclays reduced the amount of HRWRA required to achieve target flowability, regarding the same components uncombined. The type and amount of VMAs and nanocomponents also produced changes on yield stress, viscosity and structural build-up. Their effect on structural build-up of fresh paste was related to reversible and non-reversible mechanisms, comparing the reduction of spread diameter of fresh samples stirred and left at rest over time measured with the mini-cone.

1. Introduction

Non-conventional cast-in-place techniques for cement-based materials (CBM), as self-compacting ability and digital fabrication, highlight as a new industrial revolution in the field of construction technologies and building materials, enhancing freedom in architectural design [1]. These new technologies have entailed many advantages, as fast construction speed, efficient structural design, increased worker safety and reduced cost labor and framework [1].

Rheology and structural build-up have become fundamental factors to achieve CBM cast-in-place control [2]. CBM for non-conventional cast-in-place techniques must show a liquid-like state to be able to flow and be transported, and then a solid-like state to hold its shape [3]. Thixotropy (structural build-up) of CBM is a process in which reversible and irreversible mechanisms of flocculation are involved, related to the dispersion kinetics of solid particles and the continuous progression of cement hydration [4]. Reversible structural build up is related to bonding forces as colloidal flocculation and deflocculation, van der Waals forces or Brownian motion [4–6]. Irreversible structural build-up

generally increases slowly and it cannot be significantly measured until 30 min of age. It is related to C-S-H bridges, although part of C-S-H bridges could be broken down if it is applied enough mix energy, becoming a reversible mechanism (macroscopic scale) [4,6]. Roussel defined the structural build-up coefficient or thixotropic parameter (A_{thix}) as a linear increment of static yield stress over time [5,6]. Perrot proposed an exponential increase of A_{thix} after 60 min, taking into account a characteristic time [7,8], and afterwards a model combining both a linear plus an exponential model [9].

The combination of nanoparticles with polymeric admixtures is a promising alternative to improve rheology control over time of CBM [10,11]. The synergetic effects produced by their combination can be related to size, shape and morphology of NC [12–17], and also to polymer chain, morphology and molecular weight of VMAs [10,18–24].

Nanocomponents as nanosilica (NS) and nanoclays have demonstrated to be useful for modifying static yield stress, acting as inorganic rheology modifiers [10,12,18,25]. Some authors have showed the ability of attapulgite (small nano-particle size palygorskite clay) to modify rheological properties of fresh cement pastes [10,14–17,26].

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Sepiolite (medium nano-particle size palygorskite clay) has also shown an enhancement ability of stabilization due to its high-water adsorption [12,27]. Bentonite (medium nano-particle montmorillonite clay) can significantly increase yield stress reducing flowability [8,12,28–30]. On the other hand, colloidal nanosilica has been also used as inorganic rheology modifier due to its high surface area and high-water demand [31,32].

Polymeric admixtures, as viscosity modifying admixtures (VMA) and high range water reducing admixtures (HRWRA), are also used to adjust rheological properties of cement pastes [18–23,25,33–35]. VMAs are water-soluble organic polymers that increase plastic viscosity, enhancing rheology of liquid phase of CBM. The combination of VMAs and HRWRA in adequate proportions can produce mixtures with high segregation resistance and homogeneity [10,18,20,24,25]. Several types of VMAs are used to adjust cement paste rheology, as natural polymers (welan gum), semi-synthetic polymers (methylcellulose-based) and synthetic polymers (polyacrylamide, polyacrylate) [18,19,21–23,35]. Four modes of action of VMAs have been described: a) water retention, b) entanglement (polymer–polymer interaction); c) bridging flocculation (polymer–particle interaction); d) depletion flocculation (difference in polymer concentration may increase the osmotic pressure and hence its yield stress) [10,18,20].

Several testing techniques have been used to understand the effect of these components on flowability, rheology and structural build-up of cement paste, [13,36–44]. Mini-cone slump test, one of the most used field-oriented testing technique, can be used to evaluate flowability parameters of cement pastes, measuring the final spread diameter, final slump and final time of spread. This test can also be used to evaluate structural build-up over time [39,45]. On the other hand, dynamic shear rheometer test (DSR) can be used to characterize rheology of cement paste. A controlled shear stress protocol (CS) or flow curve can be

applied to evaluate yield stress and viscosity throughout the modified-Bingham model [46]. Moreover, a controlled constant shear rate protocol (CCR) or time curve can be used to assess structural build-up [8,43]. A coaxial cylinder geometry is one of the more frequent geometries used for this test [42,47].

The main aim of this study was to evaluate the synergies between nanocomponents and polymeric admixtures on cement paste rheology over time. Mini-cone slump test and dynamic shear rheometer test were carried out to evaluate flowability, rheology and structural build up behavior of cement pastes with nanoclays, nanosilica, viscosity modifying admixtures and HRWRA. Understanding the synergies between these components and, consequently, controlling the rheological properties of cement paste can help to design practical mixtures useful for non-conventional cast-in-place techniques.

2. Experimental program:

2.1. Materials and mix design

The cement paste compositions designed for this study are summarized in Table 1. The reference cement paste included a Portland cement type I 42.5 R blended with a limestone filler, 2:1 by cement weight, 0.35water to binder ratio (w/b) and a polycarboxylate ether based high range water reducing admixture (HRWRA) proportioned to achieve a fluid cement paste. The percentage of HRWRA regarding cement weight varied between 0 and 3 %, depending on the amount of HRWRA required to spread 300 ± 30 mm in the mini-cone slump test.

Then, three different types of viscosity modifying admixture (VMA) were added:

Table 1

Cement pastes compositions (components in g) and initial rheological properties measured with DSR (CS protocol): initial yield stress (τ_0) and viscosity (μ_0).

	CEMI42.5R	Lim.Filler	Water	NC	VMA1	VMA2	VMA3	τ_0 (Pa)	μ_0 (Pa s)
REF	850	425	446	–	–	–	–	8	0.4
ATT	850	425	446	17	–	–	–	24	0.5
BE	850	425	446	17	–	–	–	10	0.3
SEP	850	425	446	17	–	–	–	29	0.6
SEW	850	425	386*a	77.2*c	–	–	–	95	0.9
NS	850	425	386*a	77.2*c	–	–	–	42	0.5
VMA1	850	425	446	17	1.7	–	–	57	2.3
VMA1ATT	850	425	446	17	1.7	–	–	71	1.6
VMA1BE	850	425	446	17	1.7	–	–	48	1.6
VMA1SEP	850	425	446	17	1.7	–	–	174	2.5
VMA1SEW	850	425	386*a	77.2*c	1.7	–	–	122	2.2
VMA1NS	850	425	386*a	77.2*c	1.7	–	–	10	1.1
VMA2	850	425	446	17	–	1.7	–	36	0.9
VMA2ATT	850	425	446	17	–	1.7	–	39	0.9
VMA2BE	850	425	446	17	–	1.7	–	72	0.7
VMA2SEP	850	425	446	17	–	1.7	–	31	1.0
VMA2SEW	850	425	386*a	77.2*c	–	1.7	–	26	0.8
VMA2NS	850	425	386*a	77.2*c	–	1.7	–	40	0.6
VMA2(04)	850	425	446	17	–	3.4	–	64	1.5
VMA2(04)ATT	850	425	446	17	–	3.4	–	59	1.7
VMA2(04)BE	850	425	446	17	–	3.4	–	72	1.4
VMA2(04)SEP	850	425	446	17	–	3.4	–	97	1.8
VMA2(04)SEW	850	425	386*a	77.2*c	–	3.4	–	71	1.6
VMA2(04)NS	850	425	386*a	77.2*c	–	3.4	–	48	1.0
VMA3	850	425	446	17	–	–	1.7	17	0.5
VMA3ATT	850	425	446	17	–	–	1.7	20	0.5
VMA3BE	850	425	446	17	–	–	1.7	22	0.5
VMA3SEP	850	425	446	17	–	–	1.7	21	0.5
VMA3SEW	850	425	386*a	77.2*c	–	–	1.7	17	0.6
VMA3NS	850	425	386*a	77.2*c	–	–	1.7	35	0.4

*a Liquid water added.

*b HRWRA was employed as an increment dosage scale, by cement weight.

*c Water of the components (SEW and NS) was also considered. Sew and Ns solid residue was 22 %.

*d All samples have a water to binder ratio of 0.35.

*e The amount of HRWRA varied from 0 to 3 % in order to reach the required flowability (300 mm).

- A poly (acrylamide-co-acrylate)-based viscosity modifying admixture (VMA1),
- A polyether-methylcellulose-based viscosity modifying admixture (VMA2),
- A synthetic co-polymer viscosity modifying admixture (VMA3).

VMAs were used at 0.2 % by cement weight, and VMA2 was also used at 0.4 %. These VMAs are commercial components provided by the material supplier and not more data is available.

Finally, 5 types of nanocomponents (NC) were included at 2 % by cement weight:

- Attapulgite (palygorskite) (Att), a nanoclay with needle shaped particles and a BET surface of 144 m²/g,
- Bentonite (montmorillonite) (Be), a nanoclay with plate shaped particles with a BET surface of 138 m²/g,
- Two types of sepiolite (palygorskite), a nanoclay with needle shaped particles with a BET surface of 316 and 284 m²/g respectively, one in a powder form (Sep) and the other dispersed in water (Sew),
- A water-based colloidal nanosilica (NS), MasterRoc MS 685 supplied by BASF, with a 1.134 + 0.003 g/cm³ density and a 22 % of solid content.

2.2. Experimental methods

2.2.1. Mini-cone slump test: Flowability and structural build-up evaluation

Mini-cone slump test was carried out using plastic 3D printed mini-cones with dimensions 100 × 70 × 50 mm placed on a transparent methacrylate plastic base in order to record the spread process from below with a video camera. Final spread diameter and final time of spread were the parameters measured in this test. Final spread diameter was measured when paste spreading stopped and final time of spread was determined using the recorded video. The test was used to evaluate two different properties: flowability and structural build-up of cement paste.

The flowability of cement pastes required for structural build-up and DSR tests was achieved proportioning HRWRA to reach a mini-cone spread diameter of 300 ± 30 mm. A flowability study of the pastes with NC and VMAs was carried out, increasing the amount of HRWRA and measuring the spread diameter and final time of spread.

On the other hand, paste samples left at rest and stirred were tested with the mini-cone slump test over time to evaluate the structural build-up of the mixture. Four samples of each batch were left at rest inside a mini-cone and tested at 0, 10, 30 and 50 min, corresponding the initial

testing time to ten minutes after cement and water were mixed together. Other samples of each batch were stirred manually for one minute and tested immediately after each corresponding sample at rest.

2.2.2. Dynamic shear rheometer (DSR): Rheology and structural build-up evaluation

Dynamic shear rheometer test (DSR) was carried out in a modular rheometer (THERMO-HAAKE MARS Rheostress 600) with a coaxial cylinder geometry (bob-cup CC20TiSe) [47]. Rheological properties as initial yield stress, viscosity and structural build-up were measured with this test on fluid pastes using two different protocols: initially, a controlled stress (CS) protocol and afterwards a constant controlled rate (CCR) protocol. CCR protocol is also named static yield stress test [8,43]. Rheometer geometry and both protocols have been detailed in a previously published study [12].

Fig. 1 shows how rheological parameters were determined in CS and CCR and the protocols of both procedures. Initial yield stress and viscosity values were obtained from rheometer software using the CS protocol (Fig. 1a, according to a modified-Bingham model, which showed the best adjustment for these fluid pastes [46,47]. Immediately after the CS protocol, CCR protocol (Fig. 1b) was used to evaluate the structural build-up of pastes with nanocomponents and VMAs, considering the evolution of the static yield stress peak value over time (segment IV). This protocol was carried out over time, using the same time lapses as for mini-cone slump test (0, 10, 30 and 50). DSR test started also ten minutes after water was added in the mixing process. A pre-shear stress was applied after CCR protocol in order to homogenize the mixture. Similar rheometer protocols and procedures are reported in the literature [5,8,26,42,43].

3. Experimental results:

3.1. Effect of HRWRA on cement paste flowability

The effect of HRWRA amount on fresh paste flowability was evaluated with the mini-cone slump test. Fig. 2 presents the experimental results of final spread diameter and final time of spread of pastes with nanoclays (NC) and combined also with the three types of VMA (VMA1, VMA2 and VMA3, respectively). Two amounts of admixture, 0.2 and 0.4 % regarding cement weight were considered in the case of VMA2, while only 0.2 % was considered for VMA1 and VMA3. The amount of admixture was selected in each case after a previous study to determine proper VMAs percentages for fluid pastes [34]. These parameters have been related in the literature with rheological properties as yield stress

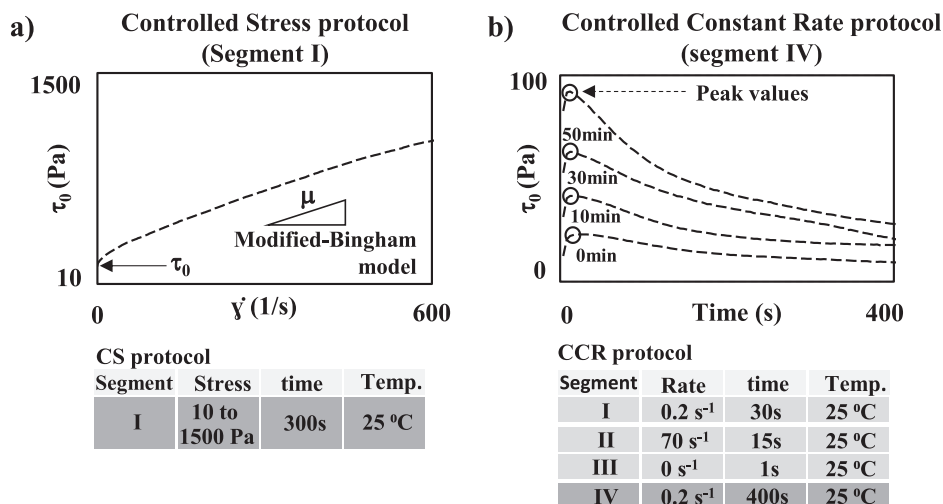


Fig. 1. Testing DSR protocols applied on paste samples. a) Controlled stress protocol (CS) according to a Modified-Bingham model; b) Controlled constant rate protocol (CCR).

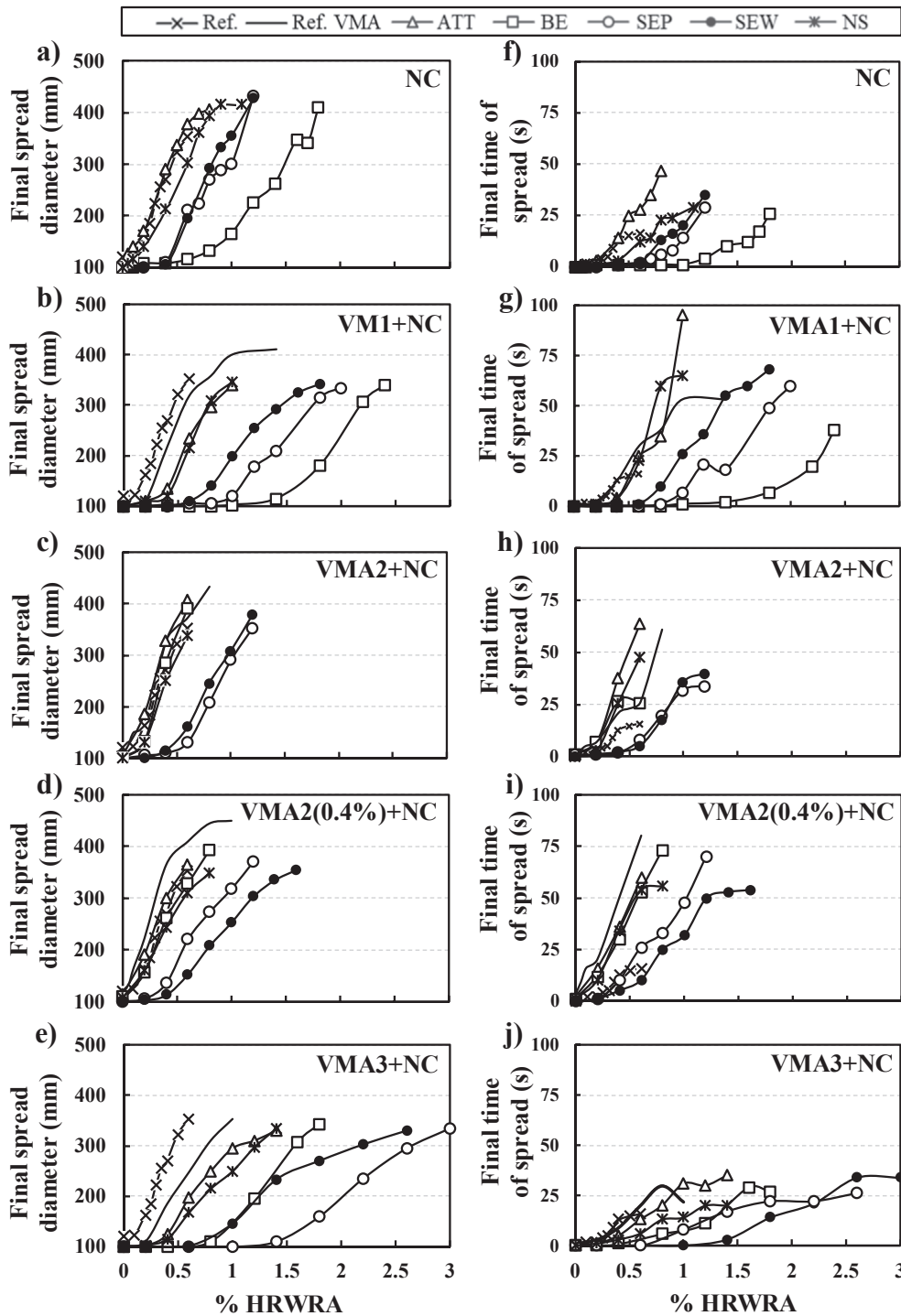


Fig. 2. Final spread diameter (mm) and final time of spread (s) of pastes with nanoclays (NC), VMAs and different amounts of HRWRA measured with the mini-cone slump test.

(τ) and viscosity (μ) [13,36–40].

Final spread diameter results (Fig. 2 showed that a minimum amount of HRWRA is necessary to increase the diameter and, above it, the diameter increase linearly with the amount of HRWRA. The reference mixture, without NC or VMA, required a very little amount (0.1 %) to activate the flowing effect of HRWRA. The incorporation of NC (Fig. 2a produced different effects. ATT and NS behaved similar to the reference mixture, while SEP, SEW (0.4 %) and especially BE (0.6 %) required larger amounts of HRWRA to reach the same flowability, due to the consumption of HRWRA by the NC particles [28,29].

When NC were combined with the VMAs, two different effects were observed. VMA1 and VMA3 (Fig. 2b and 2e, respectively) enlarged the amount of HRWRA required to achieve the target flowability, increasing HRWRA consumption up to 1.4 %. Nevertheless, both amounts of VMA2 (Fig. 2c and 2d showed a synergetic effect, reducing significantly the amount of HRWRA necessary for the mixture with bentonite (BE) to a value similar to the reference paste (Fig. 3. This interaction between BE and HRWRA [12,26,28] was cancelled with VMA2 addition, improving initial dispersion of bentonite.

The effect of HRWRA was also observed on the final spread time of

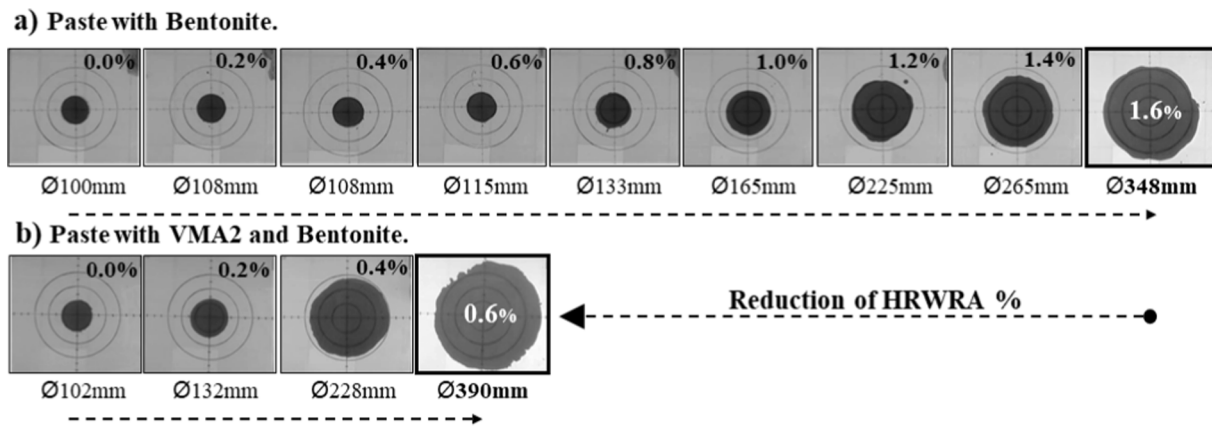


Fig. 3. Effect of HRWRA on the Spread diameter of cement pastes with bentonite: a) Paste with bentonite, b) Paste with VMA2 and bentonite.

pastes with NC and VMAs. After reaching the minimum value of HRWRA that activate the flowing effect, the larger the amount of HRWRA, the longer the final time. BE showed again the larger amount of admixture required to enlarge the spread time. The longer spread times were measured for mixtures with VMA1 (Fig. 2g, reaching final times of 75–100 s and showing a more viscous spread mechanism than the other two VMAs. On the other side, samples with VMA3 (Fig. 2j) showed a limit of spread time of 25 s and larger amounts of HRWRA did not show any further effect. This effect is related to the functionalization of VMA3 that maintains a uniform viscosity value, as can be seen in Table 1.

3.2. Influence of nanocomponents and VMAs on cement paste rheology evaluated by DSR

Initial yield stress (τ_0) and viscosity (μ_0) were measured on fluid pastes (mini-cone spread diameter of 300 ± 30 mm) using a DSR controlled stress protocol (CS) and calculated according to the modified-Bingham model [46]. Fig. 4 plots the rheological curves and Table 1 summarizes τ_0 and μ_0 values of pastes with NC and VMAs.

Mixtures with similar flowability showed different initial rheological properties. Pastes with NC (Fig. 4 a) increased τ_0 regarding the reference paste, ranging from 10 Pa (BE) to 95 Pa (SEW). On the other hand, μ_0 showed a slight increase, reaching 0.9 Pa s (SEW). The rheological curves were essentially linear.

The incorporation of VMA to the pastes with NC modified both rheological parameters (τ_0 and μ_0), although they are formulated theoretically to modify μ_0 . Pastes with VMA1 and with 0.4 % of VMA2 (Fig. 4b and 4d) presented rheological curves with high μ_0 values, ranging from 1 to 2.5 Pa s. The largest τ_0 value was 174 Pa and corresponded to VMA1 and sepiolite in powder form (SEP). On the other hand, 0.2 % of VMA2 and VMA3 (Fig. 4c and 4e) showed a linear rheological curve, with lower τ_0 and μ_0 values. In both cases, the VMA effect was slightly affected by the presence of NC. VMA3 showed the narrowest variability of both parameters. NS showed low τ_0 and μ_0 values when combined with any VMA.

3.3. Evolution of rheological properties over time: Reversible and irreversible effects.

The variation of rheological properties of fresh pastes over time is related to the development of bonding forces among solid particles dispersed in the liquid matrix of a cement paste and can be sorted in reversible and irreversible mechanisms [5–7]. The evolution of the rheological properties over time was assessed with both the mini-cone slump test and the DSR. The mini-cone was used to assess the reversible and irreversible effects while the DSR was used only to evaluate the irreversible effects because the testing procedure requires a pre-shear that breaks the reversible bonding forces [8,43].

The effect of the bonding forces developed inside the paste due to both the reversible and the irreversible mechanisms was evaluated with the variation of the spread diameter in the mini-cone slump test over time on samples left at rest inside the mini-cone until tested.

The irreversible effects were evaluated with the mini-cone slump test over time on samples stirred before testing and also with a DSR constant controlled rate (CCR) protocol, by comparing the yield stress peak values over time. Both tests were carried out after the sample was stirred, cancelling the effects of the reversible mechanisms.

It must be considered that the concepts of reversible and irreversible bonding mechanisms are applied in the literature related to flocculation and hydration processes respectively [4,5]. However, in this study the reversible bonding mechanisms are those that arise and grow over time in samples left at rest, while the irreversible bonding mechanisms are those that remain and increase over time when the sample is stirred before tested. Namely, reversible mechanisms are bonding forces that can flocculate and deflocculate if some shearing energy is applied, while irreversible mechanisms are C-S-H bridges that could not be broken down [4–6].

The use of nanocomponents and VMAs produces changes on the evolution of the rheological properties. Particularly, they were introduced to produce reversible effects, modifying initial yield stress, viscosity and structural build-up over time. Nanoclays had more effect on yield stress, above all sepiolites uncombined. Whereas, VMAs showed influence on yield stress and viscosity, with the exception of VMA3 that was mainly on yield stress.

3.3.1. Reversible effects over time: mini-cone slump test of pastes left at rest

Fig. 5 presents the final spread diameter results of different samples of the same batch of each paste composition left at rest in a mini-cone and tested at 0, 10, 30 and 50 min, respectively. It must be considered that time 0 min in this study corresponded to 10 min after water was incorporated to the mixing process. On the other hand, one hour is considered the limit when cement setting would become the main mechanism related to paste stiffening [5,7,9]. During the dormant period (first hour), a cement grains nucleation process takes place due to C-S-H bridges formation and reversible bonding forces. It can be observed that all pastes showed a reduction of diameter with time, as expected [13,40].

The type of NC modified the evolution of diameter in time (Fig. 5a). ATT, NS and BE needed 50 min to reach 120 mm of final diameter, while both sepiolites reached 100 mm at 30 min.

When combined with VMA, the pastes also showed changes in the reduction spread diameter. The reference paste with VMA1 presented a quick diameter reduction (Fig. 5b), reaching a final spread diameter of 130 mm at 30 min. The combination with ATT, BE and SEW did not modify this trend, while SEP showed a quicker reduction of final diameter reaching 130 mm at 30 min. An interaction between VMA1

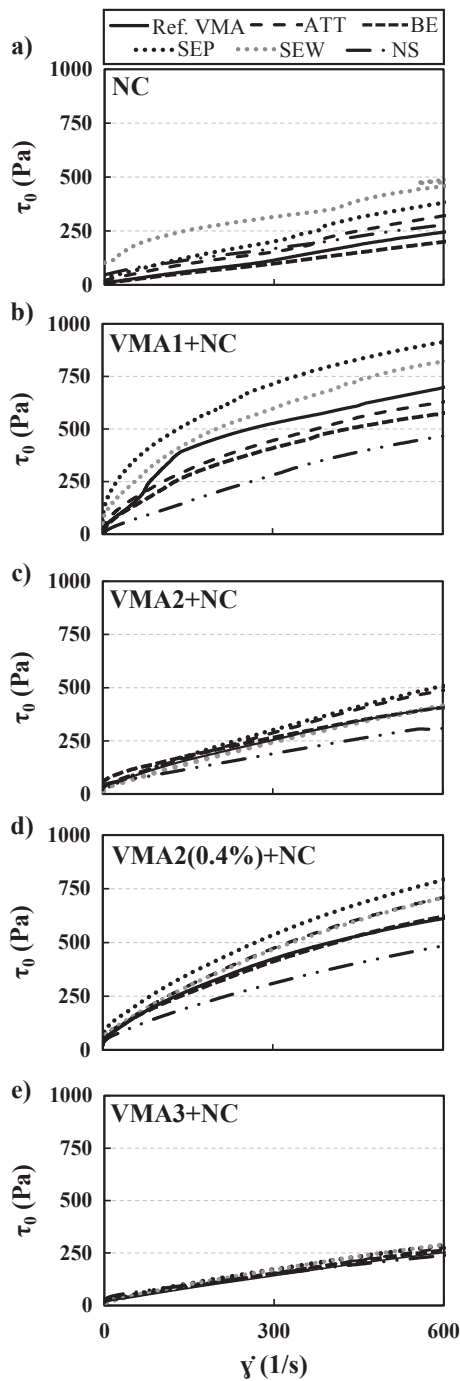


Fig. 4. DSR Controlled stress (CS) curves measured on pastes with nanoclays (NC) and viscosity modifying admixtures (VMA).

and NS was recorded, reducing the efficiency of this type of nanoparticle alone.

When VMA2 was incorporated at 0.2 % and at 0.4 % (Fig. 5c and 5d, the diameter reduction was lower than VMA1. However, the combination with NC also produced synergetic effects. Paste with 0.2 % VMA2 and BE reached 100 mm of spread at 30 min, showing a quick reduction of final spread diameter. ATT and NS produced a slower diameter reduction, reaching 100 mm at 50 min. Nevertheless, when the amount of VMA2 was increased to 0.4 %, all NC showed a similar behavior, reaching 100 mm at 50 min.

Mixtures with VMA3 (Fig. 5e produced a larger diameter reduction with ATT, SEP and NS. NS showed the quickest reduction of final spread

diameter (120 mm at 30 min), while BE and SEW presented a lower reduction of final spread diameter than the other mixtures with VMA3.

3.3.2. Irreversible effects over time: mini-cone slump test on stirred samples.

Irreversible variations of rheological properties over time were evaluated with mini-cone slump test over time on stirred samples and the results are also plotted in Fig. 5. It can be observed that the stirred samples showed a poorer reduction of final spread diameter than the samples left at rest and none of the stirred pastes reached a final diameter of 100 mm, as the minimum value reached 150 mm (VMA1 with BE).

Mixtures with NC (Fig. 5f showed the same trends as samples at rest and both sepiolites showed the largest spread reduction, reaching 160 mm at 50 min. The incorporation of VMAs to the mixtures did not improve the spread reduction compared to NC alone. VMA 1 (Fig. 5g and VMA2 at 0.4 % (Fig. 5i did not produce any significant spread reduction. VMA2 at 0.2 % (Fig. 5h and VMA3 (Fig. 5j only reduced 100–150 mm the spread diameter. These results point out that the stirring applied to the mixtures before testing cancelled the reversible bonding mechanisms. As a consequence, the spread reductions could be undoubtedly attributed to irreversible bonding mechanisms which were developed inside the fresh pastes over time.

3.3.3. Irreversible effects over time: DSR tests CCR protocol.

The variation of the peak shear value (τ_{pv}) over time (0, 10, 30 and 50 min) of pastes with NC and VMA was assessed with a dynamic shear rheometer (DSR) using a controlled constant rate test (CCR) at 0.2 s^{-1} . It must be considered that time 0 min of the tests corresponded to 10 min after water was incorporated to the mixing process. A pre-shear stirring of 70 s^{-1} was applied before each test, in order to cancel all the reversible bonding forces developed in the paste over time [5,8,26,42,43]. Accordingly, the changes of τ_{pv} could be attributed to the irreversible bonding mechanisms developed in the pastes over time [4,5].

The experimental τ_{pv} obtained from CCR curves are summarized in Table 2. Pastes without VMAs showed initial τ_{pv} ranging from 0.65 Pa (BE) to 76 Pa (SEW). The reference cement paste displayed 1.4 Pa and SEP and NS presented values around 30 Pa. The evolution of τ_{pv} over time followed a linear trend in all mixtures and a τ_{pv} growth parameter was calculated ($\Delta\tau_{pv}$) that is also presented in Table 2. Pastes with NC showed $\Delta\tau_{pv}$ larger than the reference mixture, ranging from $20.5 \cdot 10^{-2} \text{ Pa/min}$ (BE) to $104 \cdot 10^{-2} \text{ Pa/min}$ (SEP).

The incorporation of VMAs to the reference paste increased both τ_{pv} and $\Delta\tau_{pv}$, presenting values equivalent to pastes with NC, ranging from 5.2 to 22 Pa and 7.7 to $43.7 \cdot 10^{-2} \text{ Pa/min}$, respectively. However, the combination of NC and VMAs showed some synergetic effects and some negative interactions on both parameters. Pastes with NC and VMA1 showed a reduction of the shear peak value (τ_{pv}) and the growth parameter ($\Delta\tau_{pv}$), narrowing the differences observed in the samples only with NC. Pastes with NC and VMA2 increased τ_{pv} values regarding VMA2 alone. The largest synergies (increase of τ_{pv} and $\Delta\tau_{pv}$) were observed for samples with bentonite (BE) with 36.1 Pa and $93.6 \cdot 10^{-2} \text{ Pa/min}$, while the largest interaction (decrease of τ_{pv} and $\Delta\tau_{pv}$) was recorded for samples with sepiolite in water suspension (SEW), with 11 Pa and $5 \cdot 10^{-2} \text{ Pa/min}$ respectively.

Mixtures with NC and VMA3 presented a significant reduction of initial peak values in almost all cases except BE, which slightly increased to 5.2 Pa. Initial τ_{pv} ranged from 1.9 to 25 Pa, which corresponded to NS. Samples with BE and NS produced a remarkably large increase of $\Delta\tau_{pv}$, reaching 112.8 and $116.4 \cdot 10^{-2} \text{ Pa/min}$ respectively.

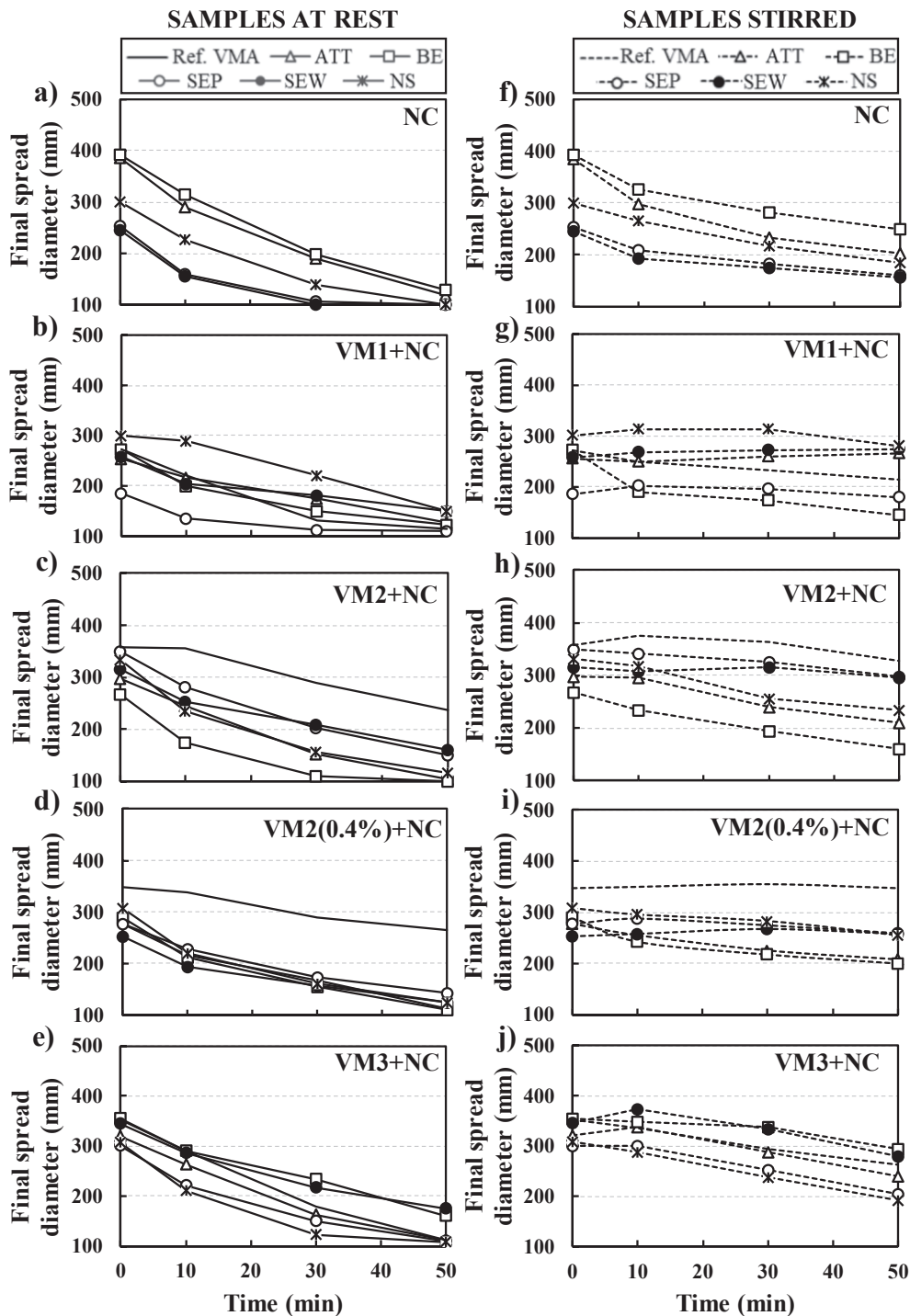


Fig. 5. Mini-cone slump test results over time. a-e) Final spread diameter of pastes at rest; f-j) Final spread diameter of stirred pastes.

4. Analysis and discussion

4.1. Synergies and interactions between NC and VMAs on cement paste rheology

According to the results obtained, low amounts of NC and VMAs can modify significantly rheological properties of cement pastes, as described in the literature [8,12,15,16,18]. Nanoclays size, shape and morphology, and VMAs polymer chain, morphology and molecular weight are linked to those synergetic effects [10,12–24].

Pastes with NC and VMA1 (a poly(acrylamide-co-acrylate)-based

viscosity modifying admixture) needed a larger amount of HRWRA than pastes without VMA1 to reach the target final spread diameter of 300 ± 30 mm. The water retention capacity of this type of VMA could be the reason behind this increase [18,22,23]. Besides, pastes with VMA1 and sepiolites in powder and dispersed in water (SEP and SEW, respectively) presented remarkably high yield stress and viscosity values. The needle shape particles of sepiolites, larger than attapulgite particles, can explain the particle entanglement due to the reduction of water by VMA1 (water retention capacity) [10,18,20]. Sepiolite dispersed in water (SEW) showed lower rheological values than sepiolite in powder form (SEP), because SEW was a functionalized component

Table 2
Peak values over time of cement paste measured with CCR on DSR.

Samples	$\tau_{pv-0min}$ (Pa)	$\tau_{pv-10min}$ (Pa)	$\tau_{pv-30min}$ (Pa)	$\tau_{pv-50min}$ (Pa)	$\Delta \tau_{pv}(10^{-2}$ Pa/min)
REF	1.4	2.5	4.1	5.4	8
ATT	9.7	–	22.7	–	43.3
BE	0.65	–	6.8	–	20.5
SEP	33	–	64.2	–	104
SEW	76.7	–	102.7	–	86.7
NS	30.9	–	53.9	–	76.7
VMA1	10.1	–	12.4	–	7.7
VMA1ATT	2.2	4.3	5.25	6	6.7
VMA1BE	2	3.2	4	5.4	6.3
VMA1SEP	19.5	15	22.4	22.8	11.4
VMA1SEW	12.7	8.7	14.8	17	12.5
VMA1NS	3	6.8	7.4	11.3	14.5
VMA2	13.6	–	26.7	–	43.7
VMA2ATT	23.3	20.9	42.25	53.6	68.1
VMA2BE	36.1	49.1	64.1	84.6	93.6
VMA2SEP	29.1	69.7	51.5	71.5	56
VMA2SEW	11	18.4	13.3	16.4	5
VMA2NS	18	39.1	42.8	57.7	68.7
VMA2(0.4)	22	–	34.8	–	42.7
VMA2(0.4) ATT	35.7	49.5	58.5	75.7	74.5
VMA2(0.4) BE	36.3	38.1	55.3	70.5	72
VMA2(0.4) SEP	83	183.8	113	145	45
VMA2(0.4) SEW	17.1	19.2	18.8	21.2	6.7
VMA2(0.4) NS	35.1	38.4	63.3	77.4	90.4
VMA3	5.2	13.4	18.6	25.9	38.5
VMA3ATT	5	8.3	18.61	25.9	43.1
VMA3BE	5.2	16.5	37.3	62.1	112.8
VMA3SEP	2.4	2.3	5.7	9.7	15.4
VMA3SEW	1.9	3.3	3.3	5.5	6.2
VMA3NS	25	20	58.2	76.1	116.4

[12,27]. However, sepiolite uncombined showed higher thixotropic behaviour than combined VMA1. Pastes with VMA1 - ATT and BE showed a much moderated increase of rheological parameters. Conversely, paste with NS and VMA1 reduced yield stress and viscosity, regarding samples only with NS, decreasing the strong viscous effect of VMA1 [32].

When mini-cone slump test results over time were compared on samples at rest and stirred, a remarkable change was observed, as samples at rest decreased diameter with time while stirred samples did not and, in some samples even increased. The release of water retained by the VMA1 and the breakage of the bonding forces due to the stirring process could explain this difference. The exception was observed for BE, as the sample stirred showed a remarkable reduction during the first 10 min, which moderated afterwards.

On the other hand, pastes with VMA2 (a polyether-methylcellulose-based viscosity modifying admixture) and NC required the same amount of HRWRA as uncombined pastes [19]. There was a remarkable exception for pastes with VMA2 and BE, which showed a large reduction of the HRWRA required to reach the target flowing diameter of 300 ± 30 mm. This synergetic effect happened for 0.2 and 0.4 % of VMA2 and could be attributed to the dispersion effect on BE plate shaped particles of VMA2, breaking the “house of cards” effect described in the literature [12,26,28]. Accordingly, there was not need of any extra HRWRA to disperse the BE plate shaped particles, increasing HRWRA efficiency up to 3.75 times. This synergy did not happen for the other NC, especially on palygorskite-based nanoclays (attapulgite and sepiolites) due to an increase of surface water adsorption by VMA2 and the entanglement of needle shaped particles [12,27].

Mini-cone slump test on samples at rest of mixtures with NC and VMA2 produced a quick reduction of diameter over time and BE samples showed the largest reduction. Accordingly, it can be said that VMA2

improved initial BE dispersion but BE started to build-up house of card adhesion forces over time when left at rest [12,26,28]. These adhesion forces were partially cancelled on stirred samples, although a slight reduction of final diameter was observed. On the other hand, when VMA2 was increased to 0.4 %, all NC produced the same diameter reduction over time for samples left at rest.

Mixtures with VMA3 (synthetic co-polymer viscosity modifying admixture) and NC demanded larger amounts of HRWRA to spread than samples uncombined or with the other VMAs, especially sepiolites. However, VMA3 produced very similar initial yield stress and viscosity values for all NC, showing a high HRWRA adsorption while properly dispersing NC particles. The evolution of spread diameter measured with the mini-cone slump test over time on samples left at rest showed the largest decrease for NS followed by sepiolite dispersed in water (SEW). A diameter reduction was observed for most of the stirred samples.

4.2. Structural build-up of cement paste: Reversible and irreversible mechanisms

Fig. 6 shows the effect of the structural build-up on the spread of a paste sample with 0.2 % of VMA2 and BE in a mini-cone left at rest and stirred before tested over time. At the initial time, which corresponded to 10 min after water and cement were mixed together, the sample produced a large spread of 300 ± 30 mm. At 10 min the difference was easily observed, as the sample left at rest reduced the slump regarding the sample stirred before tested. Afterwards, the difference increased over time. It can be observed that the effect of time on the sample at rest corresponds to the bonding forces generated by reversible mechanisms, which were mainly cancelled by stirring the sample and only irreversible bonding forces remained [5–7].

Fig. 6 also shows the evolution in time of the shear peak value of samples of the same paste tested with a CCR DSR protocol, where the sample is subjected to a pre-shear force before tested, equivalent to stirring the sample in the mini-cone. The peak value increased over time and the growth was remarkably larger than the reference paste with VMA2, pointing out a synergetic effect between NC and VMA admixture.

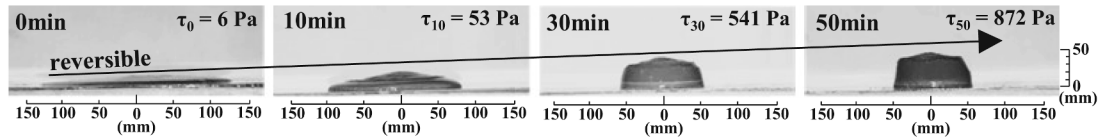
These results agree with the literature: the initial yield stress corresponds to the initial flocculation that appears almost instantly, while any further increase of bonding forces requires some minutes at rest to appear. These incipient bridges are the effect of C-S-H formation due to cement hydration and can be easily broken by stirring the paste. However, as hydration continues, the paste at rest would rebuild those bridges. Therefore, these mechanisms can be considered reversible [4–6].

On the other hand, the slight increase of yield stress of stirred samples can be attributed to irreversible mechanisms related to the increase of the roughness of the particles in suspension due to the crystallization of C-S-H on their surface [6,9]. As hydration during the dormant period can be considered steady, the increase of yield stress of stirred samples was linear [5,6].

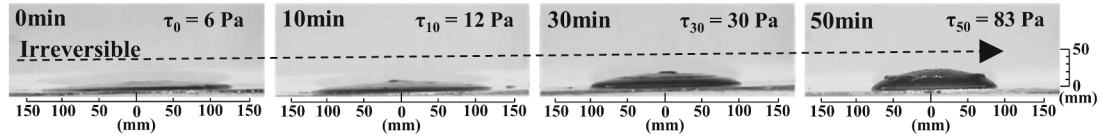
The addition of NC and VMA modified particle flocculation and, consequently, the amount of HRWRA required to achieve the target spread diameter. Some combinations, as the example presented in Fig. 6 (VMA2 with bentonite), showed synergetic effects by reducing significantly the amount of HRWRA and accelerating and maximizing the structural build-up mechanisms.

The structural build-up corresponds to the development of cohesive forces inside the fresh pastes due to flocculation and can be related to the evolution of the static yield stress (τ) over time with the thixotropic coefficient (A_{thix}) [4,5]. The static yield stress (τ in Pa) can be calculated from the final spread diameter measured in the mini-cone slump test over time of samples left at rest and stirred before testing, using (Eq. (1)) [36],

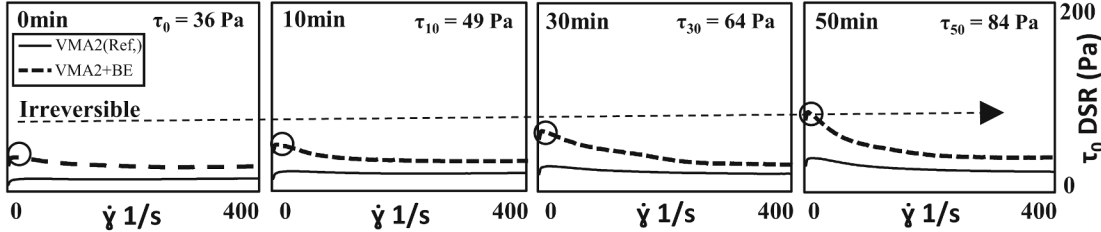
a) Minicone slump test: samples at rest (reversible structural build-up)



b) Minicone slump test: stirred samples (irreversible structural build-up)



c) DSR: pre-sheared samples (irreversible structural build-up)



* τ of minicone slump test was calculated with rousel model.
 * τ of DSR (CCR) was determined from peak value of the curve.

Fig. 6. Rheological properties evolution of pastes with VMA2 (0.2 %) and bentonite. (a) mini-cone slump test of samples at rest and (b) samples stirred before testing; (c) measured with DSR (CCR testing protocol).

$$\tau = \frac{225\rho gV^2}{128\pi^2R^5} \quad (1)$$

where ρ is the paste density (g/cm^3), g is the gravity acceleration ($9.8 \text{ m}/\text{s}^2$), V is the tested sample volume used in the mini-cone test (m^3), and R is the radius of spread (m).

The evolution of static yield stress (τ) over time can be described by the rate of structural build-up of cement paste or thixotropic coefficient (A_{thix}) and was calculated for the samples stirred as the linear increase of yield stress over time, according to (Eq. (2)) [5,7]:

$$A_{thix} = \frac{\tau_{0t1} - \tau_{0t0}}{t_{rest}} \quad (2)$$

where τ_{0t0} is the initial yield stress, τ_{0t1} is the yield stress after a specific time (t_{rest}). Eq. (2) was used to calculate the paste structural build-up rate from 0 to 50 min (10–60 min after water was mixed with cement) [5–8].

Table 3 presents the main rheological parameters calculated for samples stirred and at rest tested over time on mini-cone slump test. The evolution of τ over time of stirred samples was governed by the irreversible mechanisms and showed a linear trend, as expected [5–7]. It can be characterized by the thixotropic coefficient (A_{thix}) and the yield stress at 30 min (τ_{30}): A_{thix} ranged between 0.0 and 2.55 Pa/min and τ_{30} varied between 1.39 and 59.66 Pa. Fig. 7 shows the linear relationship between τ_{30} and A_{thix} for stirred samples. Sepiolites showed higher A_{thix} in pastes without VMAs, similar to results of reversible effects tests. However, attapulgite showed a slight increase of A_{thix} with VMA2, being a palygorskite clay with a shorter particle size than sepiolite. Nanosilica worked similarly with VMA3 and uncombined but showed larger reversible effects with VMA3. On the other hand, VMA1 with bentonite presented higher irreversible effects over time on mini-cone test (A_{thix}) while on reversible effects were remarkable with VMA2 (Table 3).

The evolution of irreversible bonding forces was also observed on the yield stress peak values of paste samples tested with DSR over time (Table 2). Although values were not exactly the same, due to the different conditions between testing techniques, paste compositions showed the same linear behavior over time. Peak values at 30 min

Table 3

Calculated structural build-up rate (A_{thix}) of samples left at rest and stirred in the mini-cone slump test over time.

	Mini-cone stirred		Mini-cone at rest	
	A_{thix} (Pa/min)	τ_{30} (Pa)	τ_{30} (Pa)	t_c (min)
ATT	0.49	12.87	35.32	30
BE	0.16	4.82	28.88	50
SEP	1.49	44.15	622.71	10
SEW	1.53	53.68	550.62	10
NS	0.73	17.99	162.81	10
VMA1	0.25	12.97	237.28	10
VMA1ATT	0.0	7.49	54.27	30
VMA1BE	2.55	59.66	120.00	30
VMA1SEP	0.52	31.59	494.30	0
VMA1SEW	0.0	5.92	47.08	30
VMA1NS	0.03	2.94	17.03	30
VMA2	0.02	1.39	4.25	50
VMA2ATT	0.37	11.18	107.99	30
VMA2BE	1.50	30.9	541.68	10
VMA2SEP	0.04	2.40	25.59	30
VMA2SEW	0.02	2.75	22.17	30
VMA2NS	0.21	8.17	98.47	30
VMA2(04)	0.0	1.51	4.15	50
VMA2(04)ATT	0.34	14.82	64.85	30
VMA2(04)BE	0.45	18	97.87	30
VMA2(04)SEP	0.05	5.51	56.83	30
VMA2(04)SEW	0.0	6.22	87.89	30
VMA2(04)NS	0.09	10.21	84.12	30
VMA3	0.11	3.87	45.77	30
VMA3ATT	0.17	4.47	77.56	30
VMA3BE	0.04	1.95	12.60	50
VMA3SEP	0.41	8.48	114.74	30
VMA3SEW	0.07	2.12	17.72	50
VMA3NS	0.58	11.53	315.85	10

($\tau_{pv,30}$) varied between 3.3 and 102.7 Pa and ($\Delta\tau_{pv}$), which can be considered equivalent to A_{thix} , ranged between 5 and $116.4 \cdot 10^{-2}$ Pa/min. A linear relationship between $\Delta\tau_{pv}$ and $\tau_{pv,30}$ was also identified for all the mixtures but those with VMA1, where $\Delta\tau_{pv}$ was very similar for all the paste compositions, independently to $\tau_{pv,30}$ (Fig. 8). This fact can be related to the initial water retention of VMA1 that would be released to

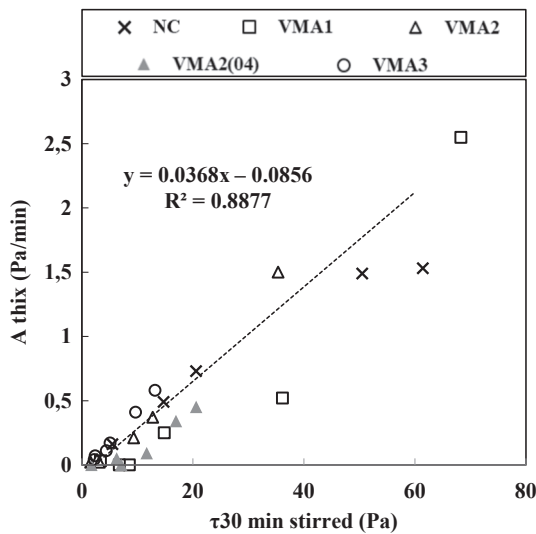


Fig. 7. Thixotropy parameter (A_{thix}) related to shear value (τ_{30}) of stirred nano-clay modified paste samples with and without VMAs tested with mini-cone slump test.

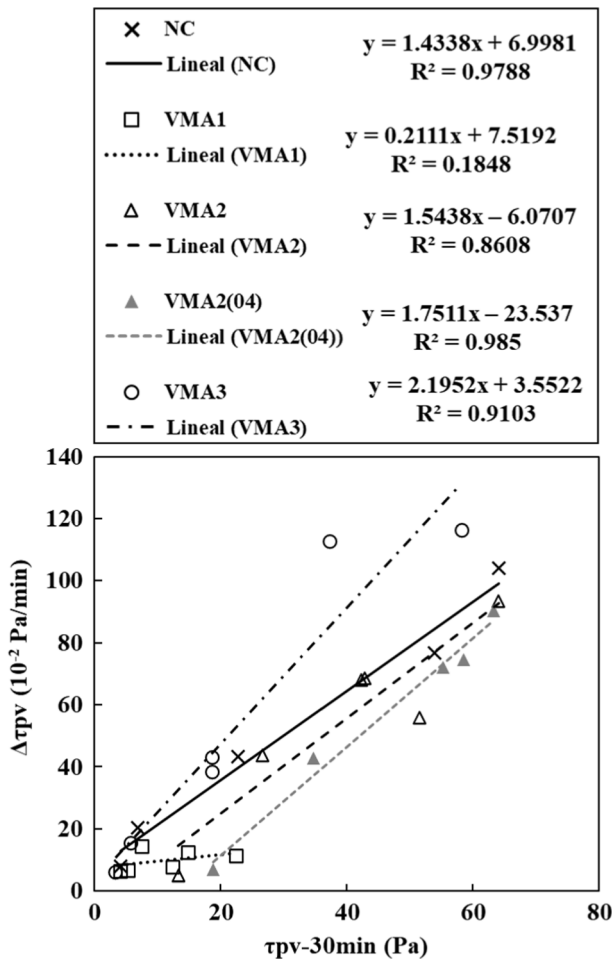


Fig. 8. Peak shear value growth parameter ($\Delta\tau_{pv}$) related to peak shear value (τ_{pv}) of nano-clay modified paste samples with and without VMAs tested with DSR CCR protocol.

the cement system during pre-shear, but would not be regained afterwards [22].

The main rheological parameters of samples left at rest over time, which corresponds to the effects of reversible mechanisms, are also presented in Table 3. Yield stress at 30 min (τ_{30}) was remarkably larger for all the mixtures considered in this study. As a general rule, the effect of reversible structural build-up mechanisms increased one order of magnitude at 30 min (τ_{30}). Some mixtures also showed a synergetic effect bringing forward the time when structural build-up initiate (t_c) before 30 min, corresponding to samples with the largest (τ_{30}): SEW, SEP, VMA1, VMA1SEP, VMA2BE and VMA3NS. It can be also highlighted that some mixtures showed negative interactions between NC and VMAs by reducing τ_{30} regarding samples only with VMA1 and

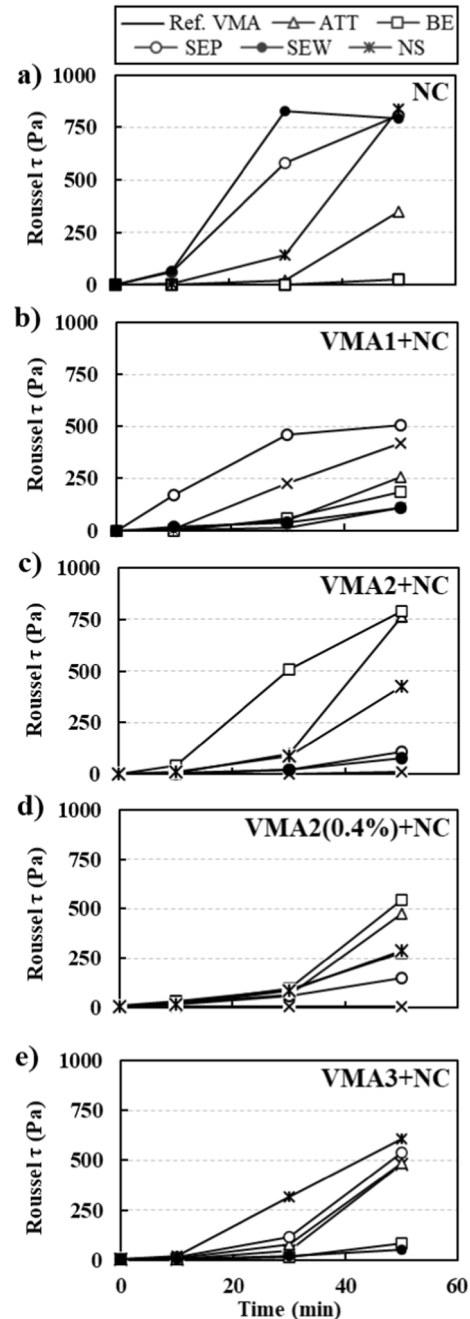


Fig. 9. Yield stress difference between samples at rest and stirred over time, corresponding to the difference between the reversible and irreversible structural build-up, respectively.

VMA3.

Fig. 9 plots the difference of yield stress calculated using Roussel model (τ) between samples left at rest and samples stirred tested with the mini-cone over time. It was observed that the reversible structural build-up of the samples at rest required a certain period of time before developing. Most of the samples showed a sharp increase of the difference at 30 min. The samples that showed synergetic effects produced this difference before 30 min by combining specific NC and VMAs, while those that presented negative interactions, delayed it further than 50 min. These pastes with enhanced thixotropic ability when left at rest are promising mixtures to be used in self compacting concretes in order to reduce the lateral formwork pressure.

5. Conclusions

An experimental study on the synergies produced by the combination of nanocomponents (NC) and viscosity modifying admixtures (VMAs) on fresh fluid cement paste rheology and structural build-up mechanisms at very early ages was presented. A commercial nanosilica (NS), an attapulgite (AT), a bentonite (BE), a sepiolite in powder form (SEP) and a sepiolite dispersed in water (SEW) were used. Three VMAs, a poly(acrylamide-co-acrylate)-based (VMA1), a polyether-methylcellulose-based (VMA2) and a synthetic co-polymer (VMA3), were considered. Paste samples were assessed with mini-cone slump test and dynamic shear rheometer test (DSR), and the difference between samples left at rest and stirred over time were evaluated.

The main conclusions were:

- The incorporation of NC and VMA to cement pastes increase the amount of HRWRA required to achieve a target spread diameter, especially bentonite and sepiolites with VMA1 and VMA3. Mixtures with lower amount of HRWRA showed larger structural build-up at very early ages.
- VMA2 at 0.2 % with bentonite showed a synergetic effect reducing the HRWRA amount needed and also decreasing the spread diameter over time on mini-cone slump test, due to an initial dispersion effect on bentonite particles of VMA2. VMA2 at 0.4 % showed a spread diameter reduction over time with all the components but more slowly and without reducing the amount of HRWRA required to achieve the target spread diameter.
- For the same spread diameter, pastes with NC and VMA showed larger initial yield shear stress (τ_0). VMA1 with NS showed the opposite effect, reducing initial yield stress regarding to components uncombined. That initial effect did not change over time as showed by the shear stress peak value rate ($\Delta\tau_{pv}$) of this paste. On the contrary, VMA3 with NS showed a highly thixotropic behaviour.
- The development of bonding forces over time produced a reduction of spread diameter over time in the mini-cone test and an increase of yield stress peak value (τ_{pv}) in the CCR DSR protocol.
- Comparing the effect on samples at rest and stirred over time on mini-cone slump test allowed to evaluate reversible and irreversible mechanisms involved in structural build-up and thixotropy.
- The effects of irreversible structural build-up mechanisms were evaluated with stirred samples tested with the mini-cone and a CCR DSR protocol. Although the values vary due to the different testing techniques, the same trend was identified. The thixotropic coefficient (A_{thix}) and the shear stress peak rate value ($\Delta\tau_{pv}$) were calculated and could be used to define the linear tendency observed over time. Both parameters were low during the test.
- Sepiolites showed better control of rheological properties uncombined. A_{thix} and $\Delta\tau_{pv}$ parameters were higher when sepiolite was not combined with any VMA. VMAs increased of HRWRA required without improving rheological properties. Whereas, attapulgite, also a palygorskite clay with shorter particle size, increase these parameters only when it was combined with VMA2.

- Reversible structural build-up was calculated with the final spread diameter of samples left at rest. In all cases, reversible effects were larger than irreversible effects, showing an increased difference after 30 min at rest.
- A few combinations produced synergetic effects between NC and VMA, bringing forward initial reversible effects before 30 min, boosting yield stress increase and maximizing thixotropy, mainly VMA2 with bentonite, VMA3 with nanosilica and sepiolite alone. These combinations could be further explored to obtain fluid cement based materials with reduced lateral formwork pressure.

CRedit authorship contribution statement

Hugo Varela: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Gonzalo Barluenga:** Conceptualization, Methodology, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Irene Palomar:** Conceptualization, Methodology, Investigation, Writing - review & editing. **Alberto Sepulcre:** Conceptualization, Methodology, Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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