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Influence of nanoclays on flowability and rheology of SCC pastes

Hugo Varela, Gonzalo Barluenga, Irene Palomar
Department of Architecture, University of Alcala, Madrid, Spain.

Abstract

SCC rheology is the key factor of fresh performance and its control is required to overcome cast in place issues regarding pumping and formwork lateral pressure that still limits its widespread use. Nanoclays are good candidates to improve rheological properties of cement pastes as yield stress, viscosity and thixotropy, controlling paste flow behavior. However, some interactions between nanoclays and admixtures can limit their efficiency. In this study, a comparative analysis on rheology and flowability of SCC cement pastes blended with limestone filler and 2 % by cement weight of four types of nanoclays, attapulgite, bentonite, and sepiolite in powder form and dispersed in water, is presented. Two water to binder ratios (w/b), 0.35 and 0.45, were considered and a high range water reducing admixture (HRWRA) was used to reach the required flowability. Water adsorption of nanoclays, flowability and rheological properties of SCC cement pastes with nanoclays were evaluated. It was found that HRWRA was less effective on pastes with nanoclays and low w/b, particularly bentonite. Sepiolite showed larger water adsorption and higher enhancing of rheological properties. It was observed that, the relation of nanoclays and HRWRA was decisive to produce flowability on pastes with low w/b. Besides, flowability was deeply affected by w/b, as water saturation of nanoclays increased HRWRA efficiency. All nanoclays modified rheological properties due to its different particles morphology characteristics, however sepiolite showed the largest effects and reached the higher values of yield stress, viscosity and thixotropy ratios used.

Keywords: SCC paste; Nanoclays; water adsorption; flowability; rheology.

1. Introduction

Self-compacting concrete has many advantages regarding conventional concrete and has gained considerable acceptance among researchers and practitioners. However, SCC presents some issues regarding its cast in place that still need to be addressed, as the possible rheopectic behavior when pumped and the higher formwork lateral pressure due to its large flowability [1, 2]. Both issues can affect construction costs, speed and safety. Effective control of rheological properties has been described to be a key factor to improve SCC cast in place. For SCC pumping, a low dynamic yield stress to enhance the flowability is preferred, while a static yield stress increase in time (effect of thixotropy) is necessary to minimize SCC formwork lateral pressure [3].

Flowability and Rheology have been widely studied in cement-based materials over the last decades and several testing techniques have been established. Some simple field-oriented tests have been proposed to evaluate flowability parameters, as geometrical values (spread, slump, height) and time values, and correlated afterwards to rheological properties as yield stress and viscosity [4-10]. Jointly with this simple tests, Dynamic shear Rheometer (DSR) is a rheology testing precision equipment that is used to evaluate rheological parameters, as yield stress, viscosity and thixotropy, applying low shear stress or rate to material through different geometries, as parallel plates, bladed vanes or coaxial cylinders [11, 12].Coaxial cylinders are a geometry used frequently on fluid cement pastes. However, the experimental results depend deeply on the testing protocol applied and the geometry used [12, 13].

Yield stress and viscosity parameters can be obtained according to modified Bingham model with a DSR controlled shear stress protocol (CS) using the rheometer software to calculate. According to the literature, modified Bingham model can explain better the non-linear behavior of cement pastes than other models as Bingham and Hershel-Buckley models [12, 14]. On the other hand, there are many methods to evaluate thixotropy parameters on SCC, as *structural break down area, breakdown percentage, drop in apparent viscosity and yield value at rest*. [15-18]. Nevertheless, a DSR protocol commonly used to evaluate thixotropy parameters on pastes is the constant controlled shear rate protocol (CCR) and different calculation procedures have been proposed [19-22]. Roussel proposed the flocculation rate or yield stress rate growth (A_{thix}) as a parameter to evaluate the effective thixotropy of paste samples at rest during a certain period of time [19, 23], while Qian proposed a thixotropy index (I_{thix}) to evaluate thixotropy as the ratio between the peak yield stress and the steady-state equilibrium value [3, 24].

A promising alternative for improving flowability and rheology is the use of nanocomponents. Among them, nanoclays such as sepiolite, attapulgite, and montmorillonite can modify the rheological properties of fresh concrete. These nanoclays have different morphology and nature, but similar size or BET surface area [25-27]. Tregger and Kawashima have demonstrated that low amounts of Attapulgite remarkably modified yield stress and viscosity of cement pastes [13, 28-31]. Besides, Quanji et al. [32] showed that thixotropy of cement paste increased with time and nanoclays contributed to increase this effect. Ferron and Fuente explained that sepiolites can improve the stability of cement flocs [33]. Kaci et al. studied the effect of bentonite on the rheological behavior of mortars and found that bentonite increased yield stress after shear and reduced the characteristic time for yield stress recovery [34]. Besides, some authors had showed that bentonites produce a formation of house-of-card microstructure when the paste is kept at rest which may cause a reduction of flowability [3, 35, 36].

Another point to be considered is the interaction between nanoclays, water and superplasticizers (High range water reducing admixtures- HRWRA) and other polymeric admixtures [37]. Nanoclays showed more affinity with water and superplasticizers than cement particles because nanoclays have a S_{BET} 17 times larger than cement [38]. In fact, with low amounts of nanoclays by cement weight it is possible change the consistency of cement paste, mortar or concrete. Besides, the high water adsorption showed by nanoclays produces a workability reduction and a viscosity increase [35, 36, 39]. Also, nanoclays are able to adsorb 3-4 times of HRWRA than cement particles [38], but this adsorption varies according to the type of nanoclay and the amount of water on the mixture. Moreover, nanoclays combined with superplasticizers enhance thixotropy, increasing the difference between the peak yield stress value and the steady-state equilibrium value [3]. Accordingly, nanoclays' particle size and shape are responsible of modifying rheological properties of SCC pastes [10].

The aim of this study was to evaluate and to characterize the influence of four different nanoclays on flowability and rheology of limestone filler-cement blended pastes with two w/b and different amounts of a high range water reducing admixture (HRWRA). Water adsorption test, mini-cone slump test and dynamic shear rheometer test were used to provide a wide comparison of nanoclays effects on cement paste fresh state. Understanding the effects of nanoclays on fresh state rheological properties, as yield stress, viscosity and thixotropy, would help to control SCC cement paste flow behavior. The paper presents these effects on cement paste in order to overcome the issues identified on SCC in the next steps of the study.

2. Experimental program:

2.1. Material and mix design

The components of the pastes designed for this study are summarized in *Table 1*. A reference paste with a Portland cement type I 42.5 R blended with a limestone filler, supplied by Omya

Clariana SL, in a ratio 2:1 was designed. Two water to binder ratios (w/b), 0.35 and 0.45, were considered. In order to reach a large paste fluidity, a polycarboxilate based high range water reducing admixture (HRWRA) supplied by BASF construction chemicals Spain SL was used. The amount of HRWRA varied from 0 to 2% by cement weight, depending on the amount required to reach the target spread. Then, 2% by cement weight of four nanoclays supplied by TOLSA S.A. Group were added: attapulgite (*Att*), bentonite (*Be*) and two sepiolites, one in powder form (*Sep*) and the other dispersed in water (*Sew*). Attapulgite (or palygorskite) and Sepiolite are the same hydrated aluminum silicate mineral with the same needle particle shape, although sepiolite has a larger particle length and BET surface area (S_{BET}) [25, 26]. In contrast, Bentonite (Montmorillonite) is a smectite mineral clay with a plate particle shape but with similar S_{BET} than Attapulgite [25, 27]. *Table 2* presents the main particle characteristics of the nanoclays provided by the manufacturers.

2.2 Experimental methods

2.2.1. Water adsorption of nanoclays: Tea-bag test

The tea-bag test was carried out to evaluate water adsorption of nanoclays according to the literature [37]. A tea-bag was filled with 0.3 g of nanoclay and was submerged in water. The bag was weighted in wet conditions at times 0 - 180 minutes and water adsorption (*Ad*) of nanoclays over time was calculated according to (*Eq. 1)* [37].

$$Ad = \frac{(m_2 - m_1)}{m_0} \qquad \text{(Eq. 1)}$$

Where m_1 is the tea-bag wet weight at 0 minutes, m_2 is tea-bag wet weight at time t, m_0 is the weight of the dry clay sample.

Two different pH water solutions were considered: tap water (pH - 6) and a cement pore solution prepared with ordinary Portland cement and water with a 4:3 water to cement ratio (pH - 11).

2.2.2. Paste Flowability: Mini-cone slump test

A mini-cone with dimensions 100 x 70 x 50 mm was used to evaluate cement paste spread diameter, final slump and final spread flow time. A transparent methacrylate plastic base was used to videotape the spread process from below. Spread diameter has been related in the literature to yield stress while final spread time has been associated to paste viscosity [4-6]. The mini-cone test was used to evaluate the effect of water on pastes spread with nanoclays and, afterwards, the effect of a HRWRA on flowability parameters of pastes with nanoclays and 0.35 and 0.45 w/b ratio. The combination of both sets of results were then used to evaluate the interactions among nanoclays, water and HRWRA on cement paste flowability.

2.2.3. Rheological parameters: Dynamic shear rheometer (DSR)

Dynamic shear rheometer test (DSR) was carried out to evaluate yield stress, viscosity and thixotropy of fluid cement pastes with nanoclays. A modular rheometer (THERMO-HAAKE MARS Rheostress 600) with a coaxial cylinders bob-cup geometry (CC20TiSe) was used. The cup radius is 27mm, and the bob radius and height are 20mm and 34.5mm, respectively. All samples were tested using a universal temperature controller (UTC) and a cryostat set at 25 ± 1 ºC of temperature.

DSR test started 10 minutes after water was incorporated to the paste in the mixing process. Two testing protocols were applied in this study, summarized in *Figure 1*. The first testing protocol was a flow curve or controlled stress protocol (CS) that consisted in an upward ramp from 10 to 1500 Pa in 300 seconds. Yield stress and viscosity were calculated using a modified Bingham model [14]. The second protocol started afterwards and consisted on a time curve or constant controlled rate protocol (CCR), to evaluate structural build-up and thixotropy index of pastes with nanoclays. CCR procedure consisted on: a) low constant rate of 0.2 s^{-1} for 30 seconds; b) high constant rate of 70s^{-1} for 15 seconds; c) a stop (zero point) for 1second to avoid data-acquisition errors and d) low constant rate of 0.2s^{-1} for 400 seconds. According to the literature, CS protocol comprised 200 data points, while 100 data points were recorded in each stage of CCR protocol [12].

3. Experimental results:

3.1. Water related results

3.1.1 Water adsorption of nanoclays

The experimental results of nanoclays water adsorption between 0 and 30 minutes in two water solutions with different pH are reported in *Figure 2*. Water adsorption was measured for 180 minutes, although all nanoclays showed a constant value before 30 minutes. All nanoclays showed higher water adsorption values in cement pore solution (Alkaline pH - 11 solution) than in tap water. Dry nanoclays may adsorb different amount of water according to morphology, nature, size or BET surface area [36, 39]. The highest adsorption in alkaline solution was measured for *Sew* (sepiolite dispersed in water), although it must be considered that the measurement was done on a sample previously dried, grounded and sieved, to obtain a homogeneous sepiolite powder, and re-watered afterwards. *Att* was the nanoclay with lower adsorption, around half of *Sew* value. On the other hand, all nanoclays showed a similar water adsorption value in tap water.

3.1.2. Flowability of pastes with nanoclays and different w/b.

Results of mini-cone slump test of cement pastes with nanoclays and different w/b are summarized in *Figure 3*. Final spread diameter (Figure 3a) and final spread flow time (Figure 3b) are plotted. Final spread diameter of the reference paste was the largest for each w/b, as the incorporation of nanoclays required larger amounts of water to reach the same spread diameter values than reference mixture. Paste with sepiolite in powder form (SEP) showed the largest water demand to achieve the same final diameter as the pastes with the other nanoclays. At 0.35 w/b, none of the pastes had started to spread, showing a dry consistency. However at 0.45 w/b, REF, ATT, BE and SEW had reached around 180 mm of final spread diameter while SEP had not started to spread yet. Regarding final spread flow times (Figure 3b) all the samples showed very short values regardless the type of nanoclay and the w/b. Hence, nanoclays by themselves did not change the spread mechanism related to viscosity of reference cement paste.

3.2. Flowability of pastes with nanoclays and HRWRA

The mini-cone slump test was also used to evaluate the effect of HRWRA on flowability of cement pastes with nanoclays. This field-oriented test are useful for correlate final spread diameter and final spread flow time with the rheological parameters as yield stress and viscosity [4-10]. Two w/b were considered: 0.35 and 0.45. *Figure 4 and Figure 5* presents the final spread diameter and final spread flow time values of pastes with nanoclays and different percentages of HRWRA, for w/b of 0.35 and 0.45 respectively. It can be observed that the effect of HRWRA depended strongly on w/b. While for 0.35 w/b (Figure 4) the different type of nanoclay showed changes on HRWRA effectiveness, these differences were drastically reduced for 0.45 w/b (Figure 5).

In the case of pastes with 0.35 w/b, final spread diameter and spread flow time for the same amount of HRWRA were larger for reference and ATT pastes, followed by both sepiolites and, at last, by BE. To achieve a fluidity of 330 ±30 mm required for a SCC paste, reference and ATT needed around 0.5 % of HRWRA while sepiolites needed 1 % and BE 1.5 %. On the other hand, the final spread flow time values measured for pastes with 330 ± 30 mm final diameter were similar for all pastes with values around 15 seconds.

When w/b ratio was raised to 0.45 (Figure 5), all pastes with nanoclays required 0.4-0.6 % of HRWRA to reach 330 ± 30 mm final diameter, with final spread flow time values around 10 seconds. This increase of w/b improved HRWRA effectiveness reducing viscosity.

3.3. Rheology evaluation of fluid cement pastes with nanoclays.

Two protocols were considered to evaluate rheological properties of fluid cement paste with nanoclays: controlled stress protocol (CS) and a constant controlled rate protocol (CCR) (Figure 1). The CS protocol was used to evaluate yield stress and viscosity and a CCR protocol was used to evaluate structural build-up. To carry out this test, only mixtures with a mini-cone final spread diameter of 330 ± 30 mm were considered.

3.3.1. Yield stress and viscosity

Figure 6 plots the rheology curves of fluid cement paste with nanoclays and two w/b ratio (0.35 and 0.45) obtained with CS protocol and analyzed through the rheometer software. A Bingham modified model was used to calculate the rheological parameters of yield stress and viscosity, as the quadratic approximation produced the best adjustment in these flow curves [12, 14]. Others models were used as Bingham, Herschel–Bulkley, ect. However the results obtained were not robust. The yield stress and viscosity obtained with CS protocol are summarized in *Table 3*. The shear stress limit value of the CS protocol of 1500Pa was not reached with these pastes. The obtained flow curves (figure 6) showed maximum values of shear stress down to 500 Pa due to these pastes reached first the shear rate limit value of the rheometer (around 600 s-1) because of the flow consistency of these pastes.

Pastes with nanoclays and 0.35 w/b *(Figure 6a)* had yield stress values that ranged from 8.3 to 94.8 Pa and viscosity from 0.29 and 0.95 Pa·s. Among them, SEW showed the highest yield stress (94.8 Pa) and viscosity values (0.95 Pa·s). SEP and ATT exhibited similar yield stress values (28.9 and 23.9 Pa, respectively) but SEP presented higher viscosity (0.65 Pa·s) than ATT (0.46 Pa·s). BE and reference pastes had practically the same yield stress (10.0 and 8.3 Pa), although REF showed a viscosity (0.57 Pa·s) similar to ATT.

For pastes with 0.45 w/b *(Figure 6b)*, yield stress values ranged from 10.6 to 48.2 Pa and viscosity form 0.06 and 0.34 Pa·s. SEW showed again the highest yield stress, although it was half of the value of SEW pastes with 0.35 w/b. BE was the only paste with nanoclays that increased yield stress regarding 0.35, while the other pastes reduced yield stress with the increase of w/b. Yield stress of the reference paste (REF) remained very similar for both w/b. Besides, all pastes presented a sharp reduction of viscosity.

3.3.2. Structural build up evaluation

Structural build-up process was evaluated using the constant controlled shear rate protocol (CCR). In this study, two parameters described in the literature were calculated: thixotropic Index (I_{thix}) and the rate of reversible structural build-up (A_{thix}). Structural build-up process was measured with a low constant shear rate of 0.2 s^{-1} after a pre-shear of 70 s^{-1}. Figure 7 plots the curves showed by the pastes with 0.35 w/b tested at 0 and 30 minutes (10 and 40 minutes after mixing of water, respectively) and the pastes with 0.45 w/b at 0 minutes (10 minutes after mixing water). All curves showed an initial peak value followed by a decline until reaching a steady-state value.

3.3.2.1. Thixotropy index (I_{thix})

Thixotropy Index (I_{thix}) was calculated from the CCR protocol results (Figure 7) according to (Eq. 2) [3, 24]:

$$I_{thix} = \frac{\tau_i}{\tau_e} \qquad \text{(Eq. 2)}$$

where τ_i is the peak value and τ_e is the steady-state equilibrium value. I_{thix} is related to the instantaneous structural break down and describes a relation between dynamic and static yield stress in that point.

I_{thix} was calculated for pastes with 0.35 and 0.45 w/b. The rheological values measured using the CCR protocol of pastes with nanoclays and different w/b ratio are summarized in Table 4. Pastes with 0.35 w/b exhibited higher peak values and equilibrium values than pastes with 0.45 w/b, except in the case of BE (0.63 and 0.8 for 0.35 w/b and 11.48 and 7.57 for 0.45 w/b, respectively). I_{thix} ranged from 0.76 to 3.91 and was higher at 0.45 w/b for all the pastes with nanoclays, except ATT that remained constant at 1.02. Reference paste had slight changes of I_{thix} between both w/b ratios. SEW was the paste that presented higher I_{thix} in pastes with both 0.35 and 0.45 w/b. The characteristic time (T_{ch}), the time needed to reach the steady state equilibrium value ranged from 34 to 276 s, showed to depend on w/b and were higher for 0.35 w/b than for 0.45 w/b.

3.3.2.2. Rate of reversible structural build-up (A_{thix})

The rate of reversible structural build-up of a cement paste (A_{thix}) can be measured as the linear increase of yield stress of the paste at rest during time, and can be calculated from CCR protocol (Figure 7) according to (Eq. 3) [19, 23] :

$$A_{thix} = \frac{\tau_{pv\text{-}t} - \tau_{pv\text{-}0}}{T_{rest}} \quad \text{(Eq. 3)}$$

where τ_{pv-0} is the peak value at initial time, τ_{pv-t} is the peak value at a specific resting time (T_{rest}). The rheological parameters measured to calculate A_{thix} of pastes with nanoclays and 0.35 w/b at 0 and 30 minutes resting times are summarized in Table 5.

The reference paste (REF) showed zero A_{thix}, as both peak yield stress at 0 and 30 minutes were 1.47 Pa. Nevertheless, the peak value raised from 0 to 30 minutes for all the pastes with nanoclays, producing A_{thix} ranging from 0.21 to 1.04. The highest values of A_{thix} were measured for pastes with sepiolite (1.04 for SEP and 0.87 for SEW), showing similar increments from 0 to 30 minutes (31.34 and 26.03 Pa, respectively). ATT and BE showed lower A_{thix} values (0.43 and 0.21 Pa, respectively).

4. Discussion

4.1 Influence of nanoclay type on cement paste flowability and rheological parameters

The experimental results pointed out that the type of nanoclay has a main effect on its influence on flowability and rheology of cement pastes. The different effect can be related to the particle size, shape and structural morphology differences of nanoclays [10, 25].

Cement paste with Attapulgite (ATT), a nanoclay that has a needle particle shape of short length, exhibited a flow behavior similar to the reference paste with limestone filler (REF). Its low water adsorption (Figure 2) did not affect the HRWRA efficiency (Figures 4 and 5). When compared to reference paste with the same flowability, ATT showed an increase of yield stress, I_{thix} and A_{thix} as expected [28-30], while viscosity remained very similar.

Pastes with sepiolite, a nanoclay with needle particle shape and larger length than ATT required larger amounts of HRWRA to reach flowability when w/b was low (0.35). In this case, the larger water adsorption of sepiolite due to probably to its higher BET surface area

(Figure 2), explain the reduction of HRWRA efficiency with this nanoclay particle. Both sepiolites, dispersed (*Sew*) and in powder form (*Sep*), showed a similar flowability in pastes with HRWRA (Figure 4), although *Sep* needed larger w/b in pastes without HRWRA (Figure 3). This different evolution of flowability could be due to an entanglement produced by needle particle shape on samples with sepiolite in powder form [33]. That not happened with *Sew* because of it is a functionalized component. Both sepiolites increased yield stress, viscosity, I_{thix} and A_{thix}., with high values, larger than ATT. Although both are the same type of clay, the larger particle size of sepiolites improved their effect on paste rheology [25, 26]. *Sew* produced the highest values of yield stress and increased I_{thix} due to its functionalization. Bentonite (*Be*), which has a plate particle shape, showed a high demand of HRWRA to spread with 0.35 w/b (Figure 4) due to its particle structural morphology and size [27, 36, 38, 39]. Moreover, cement paste with *Be* is clearly affected by the house-of-card network microstructure that reduced the flowability of this pastes and is formed by this nanoclay [3, 35, 36]. The large amount of HRWRA required to get flowability reduced yield stress, viscosity, I_{thix} and A_{thix}. Increasing w/b to 0.45 (Figure 5), improved HRWRA efficiency as the nanoclay got saturated of water. Rheological parameters were also increased for BE and 0.45 w/b.

4.2. Assessment of rheological properties on cement paste with nanoclays.

Dynamic shear rheometer (DSR) results showed a non-linear behavior of pastes with nanoclays (Figure 6). As described elsewhere, the modified Bingham model produced a better adjustment than other models to calculate yield stress and viscosity, due to the effect of nanoclays [14]. The increment of w/b reduced the rheological parameters, particularly viscosity (Table 3). This reduction can be also identified by the final spread flow times measured with the mini-cone (Figure 3 and Figure 5), due to the water saturation of nanoclays in 0.45 w/b pastes. It must be highlighted that yield stress reduction was not as substantial as viscosity.

Thixotropy Index (I_{thix}) was higher for pastes with 0.45 than those with 0.35 w/b. Nevertheless, yield stress peak and equilibrium values of pastes with 0.45 w/b were significantly lower than pastes with 0.35 w/b, but equilibrium values had a larger reduction. The lower viscosity is behind this larger reduction of 0.45 w/b pastes. Therefore, I_{thix} is a relative index that needs to be complemented with the reference peak value to fully understand the instantaneous structural build-up of cement pastes.

When structural build-up was studied with A_{thix} (Roussel model), all peak values increased over rest time, with the exception of the reference paste [19, 23]. Hence, all nanoclays showed build-up capacity to modify the rheology of fluid cement pastes after a resting time [28-32]. Both sepiolites produced the highest A_{thix} value, although it was slightly higher for SEP, probably due to the *Sew* functionalization. ATT produced lower A_{thix} than sepiolites possibly due to its smaller particle length [25].

4.3. Interactions of nanoclays with HRWRA and w/b: effects on paste flowability and rheology

The amount of HRWRA required to reach 330 ±30 mm spread diameter in the mini-cone test depended on the type of nanoclay and w/b. The effect on flowability and rheological properties of pastes can be related to the interactions among nanoclays, HRWRA and water. Water adsorption of Nanoclays showed to be affected by solution pH and cement pore solution increased adsorptivity regarding tap water. The reduction of water available in the fresh cement paste due to water adsorption of nanoclays produced a loss of flowability.

Above a certain w/b, nanoclays were saturated of water (*saturation threshold*) and all nanoclays spread similarly (Figure 3).

The experimental results showed that only when this threshold was not reached (0.35 w/b), interactions among nanoclays, water and HRWRA occurred [35, 36, 39]. These interactions can be associated with clay particle size, shape and S_{BET} of nanoclays (Table 2.) [10, 25, 26, 38]. On one hand, Sepiolites had higher S_{BET} which corresponded to a higher water adsorption. However, their needle particle shape produced lower water adsorption than bentonite (*Be)*, with plate particle shape, which demanded larger amounts of HRWRA in order to change the flowability of pastes [27, 34, 39]. This negative interaction between *Be* and HRWRA of paste with 0.35 w/b can also be appreciated on the lower values of BE for structural build-up parameters (I_{thix} and A_{thix}) than those of sepiolites (Tables 4 and 5).

Another effect of this interactions is the increase of viscosity of the paste when HRWRA was added, as the final spread flow time (Figure 3) only reached several seconds after the incorporation of HRWRA on pastes (Figures 4 and 5). Hence, HRWRA was able to change the spread mechanism of pastes related to viscosity, further than only increasing fluidity [4-6]. However, final time values were slightly affected by nanoclays, as all pastes showed similar times values at 330 ± 30 mm final spread diameter (Figures 4 and 5). The increase of water in the paste (0.45 w/b) produced a shorter final time because less amount of HRWRA was required to reach the target diameter [7]. Besides, It must be considered that mini-cone slump test is a method with some limitations, although the results obtained in this paper with mini-cone slump test were correlated with rheological parameters measured with DSR.

5. Conclusions

This paper presents a study on cement-limestone filler blended SCC pastes with 2 % of four types of nanoclays: attapulgite, bentonite and sepiolite in powder form and dispersed in water. Their effect on flowability and rheology parameters of the pastes was evaluated. Two water to binder ratios (0.35 and 0.45 w/b) were used and a high range water reducing admixture (HRWRA) was incorporated to reach a target flowability of 330 ± 30 mm in a mini-cone test. The main conclusions of the study were:

- The pH of the water solution influenced nanoclays water adsorption regardless the nanoclay type. The alkaline pH of cement pore solution increased substantially adsorption nanoclays water adsorption.
- Water adsorption of nanoclays is related to their particle size and shape. The needle particle shape with large particles of Sepiolite in powder form reduced drastically paste flowability. The introduction of a HRWRA in the paste minimized this effect. Sepiolite dispersed in water did not show this problem due to its functionalized particles.
- The water adsorbed by nanoclays reduced the water available in the paste, reducing paste flowability, especially for low w/b (0.35). Overpassing an adsorption threshold with a higher w/b (0.45) minimized this undesirable effect and increased HRWRA effectiveness.
- The incorporation of a HRWRA in pastes with nanoclays modified both yield stress and viscosity.

- Paste with bentonite and 0.45 w/b required the same percentage of HRWRA to reach large flowability than all other nanoclays due to the *saturation threshold* of this nanoclay was overpassed and HRWRA worked effectively.
- All nanoclays used in this study modified the rheological properties on fluid cement pastes, particularly sepiolites reached the higher values of yield stress and viscosity.. The increment of water produced a reduction of viscosity in all nanoclays. Thus, peak value and steady-state value were lower with 0.45 w/b and thixotropy index (I_{thix}) was higher than pastes with 0.35 w/b. Moreover, resting time increased yield stress (peak values) with nanoclays and improved the rate of reversible structural build-up (A_{thix}).

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Table 1. Cement pastes' compositions

	REF	ATT	BE	SEP	SEW	REF	ATT	BE	SEP	SEW
cement	850	850	850	850	850	850	850	850	850	850
Filler	425	425	425	425	425	425	425	425	425	425
Water *	446	446	446	446	386	574	574	574	574	514
HRWRA **	0 - 2%					0 - 1%				
ATT	-	17	-	-	-	-	17	-	-	-
BE	-	-	17	-	-	-	-	17	-	-
SEP	-	-	-	17	-	-	-	-	17	-
SEW ***	-	-	-	-	17*	-	-	-	-	17*
w/b** **	0.35	0.35	0.35	0.35	0.35	0.45	0.45	0.45	0.45	0.45

* Liquid water added.
** HRWRA was employed as an increment dosage scale, by cement weight.
*** Solid residue 22%.
**** Water of the components (HRWRA and SEW) was also taken into account.

Table 2. Nanoclays' properties.

Component	S_{bet} (m^2/g)	D[4,3] (μm)
Attapulgite *(Att)*	144	21,97
Bentonite *(Be)*	138	38.42
Sepiolite *(Sep)*	316	39.66
Sepiolite* *(Sew)*	284	57.7

* Dispersed in water.

Table 3. Rheological properties of pastes with Nanoclays (measured using DSR with CS protocol).

w/b	Sample	yield stress (Pa)	viscosity (Pa·s)
0.35	**REF**	8.3	0.57
	ATT	23.9	0.46
	BE	10.0	0.29
	SEP	28.9	0.65
	SEW	94.8	0.95
0.45	**REF**	10.6	0.06
	ATT	15.9	0.17
	BE	29.2	0.21
	SEP	24.8	0.22
	SEW	48.2	0.34

Table 4. Rheological properties of pastes with nanoclays calculated using DSR with CCR protocol (I_{Thix} calculated according to Qian model [3, 24]).

w/b	Sample	$\tau_{i\ (Pa)}$	$\tau_{eq\ (Pa)}$	$\tau_i - \tau_{eq\ (Pa)}$	$T_{ch\ (s)}$	$T_i - T_{eq\ (s)}$	I_{Thix}
0.35	**REF**	1.47	1.93	-0.46	214	162	**0.76**
	ATT	9.68	9.46	0.22	84	50	**1.02**
	BE	0.63	0.8	-0.17	172	134	**0.79**
	SEP	32.9	27.65	5.25	240	224	**1.19**
	SEW	76.67	37.6	39.07	276	272	**2.04**
0.45	**REF**	1.26	1.3	-0.04	34	-0.04	**0.97**
	ATT	3.4	3.33	0.07	54	0.07	**1.02**
	BE	11.48	7.57	3.91	102	3.91	**1.52**
	SEP	9.695	6.47	3.23	136	3.23	**1.50**
	SEW	39.57	10.13	29.44	240	29.44	**3.91**

Table 5. Rheological properties of pastes with nanoclays calculated using DSR with CCR protocol. (A_{Thix} was calculated according to Roussel model [19, 23]).

w/b	Sample	$\tau_{pv\text{-}0\ (Pa)}$	$\tau_{pv\text{-}30\ (Pa)}$	$\tau_{pv\text{-}30} - \tau_{pv\text{-}0\ (Pa)}$	$T_{Rest\ (min)}$	$A_{Thix\ (Pa/min)}$
0.35	**REF**	1.47	1.47	0	30	**0.00**
	ATT	9.68	22.66	12.98	30	**0.43**
	BE	0.63	6.848	6.22	30	**0.21**
	SEP	32.9	64.24	31.34	30	**1.04**
	SEW	76.67	102.7	26.03	30	**0.87**

Figure 1 – DSR protocols: CS, Shear stress control; CCR, Shear rate control.

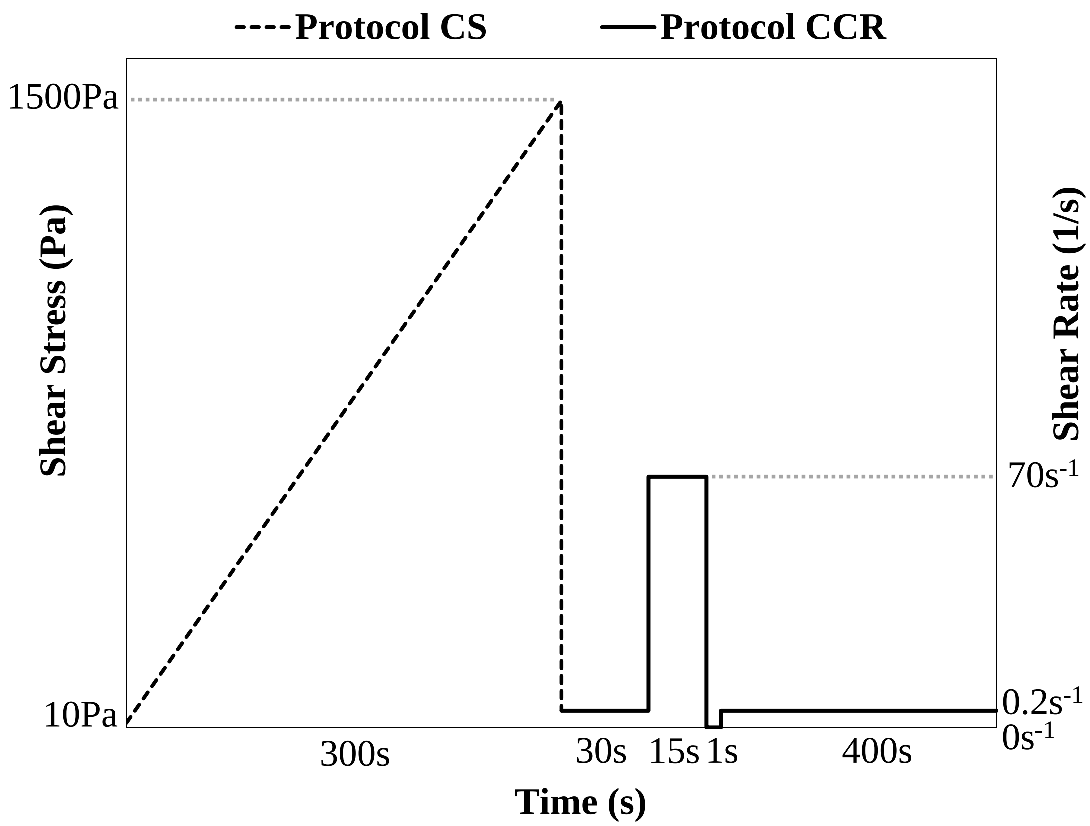


Figure 2 – Water Adsorption values over time of nanoclays. a) water adsorption on alkaline water (cement pore solution); b) water adsorption on tap water.

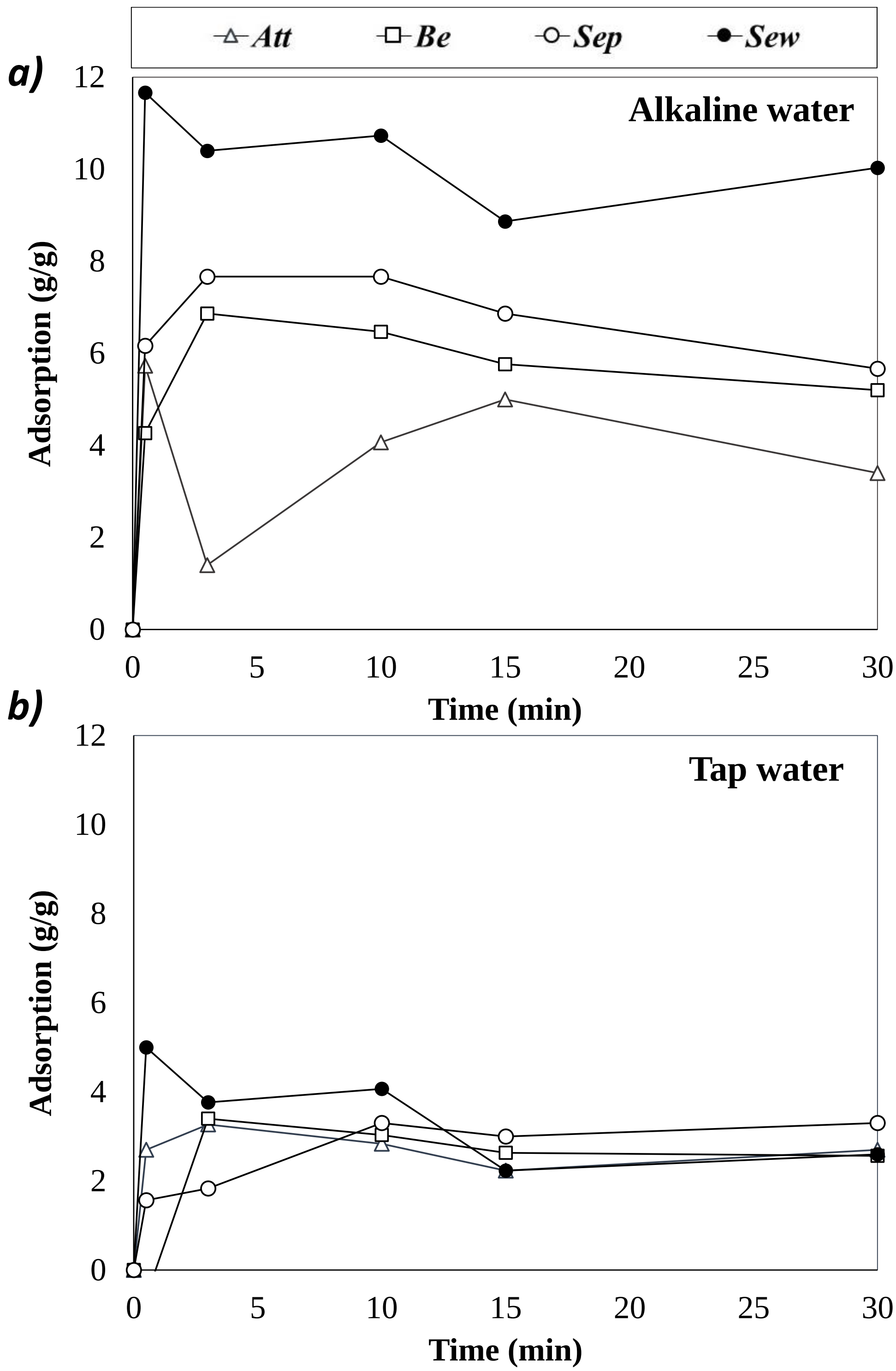


Figure 3 – Mini-cone slump test of pastes with different w/b. a) Final spread diameter; b) Final spread time values.

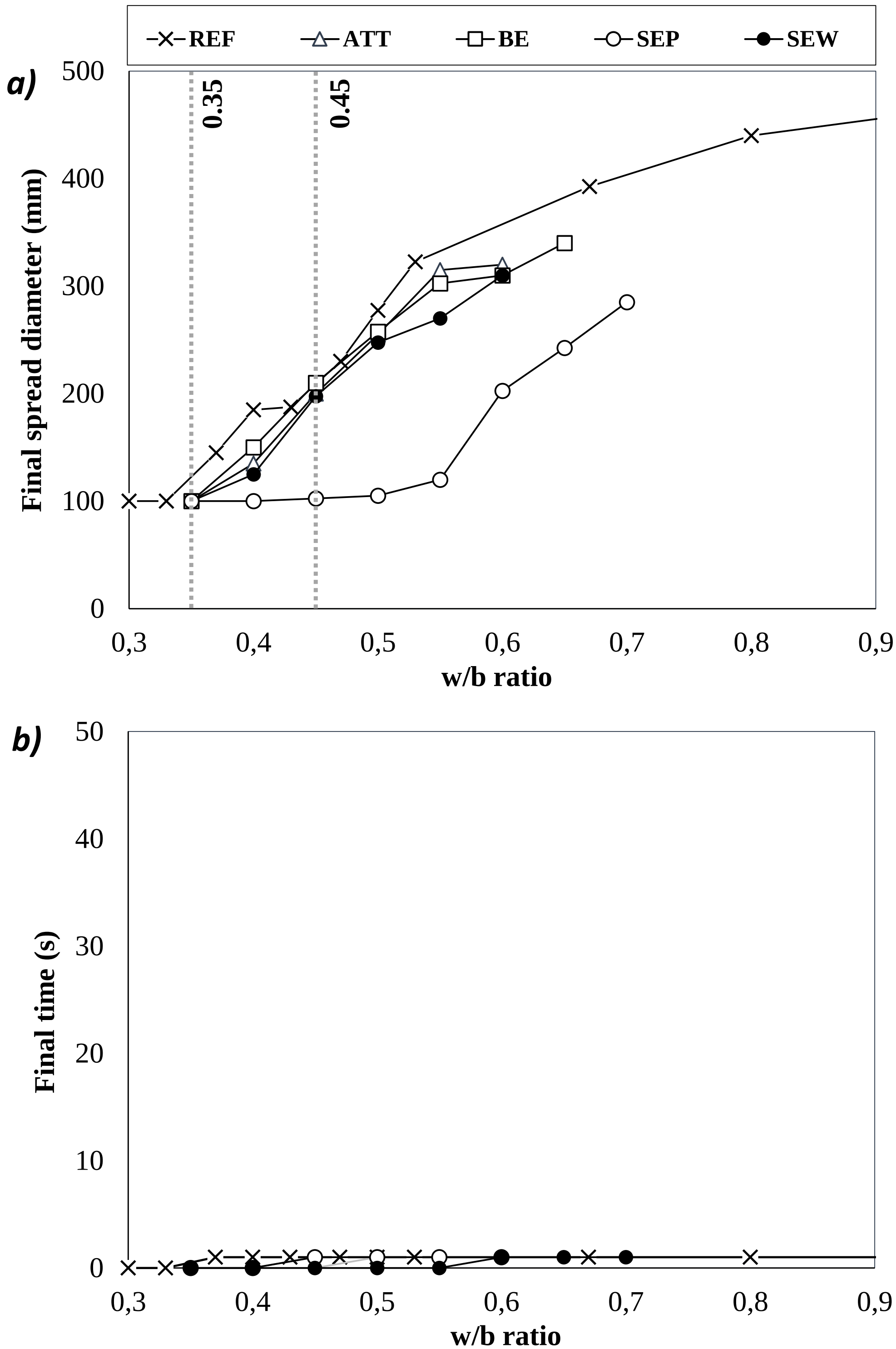


Figure 4. Mini-cone slump test of pastes with nanoclays and HRWRA (w/b - 0.35). a) Final spread diameter; b) Final spread time

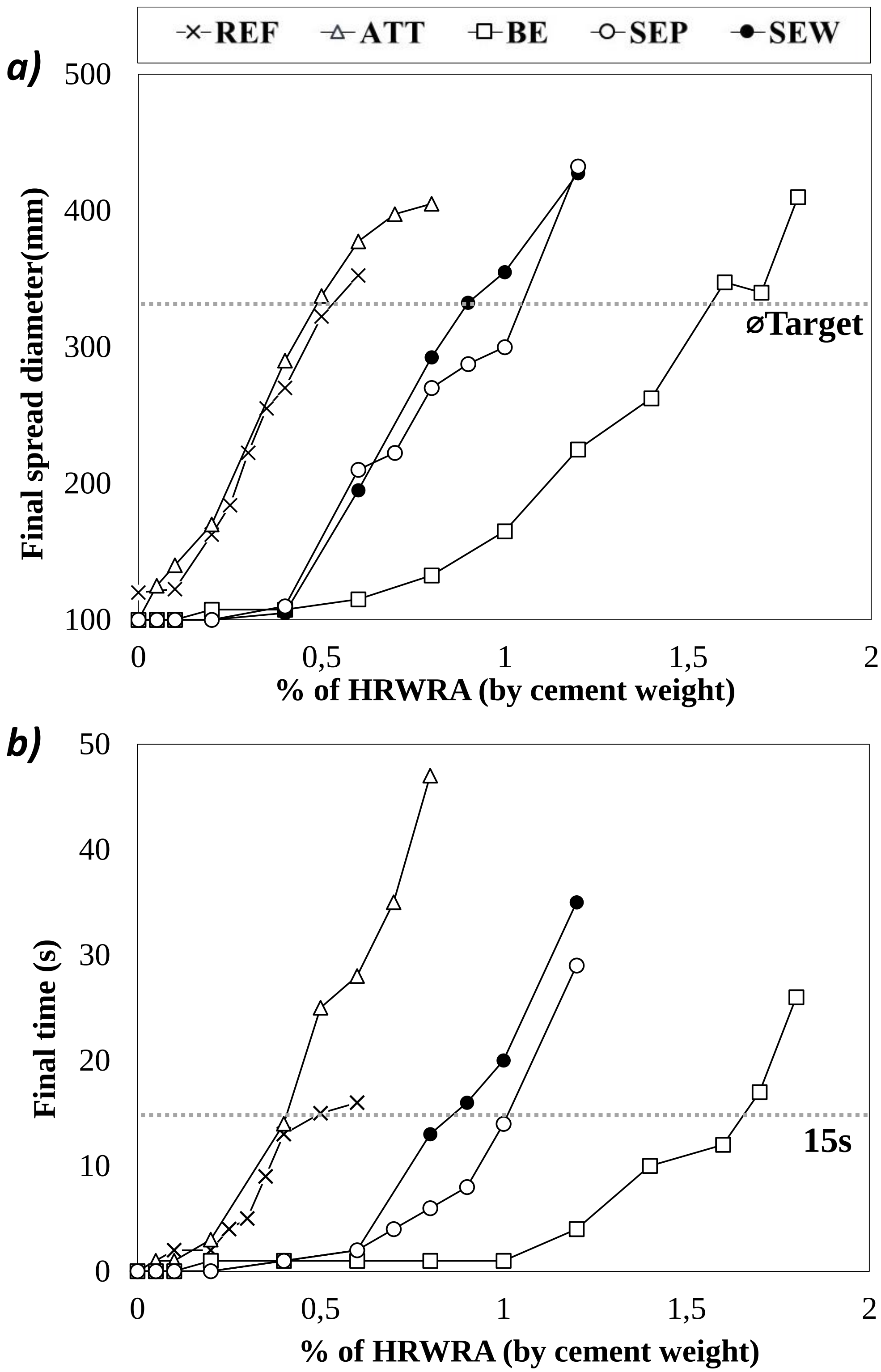


Figure 5. Mini-cone slump test of pastes with nanoclays and HRWRA (w/b - 0.45). a) Final spread diameter; b) Final spread time.

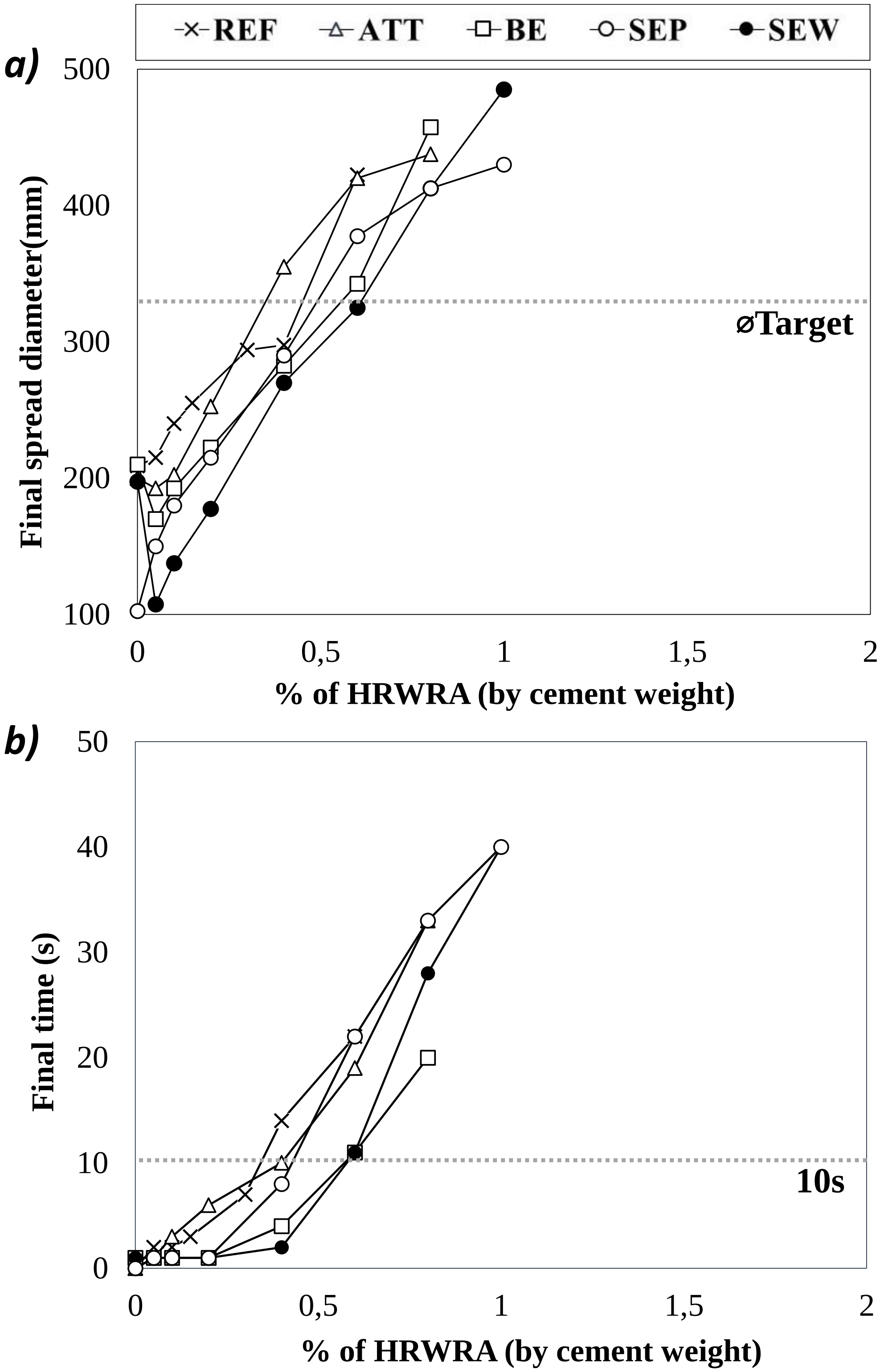


Figure 6 – DSR results of CS protocol. a) Shear stress vs rate for 0.35w/b; b) Shear stress vs rate for 0.45w/b. (In brackets the amount of HRWRA)

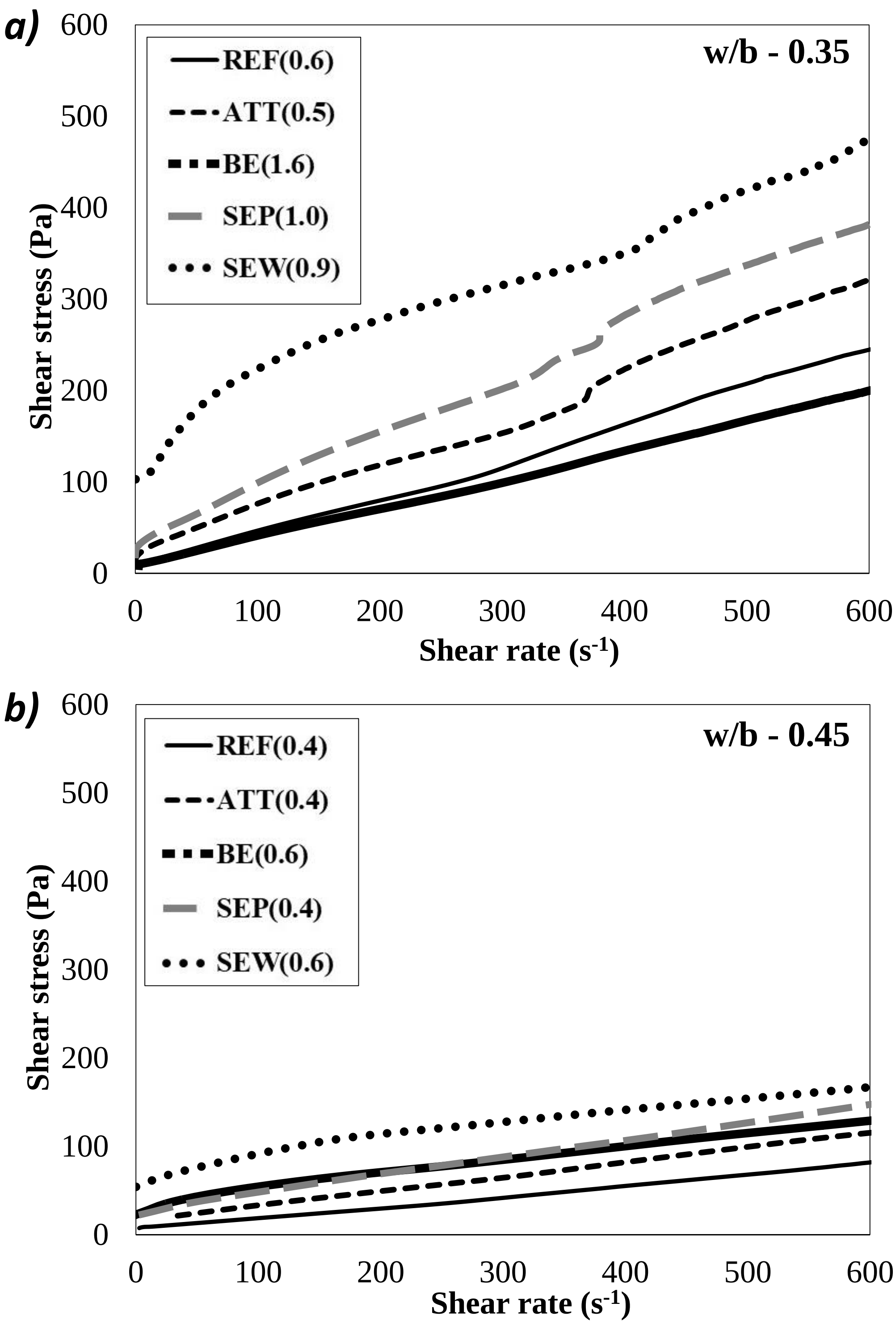
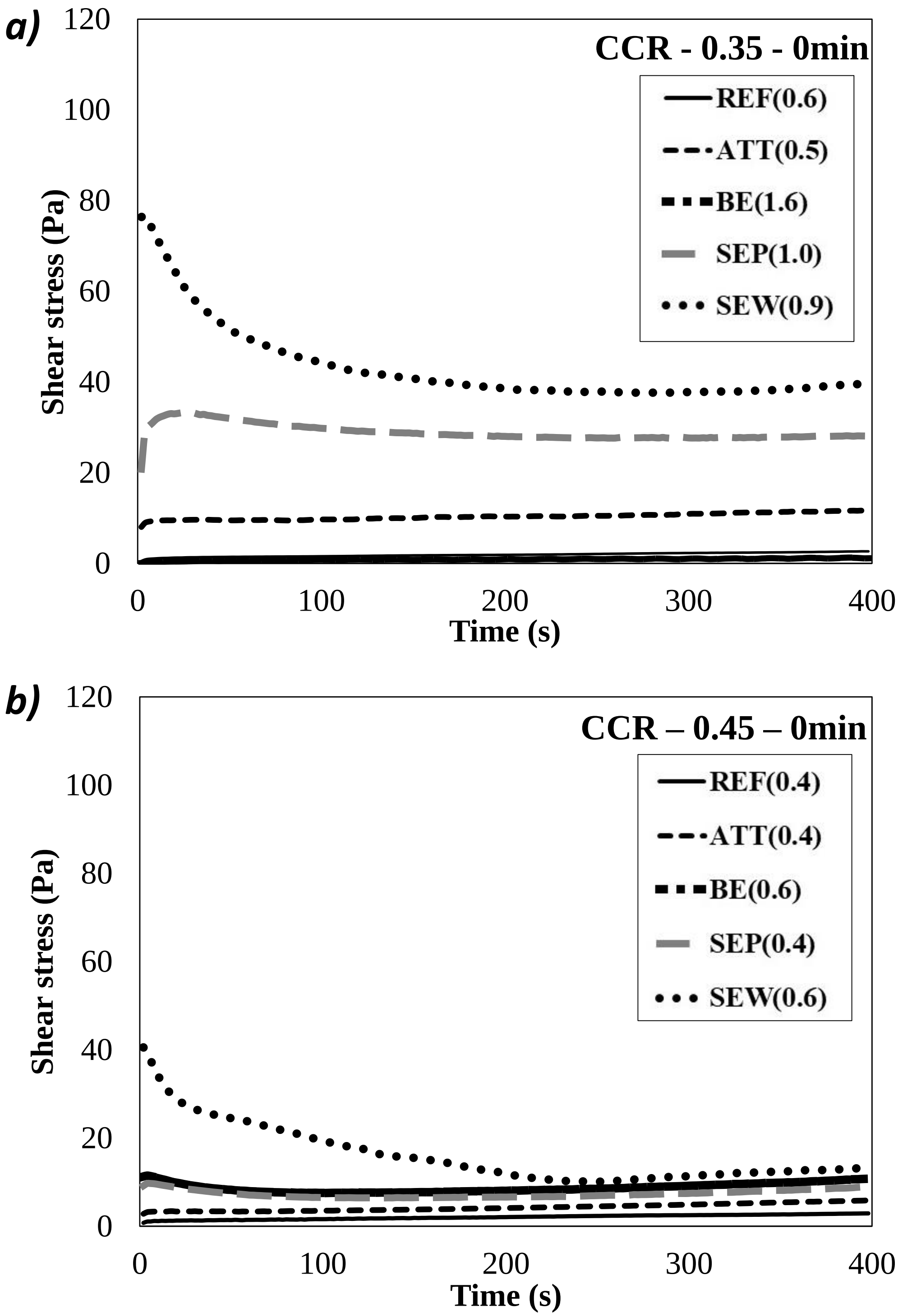
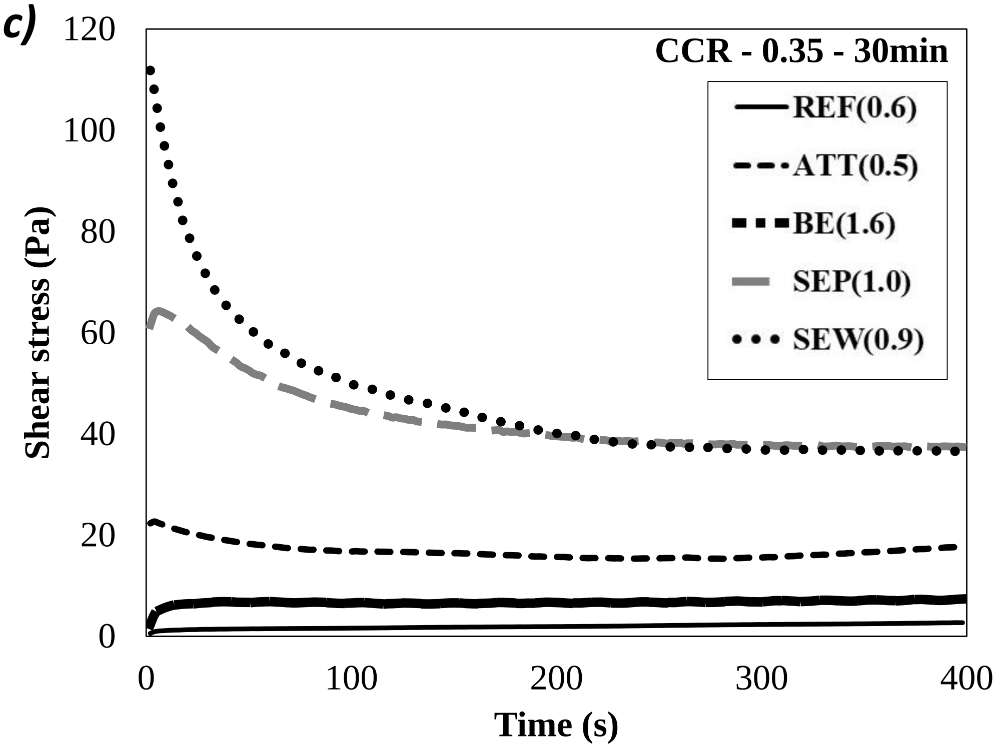


Figure 7 – DSR results of CCR protocol. a) Shear stress vs time with w/b of 0.35 and 0min; b) Shear stress vs time with w/b of 0.45 and 0min; c) Shear stress vs time with w/b of 0.35 and 30min. (In brackets the amount of HRWRA)



c)



CCR - 0.35 - 30min
REF(0.6)
ATT(0.5)
BE(1.6)
SEP(1.0)
SEW(0.9)
Shear stress (Pa)
Time (s)
0
20
40
60
80
100
120
0
100
200
300
400