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I- How admixtures affect the yield stresses of cement?

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III. Biographical Sketches

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Malo Charrier is a French engineer graduate from Arts et Métiers ParisTech and holder of a Master of Applied Science in construction engineering obtained at École de Technologie Supérieure de Montréal. After an internship at XtreeE, a startup specialized in 3D printing for construction, he joins Build'In as a research engineer, the technological platform of the École des Ponts ParisTech's Co-innovation Lab. He is interested in 3D printing issues for several construction materials as well as the integration of robotics and tailored measurement methods for the monitoring of complex processes.

ACI member Claudiane Ouellet-Plamondon is an associate professor at École de technologie supérieure, Canada. She received a degree in engineering from Dalhousie University in Canada and a Master's degree in sciences from Université de Montréal, Canada. She was a Commonwealth Scholar for her PhD at the University of Cambridge in the United Kingdom. Afterward, she was a postdoctoral fellow at ETH Zurich. She was part of the organizing committee for the ACI Convention in Québec City in 2018. She is a member the ACI committees 552 – Cementitious Grouting and 564 – 3D Printing with Cementitious Materials. Her interests are in alternative cements and material characterization.

IV Abstract

A factorial experimental design plan was used to compare the admixtures (superplasticizer, viscosity modifying agent, accelerator, CSH seeds, and nanoclay) in a blend of cement and silica fume. Two methods are tested to measure the structuration rate: the constant velocity method and the creep recovery method. The measurements were done with a rotational rheometer with a double-helical spiral geometry to reduce slippage. The evolution of yield stress and thixotropy of the mixtures at four resting times were evaluated, which can provide insight on the stress that the recently printed structure can withstand. The creep recovery method generally provides a higher static yield stress than the constant velocity method, except for the stronger mixes, which raises additional questions on the effect of the paste history on microstructural buildup mechanisms. When the extruder begins, shear is applied and the microstructure is broken causing. The dynamic yield stress to be lower than the static yield stress. The effect of the admixtures on thixotropy is discussed.

V Key words: Admixtures, Yield stress, creep recovery method, CSH-Seed, Thixotropy.

VI Body of Main Text

Introduction

The growing interest for large-scale additive manufacturing processes in construction stimulates research in computer-controlled placements of cementitious materials to create structures. This drives a fresh look at rheology to describe the early behavior of cement paste that is required: flowability for extrusion and material structuration for buildability. Admixtures affect the buildability of the paste. The microstructure of the cement paste can resist certain stress before it is broken down and starts to flow. At rest, the microstructure strengthens due to colloidal flocculation during the first five minutes. After the bonds between the hydration products starts to fill the volume and the admixtures change the cement dormancy period and the rate of structural buildup.

The yield stress can be defined in many ways. A definition common to many materials is that the yield stress is the change from the elastic to the plastic behavior of materials. Cementitious materials are visco-plastic Bingham materials. They flow only when a critical threshold value yield is reached (1). The static yield stress is the critical stress that allows a paste to flow from the rest. The dynamic yield stress is the critical stress when the paste is in movement. These yield stresses will change with time, due to the forces intrinsic to the cement. During the flocculation phase, there is competition between the attractive colloidal forces between the network of cement particles and the viscous dissipations in the interstitial water resist to the flow (1). Pumping and extrusion happen at this stage and the material yield stress and viscosity should be as low as possible. With time, during the structuration phase, the yield stress increases with the number of hydrates bridges between the cement particles. For 3D printing, the structuration rate must be fast. High static yield stress is required to ensure the stability of the extruded layers after deposition (2).

Static yield stress is the stress to initiate flow of an undisturbed microstructure. The characterization of the static yield is essential to define the printing parameters and the methodology remains a subject of debate. The static yield stress is measured at the flow onset depends on the network of colloidal interactions in the cement particles (2). The small amplitude oscillatory shear (SOAS) test is linked to the C-S-H formation at the contact point between the cement grains. This article will focus on the static yield stress at the flow onset. Three types of measurements have been suggested. The most common method is to apply a constant very low shear rate. At first, the microstructure deforms elastically and then the elastic limit is reached and the paste flow. The constant speed varies among studies, from 0,001 rad/s (3, 4), 0,01 rad/s (4-7) to 0,2 rad/s (4, 8). The shear rate affects the paste deformation, which means that the results are comparable only for the same velocities. The second method is to use a constant deformation rate for studies to determine the structuration rate for 3D printing which was recommended by a study of the static yield stress with varying constant shear rate levels between 0,08 and 0,24 rad/s (2). This constitutes the second measurement type. The third method, known as the creep recovery method, is to control the torque of the rheometer. By gradually increasing the angular velocity, the microstructure breaks and deforms rapidly, the static yield stress is determined from the rapid change in torque (9). Thus, the challenge becomes later to select experimental parameters that are representative of the printing system.

The concrete must be in movement during transportation to prevent the 3D network to form too rapidly. In the concrete flow history, the maximum shear rate is approximately 10-60 s-1 for mixing and 20-40 s-1 for pumping (10). The dynamic yield stress is measured from a paste in rotation. In this context, the dynamic yield stress is also the stress that keeps the paste flowing, as described in the steady state models, such as the Bingham model. In the measurement procedure, the rotational speed is increased than reduced to 0. The upward change in speed brings the particles in a more neutral state. The decreasing trend is used to determine dynamic yield stress with the rheological parameters. The shear rate varies from 0 to 100 s-1 for cement and slag paste (11-13), 0 to 40 s-1 for kaolin paste (6) and 0,03 to 30,3 s-1 for cement paste (14). This measurement creates a hysteresis loop, which is indicative of the thixotropy of the materials. The dynamic yield stress can also be measured with a shear rate controlled protocol, by varying the torque (9). However, this alternative procedure has not been considered in this study. Thixotropy is the reversible processes in the flow history (4). The more thixotropic the material is the more fluid it becomes when shear is applied. For 3D printing, thixotropy is required for the mixing, extrusion and the pumping steps. Once the material is deposited, the structural and network formation between the particles inhibits further flow.

A number of admixtures have been proposed for 3D printing of concrete (3) and the most effective candidates and dosages have not yet been identified. This work presents a factorial design plan of a blended cement with polycarboxylate superplasticizer and a combination of four other admixtures to see the effect of each admixture on the static and dynamic yield stress. Results at the mortar level are available in another study (15). The number of admixtures should be kept minimal for economic and environmental reasons. In northern climate, concrete often has more than two admixtures. This study adds one admixture at a time to observe the effects of each additional admixture on the yield stress and thixotropy. The study highlights the interactions of the selected admixtures on the rheology.

Research Significance

Rheology, thixotropy, and the structural breakdown of cement paste are useful in tailoring them to meet the multiple engineering properties required for successful engineering accomplishment and performance. The potential benefits of using a variety of combinations of admixtures on rheology of 3D printing cement paste is not well documented. The study presented herein aims at filling these gaps in the literature on mixtures of two to five admixtures. Sixteen different combinations with superplasticizer, viscosity modifying agent, accelerator, CSH seeds, and nano clay were used to control the printability and buildability of mixes. A systematic investigation was carried out to clarify the variation of rheological and thixotropic properties as well as stability of the fresh pastes for different combinations of admixtures.

Materials and methods

Pastes composition and mixing procedure

In the present investigation, a commercially available silica fume blended Portland cement which is classified in Canada as GUb-8SF was used in all the mixtures. It consists of 8% of silica fume by weight of cement. According to the manufacturer of the cement, the cement had a Blaine fineness of 617 m^2/kg and an initial setting time of 130 min, conforming to CSA A3000-18 - Cementitious materials compendium (4) and ASTM C1157/C1157M-20 (5). The chemical composition of the cement is presented in Table 1. Five different types of chemical admixtures are in the present study, and they were chosen to achieve different levels of yield stress, viscoelastic behaviour and compositions. All of them (polycarboxylate superplasticizer (SP), viscosity modifying agent (VMA), Accelerator (A), CSH seed (X) and nano clay (NC) are used in the construction industry. The solid concentration of the admixtures was determined by using ASTM C494 (6) and are as follows: 25.8% for SP, 1.04% for VMA, 47.2% for A, and 30.1% for X with a density of 1.050, 1.002, 1.350 ,1.120, and 1 for SP, VMA, A, X and NC, respectively. All of the mixtures were prepared using tap water. The mixture proportions were kept constant with a water-cement ratio of 0.345. Water content in the admixtures is considered when formulating the mixtures. The paste with SP was considered as the "control" mixture. The design details of the sixteen formulations are presented in detailed in Table 2. Samples were prepared according to the procedure certified by following the NIST procedure (7). A high shear mixer was used for preparing the mixers. A high shear mixer consists of two units: the control unit and a water bath. The control unit maintains the mixing process at the preset speeds, and the water bath circulates water around the mixing container to control the temperature while mixing. Initially, after setting up the water bath and adjusting the temperature in it, admixtures and water were added to the mixer. Total cement was added in the 60 s to the mixer. The mixture is blended for 30 seconds at a speed of 10,000 rpm and is followed by a pause of 150 seconds. During these 150 seconds, any mixture clinging to the walls of the high shear mixer was reincorporated using a spatula. A final mix of 30 seconds at the same speed completed the process. Utmost care was taken to apply identical an identical mixing process for each mixture and to maintain the temperature of 20 ± 2.0 °C at mixing to avoid any microstructural inhomogeneity which can cause a significant variation in rheological properties (7).

Table 1: Composition of compounds as %wt.

Parameters	%wt
SiO_2	24.4
Al_2O_3	4.3
Fe_2O_3	3.1
CaO	54.1
MgO	2.3
SO_3	3.8
K_2O	1.06
Loss of Ignition	2.8
Free lime	1.2
Silica fume addition	8.30%

Table 2: Relative mix design details (Note: the w/c was constant at 0.345, the varying amount is to consider the water in the admixtures, the admixtures are given in solid content)

Notation	Cement	Water	Admixtures				
			SP	X	A	C	VMA
SP	100	33.8	0.26				
SP VMA	100	33.4	0.26				0.004
SP C	100	33.8	0.26			0.5	
SP VMA C	100	33.4	0.26			0.5	0.004
SP A	100	33.0	0.26		0.7		
SP A VMA	100	32.6	0.26		0.7		0.004
SP A C	100	33.0	0.26		0.7	0.5	
SP A VMA C	100	32.6	0.26		0.7	0.5	0.004
SP X	100	33.0	0.26	0.3			
SP X VMA	100	32.7	0.26	0.3			0.004
SP X C	100	33.0	0.26	0.3		0.5	
SP X VMA C	100	32.7	0.26	0.3		0.5	0.004
SP A X	100	32.3	0.26	0.3	0.7		
SP A X VMA	100	31.9	0.26	0.3	0.7		0.004
SP A X C	100	32.3	0.26	0.3	0.7	0.5	
SP A X VMA C	100	31.9	0.26	0.3	0.7	0.5	0.004

Test program and methodology

To study the viscoelastic characteristics of cementitious materials modified with different admixtures, three different types of test methods are chosen, which includes mini-slump test, rheometer method test for the static yield stress and dynamic yield stress.

Mini-Slump Test

The slump test consists of filling a cone with a freshly mixed cement paste and lifting it slowly to allow the paste to flow under its own weight. The cone is comparable to the Abrams cone used to measure the slump. The top diameter, bottom diameter of the cones is 19 mm and 38 mm respectively. The height of the cone is 57 mm. It was arranged on an acrylic plate. Initially, cement paste was poured into the cone. At 15, 30, 50 and 70 min after the end of the mixing, the cone was removed and 5s later the diameter was measured.

Static yield stress

To study the effect of shear rates, the static yield stress test was conducted on these pastes at a constant speed. For the constant speed method, the speed was 0,018 rpm, the torque was measured in 60 points in 2-second intervals. The shear stress was calculated from the torque with the calibration factors. The calibration factors used in the calculation are 11916.213 Pa/Nm and 2.711 for $KK\tau\tau$ and $KK\mu\mu$, respectively. After each test, rest time was allowed for the mixture to undergo structural build-up for the subsequent measurement. With the torque increase method, the torque was increased from 0 to 8 mN.m or up to 150 rpm. The rotational speed was measured every 3 seconds in 60 points. The time between the measurement allows the paste to stabilize. From the torque and rotational speed, the shear stress and the shear rate are calculated. The linear regression on the two last points enables extrapolation to the axis to identify the tangent. The temperature was maintained at 20 °C during the test. Measurements were completed at 15, 30, 50 and 70 minutes, with, first the constant speed method, followed by the torque increase method at each time interval.

Dynamic yield stress

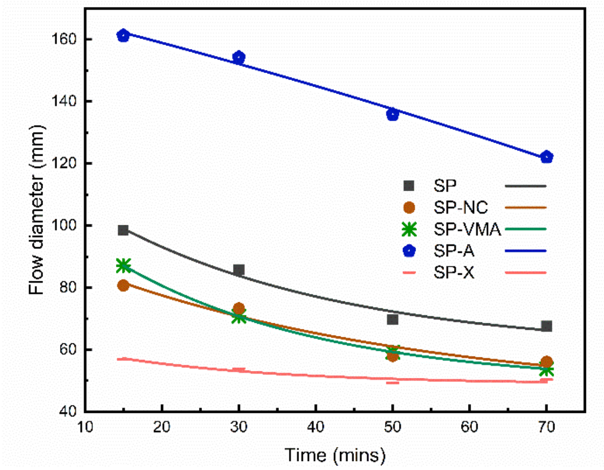
The paste was kept at a temperature of 20 °C during the test. The rotational rheometer was configured with a double spiral spindle with a diameter of 25 mm and the length of 55 mm from bottom to top of the spindle. The conversion of angular velocity and torque to shear stress and shear strain, respectively, was possible from NIST calibrated models with the calibration factors $K\tau$ and $K\mu$, 11939 Pa/Nm and 2.190, respectively. Dynamic yield stress is obtained by fitting the equilibrium flow curve with a steady-state flow model. The measurement of the dynamic yield stress was initiated 5 min after the mixing procedure. A total of 35 measurements were recorded by increasing and decreasing the angular velocity in the range of 0.1 rpm to 30 rpm in a hysteresis loop. The full test was conducted in 17 min with a measurement every 30 s or until the torque stabilized. From the collected data of the 16 mixtures, the shear stresses were computed as functions of the shear strain for each increasing and decreasing angular velocity.

Results and Discussion

Measurement of flow diameter

Fig. 1(a) to (c) illustrate the impact that the admixture type has on the flow behaviour of fresh concrete mixed at the different time periods. The results for fresh cementitious materials incorporating SP (Reference sample) and SP with VMA, NC, X and A are shown in Fig. 1(a). As anticipated, the flow diameter of these samples are decreasing with a time period. The addition of A to SP cement results in an increase in the flow diameter of cementitious materials by approximately 40%. This clearly depicts that the accelerator has a plasticity-maintaining effect on the cement hydration in the initial period (16). Moreover, the accelerator acts as a water reducing agent which influences the flow of cement paste in the initial period when compared to other admixtures. However, with time the flow diameter with accelerator decreases drastically. The addition of VMA, NC and X decreases the fluidity of the cementitious materials. The addition of VMA into the paste causes the water-soluble polymer chains of VMA to absorb some of the free water in the paste and increases the overall internal friction of the paste (17). NC shows a high adsorption capacity and very high specific surface area, both of which contribute to a reduction of the slump flow (18). The maximum amount of reduction in the slump flow was obtained with the CSH-seed. This may be attributed to the enhancement of early hydration characteristics with the addition of CSH-seed. Fig. 1b presents the final spread radius with time for different mixtures.

Interestingly, the maximum slump flow is observed for NC and A modified SP-based cementitious materials. However, with time, the difference between the values decreases when compared with SP-A. The accelerator (A) act as a flowability aid for SP-based cementitious materials and as a lubricating agent to SP-NC. The A contributed to filling the void spaces between larger particles of cementitious materials which decreased the internal frictional forces in SP-A-NC pastes. A maximum reduction of 37.5% flow was observed for the system containing SP-A-X-VMA-NC. A similar trend is maintained throughout the entire time period. Fig. 1c illustrates the slump flow diameter for high thixotropic materials. The minimum slump flow is observed for SP-X-VMA. As anticipated VMA increases the viscosity of SP-based cementitious materials which further contribute with NC to reduce the flow characteristics. Interestingly, SP-X flow characteristics have changed very little over time when compared with other admixtures.



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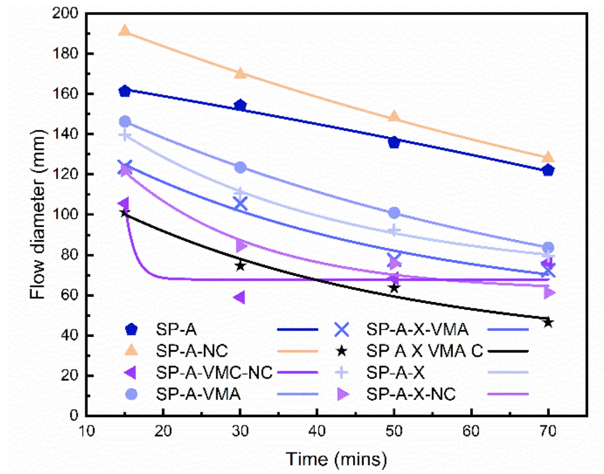

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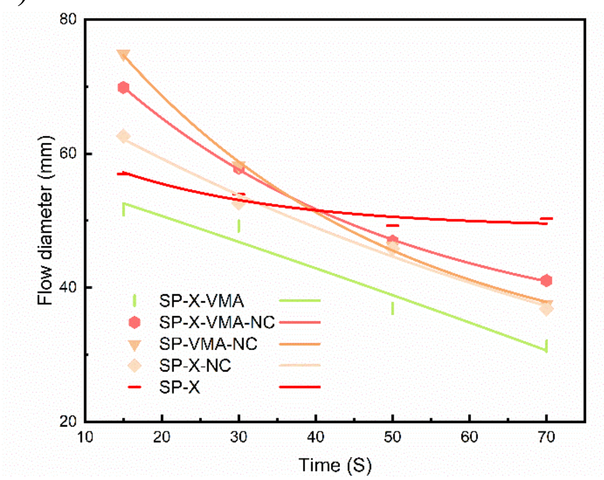

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Figure 1: Variation of flow diameter for different admixture modified mixtures with time period

Measurements of static yield stress

Constant velocity method.

The static yield stress measurement with the constant velocity method is carried out using a rheometer at different time periods: 15, 30, 50 and 70 min. The thixotropic behavior of these cementitious materials and the unstable nature of static yield stress makes it challenging to compare the effect of varying shear rates with the effect of different admixtures. To mitigate this, all the samples were prepared and tested under identical conditions. Pre-shearing (100 s− 1 for 60 s) was applied to the sample prior to the stress tests to ensure an identical state of the paste prior to testing (23). The evolution of shear stress with time of various admixtures modified cementitious material at 70 min after mixing are presented in Fig. 2. An initial peak corresponding to the static yield stress can be observed, followed by an increase in the stress. The initial point of contraflexure of shear stress is considered as static yield stress. The static yield stress values of cement pastes made with SP and one admixture are present in Fig 2.a. The admixture with high thixotropy has maximum yield stress and takes less time to reach peak value or plateau. Due to its water-reducing tendency, the addition of A induces a lower yield stress when compared to other admixtures. The maximum yield stress was observed for CSH-seed followed by VMA and NC, which means that they increase the flocculation as this testing method highlights this phenomenon in cement paste. Fig 2.b illustrates the relation to shear stress with time for different blended of admixtures modified SP-A cementitious materials. The maximum yield stress is observed for SP-A-X-VMA-NC. SP-A, SP-A-NC and SP-A-VMA have considerably lower yield stress when compared to SP alone. Remarkably, the maximum time required to reach yield stress was found to be with SP-A-VMA because the pseudoplastic behavior increased with the addition of VMA. Fig 2.c, d, e presents the variation of shear stress with time for different blended admixtures modified SP-VMA, X, NC respectively. A drastic upward shift in shear stress to time curve was observed for the SP-X-VMA-NC, SP-X-VMA, and SP-X-NC. The nano clay and CSH-seed addition in cementitious materials agglomerate the microstructure even in the presence of SP which contributes to an increase of shear stress from the lowest to a high value (19). Interestingly, the minimum static shear stress is observed for SP-A-NC. It may because of dominating effect of water reducing admixture (A).

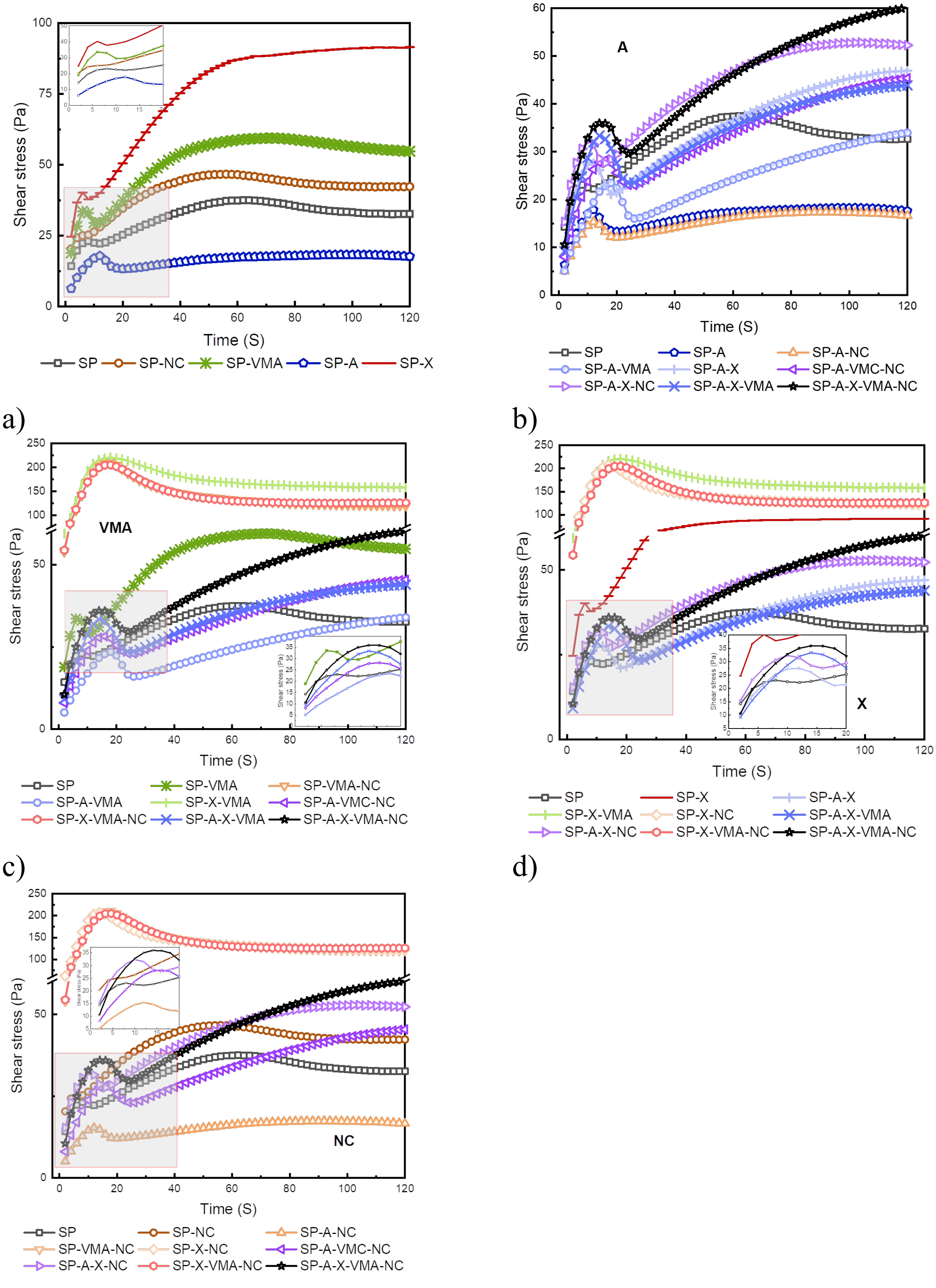
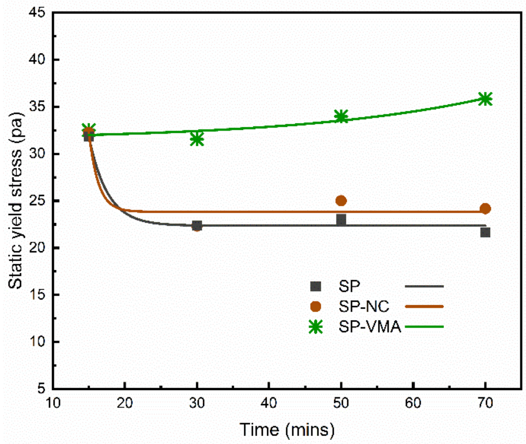


Figure 2: Variation of static shear stress with time for different admixture modified mixtures at 70 min for constant velocity method.

In static yield stress testing, it is crucial to ensure the constant shear rate be as low as possible to simulate static conditions. The selected constant shear rate is feasible for testing at all ages of interest. Furthermore, it can be reached in a short time span after initiating the test, minimizing variations attributed to ongoing aging of the sample during the test. In order to study the effect of the applied constant shear rate on structural build-up rate, four different time durations were considered (15, 30, 50, 70 mins) for each paste. These values are higher in comparison to other researchers due to the use of different admixture combinations. Fig. 3a presents the variation in the static yield stress with time for SP, SP-NC and SP-VMA. The static yield stress is decreasing or almost constant at different time periods for these admixture combinations. Fig. 3b illustrates that the yield stress variation with time for the blended admixtures increases the static yield stress slowly, which is attributed to the presence of this specific accelerator (A) admixture. For admixtures with NC and X, a rapid increase in the yield stress was observed with time (Fig 3c).



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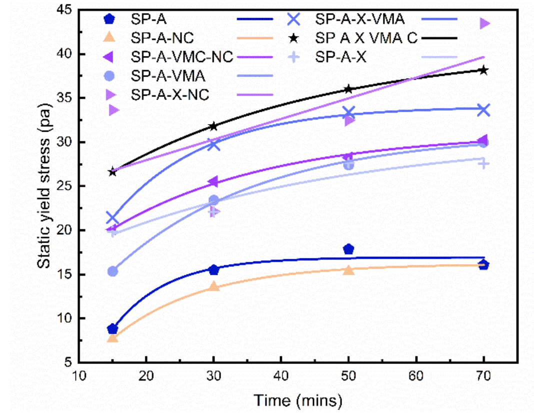

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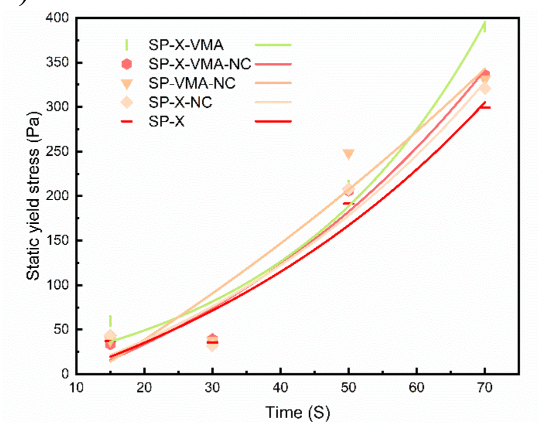


c)

Figure 3 Variations of static yield stress with time period for constant velocity method, a) selected mixes with SP, b) mixes with the accelerator, c) mixes with a higher static yield stress.

Creep recovery method

Cementitious materials with different admixtures are thixotropic and exhibiting flocculation mainly because of diffusion-coagulation processes and the formation of CSH bridges due to early hydration at rest. When the applied stress is insufficient, structural rebuilding is dominant over shear rejuvenation, and the material stops flowing. With higher stress, shear rejuvenation becomes dominant and the material exhibits continuous flow that accelerates until the steady state is reached (20). A typical figure for torque to angular velocity is presented in Fig. 4 for admixture blended cementitious materials. This test was performed two minutes after the measurement with the constant speed method. The torque increase measurement method generally provided higher static yield stress values than the constant speed method, except for the mixtures presented in the Fig. 3c, which means that the constant speed method test has lower impact on the microstructure. For the mixes with the higher static yield stress at 50 and 70 min, e.g. those with X without A, the constant speed test conducted before affected the bonds in the microstructure. The impact of the admixtures on the static yield stress measured with the torque increase method did not differentiate as much the behavior of admixtures over time as in the constant velocity method for mixes which exhibit slow static yield stress growth. Many pastes were so viscous that the applied torque did not shift the angular velocity, which means that the torque amplitude must be carefully determined (21).

Fig. 5 illustrates the variation of static yield stress with time for creep recovery method. Fig. 5a. represents the variation of static yield stress with time for SP, SP-NC and SP-VMA. Unlike in the constant velocity method, the yield stresses increase slightly with time during creep recovery test. In addition to this, the yield stress values of these admixtures modified cementitious materials have increased drastically for every period when compared constant velocity method. Fig. 5b. illustrates the yield stress variation with time for mixes that gain static yield stress slowly. For creep recovery method, a considerable increase in static yield stress was observed for all the mixtures when compared with constant velocity method. However, the trend of developing yield stress remains constant for these mixtures. Fig. 5c illustrates the yield stress variations in mixes that gain static yield stress quickly over time in the constant velocity method. Interestingly, in the creep recovery method, the static yield decreases drastically for these mixtures. A possible explanation is the gradual decrease in flocculation with time. For mixes blend with admixtures SP-X, SP-X-VMA-

NC, and SP-X-VMA, the static yield stress is decreasing or constant during the period of time. For SP-X-NC and SP-VMA-NC, the static yield stress is increasing with time, but these values are still lower than when compared to the constant velocity method.

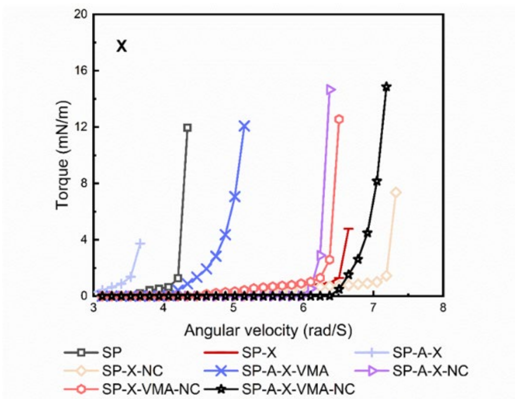
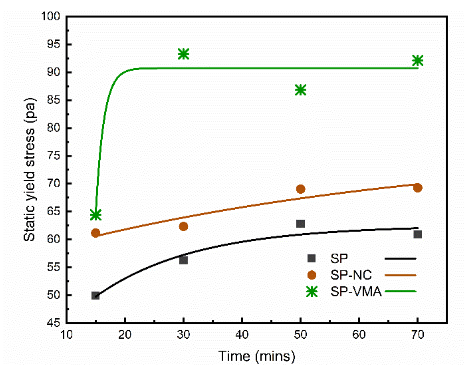


Fig. 4 Typical plot for torque to angular velocity for different admixtures at 15 min



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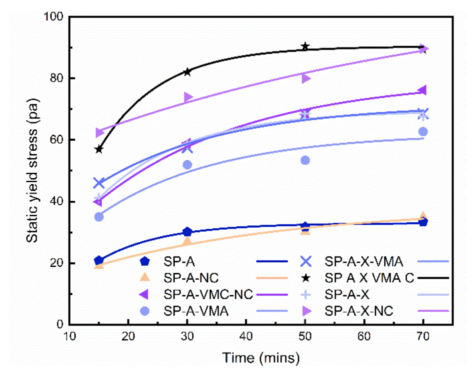

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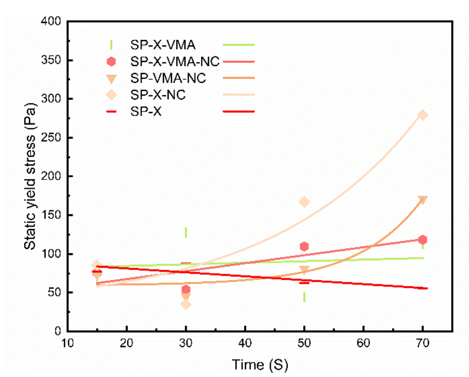


c)

Figure 5 Variations of static yield stress with time period for creep recovery method over time.

Dynamic yield stress

The dynamic yield stress measurement was conducted by increasing the shear rate. The downward curve is used to calculate the rheological properties depending on the applied model (22). Fig. 6 illustrates the rheological properties of cement paste with various admixtures. The downward shear stress–shear rate curves of different admixture modified SP-A based cementitious materials as compared to SP. The curves shift upward for SP-A-VMA-NC, SP-A-X-VMA, and SP-A-X-VMA-NC, while for all other admixtures it is decreased. Similar observations are also noticed for mini-slump flow. In these mixtures, VMA helps in stabilizing the mineral suspensions, which increases their robustness and viscosity (23). SP-A-NC, SP-A-VMA and SP-A-X mainly affect the free water in the mixtures while SP-A-VMA-NC, SP-A-X-VMA, and SP-A-X-VMA-NC most probably interact with the cement particles, which further needs investigation. The effect of different admixtures on VMA-SP based cementitious materials on shear stress to rate was graphically plotted in Fig. 6b. Interestingly, with the concentration of SP, the addition of the VMA also increases the degree of pseudo-plasticity or shear thinning of cement paste. This may be attributed to the fact that as the dose of the VMA increases, the degree of water retention and the free water needed to lubricate the paste also increases (24). As the accelerator acts a water reducing agent, the shear stress to rate curve of the SP-A-VMA is also lower when compared to SP based cementitious materials. As anticipated, SP-X-VMA-NC has a maximum upward shift, followed by SP-X-VMA and SP-NC-VMA. This is mainly because of the reaction between cementitious materials with X and NC, which is further enhanced by the presence of VMA. Fig. 6c. Illustrates the flowability characteristics of X-SP based cementitious materials, modified with different admixtures. Apart from the accelerator admixture (SP-A-X), all the other combination of admixtures with X show an upward shift when compared to SP. In all these mixtures, the synergistic effect of ultrafine particles of X stimulates the acceleration of hydration reaction with cementitious materials which aids in the enhancement of flowability characteristics (25). The maximum upward shift was observed for SP-X-VMA-NC, followed by SP-X-VMA and SP-X-NC. For these mixtures, flowability characteristics are significantly enhanced even when compared to SP-X. VMA and NC help to increase the viscosity and reactivity of cementitious materials at an early age. Fig. 6d presents the variation of workability characteristics of NC-SP based cementitious materials with different admixtures. Also, here as well, the accelerator admixture SP-A-NC shifted downward when compared with only SP. The maximum upward shift was observed for SP-X-VMA-NC, followed by SP-VMA-NC and SP-A-VMA-NC. At the initial shear rate, SP-VMA-NC is higher than SP-A-VMA-NC. However, as the shear rate increases SP-A-VMA-NC increases, it clearly shows that with the increase in the shear rate, the entangled chains dislodge and align in the direction of flow for SP-VMA-NC, thus decreasing the resistance of the cementitious material to undergo deformation. Even for SP-X-NC we can observe the drastic change in the slope for higher shear rate. This may also be related to local increases in temperature which tend to increase the dynamic yield stress (21).

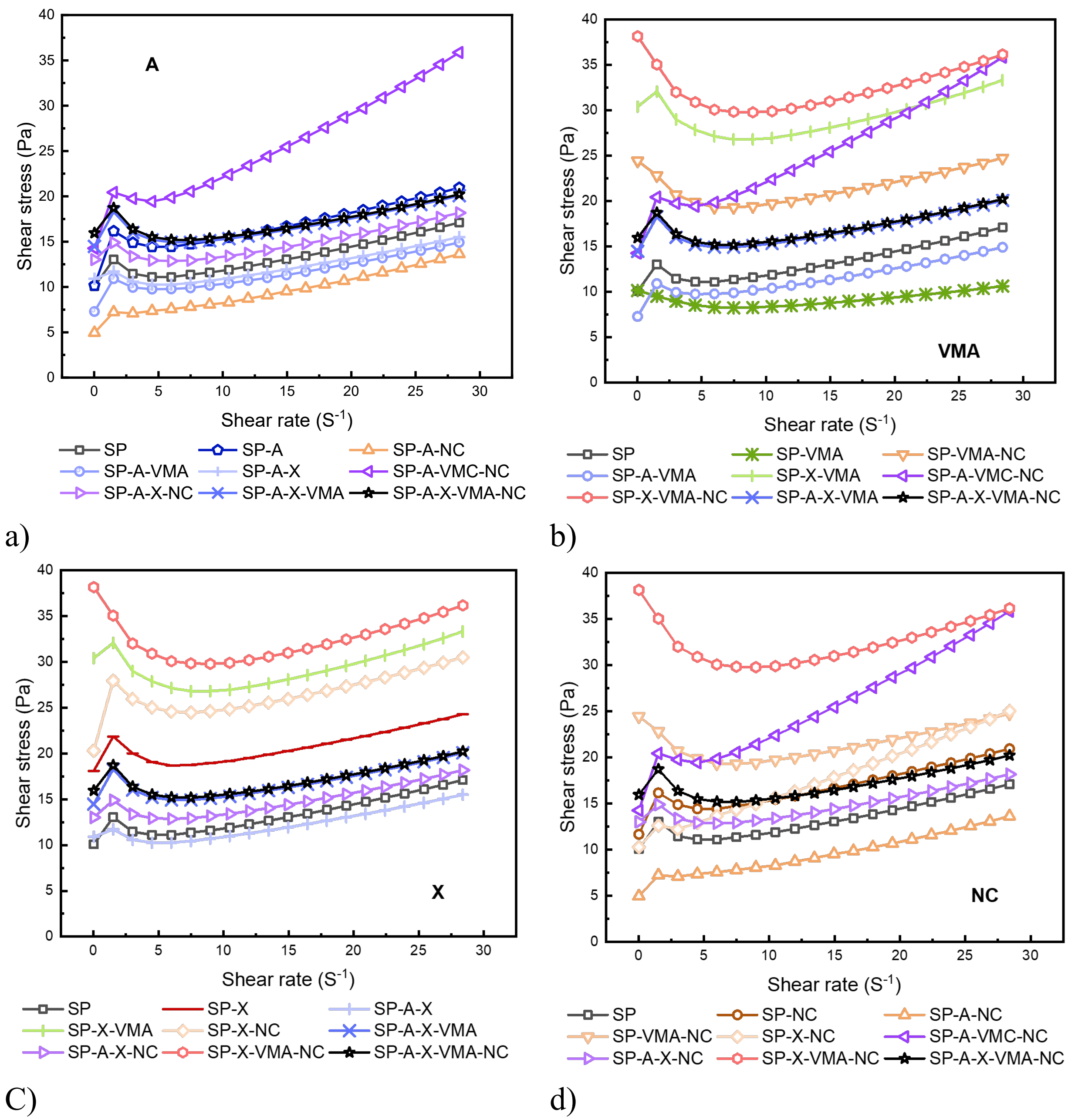


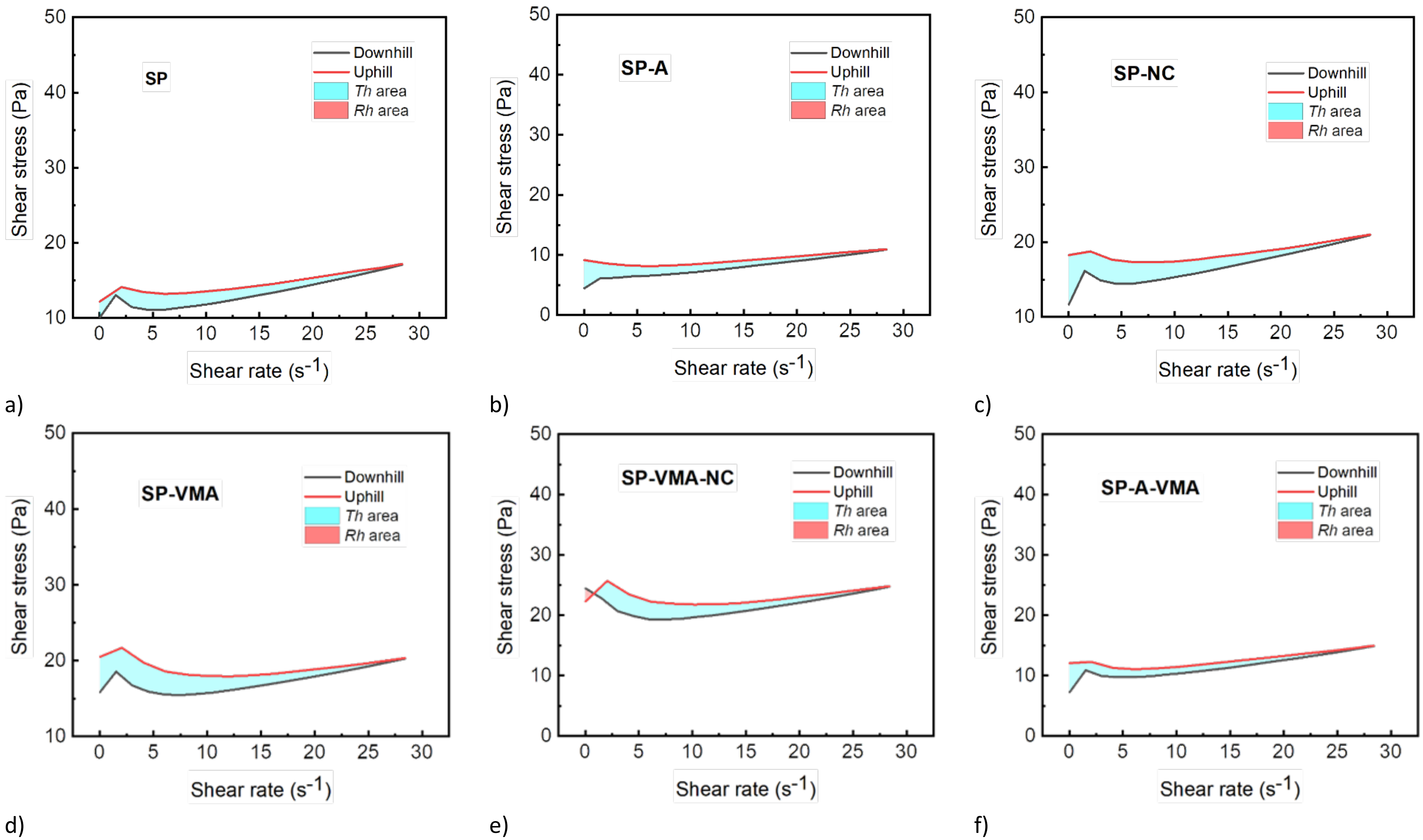
Figure 6: Dynamic yield stress measurement of cement paste with admixtures, mixes with a) the accelerator, b) the VMA, c) CSH-seed, d) nanoclay

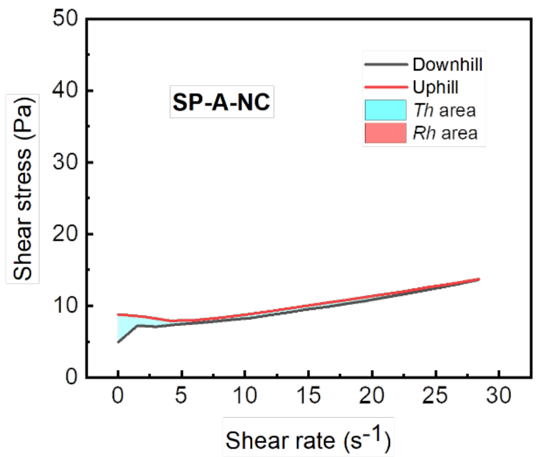
Fig. 7 shows a hysteresis loop of different admixture modified cementitious materials. From a macroscopic perspective, an increase in viscosity occurs at rest and a decrease under shear for thixotropic materials. The emphasis of this figure was to trace changes in the cement paste structure related to different shear rate in the presence of various admixtures during continuous mixing.

Thixotropic properties are closely related to the microstructure of a fresh cement paste. The rise-and-fall pattern (loop) is observed as an ascent curve and a descent curve. The integrated hysteresis loop area represents the degree of thixotropy in the present investigation. All the samples display thixotropic properties, indicating possible structural changes in the cement pastes. In the ascending stage, the cement pastes have large flocculated structures that are hard to break, resulting in higher shear stress at lower shear rates. As most of the flocculated structures are disrupted by the spindle at ascending stage, many free particles and small flocculation's are formed in the descending stage, which reduces the internal friction of the pastes, enabling lower shear stress at the same shear rate than the ascent stage (26). Therefore, the larger the number of flocculated structures in the initial paste, the larger is the area encircled by the hysteresis diagram, which indicates that fresh cement pastes have a high thixotropy. The maximum area of hysteresis loop, shown in Fig. 7, was observed for SP-X-VMA and SP-X-VMA-NC, mainly due to the increased early reactivity of the cementitious materials.

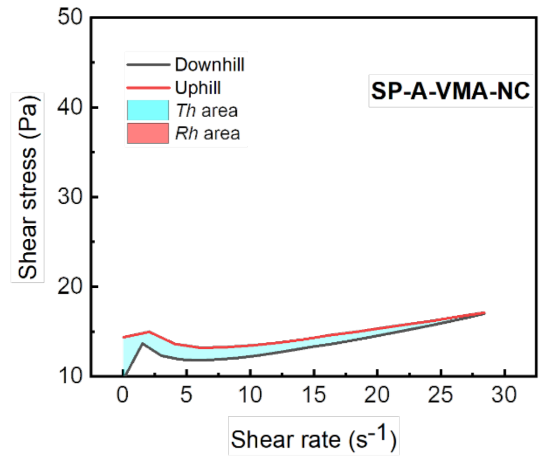
Each blend of admixture affects the rheological properties differently, for understanding purposes, these thixotropy values are represented in four histograms as shown in Fig 8. The outcome of different admixtures on SP-A based cementitious pastes are presented in Fig 8a. There is no significant impact of different admixtures on SP-A based cementitious pastes on thixotropy. A reduction of thixotropy is observed for SP-A-NC, SP-A-VMA, SP-A-X-NC, SP-A-VMA-NC, SP-A-X-VMA-NC. Maximum reduction of thixotropy is observed for SP-A-NC, i.e., of 60.91%, when compared with SP. During the early stages, thixotropy is mainly related to the interaction between particles forming the flocculant (27). Thus, yield stress occurs when shear stress is strong enough to separate pairs of flocs. It is clear from these results that interactions with accelerator (A) distinguish different admixtures from each other and causes them to act differently, especially for

NC. While there is slight increase observed for SP-A-X and SP-A-X-VMA, this may be because of their viscous nature. Fig. 8b illustrates the effects of different blends of admixtures in SP-NC modified cementitious materials on the thixotropy. SP-NC shows an increase in thixotropy when compared to SP alone, approximately 23% of the thixotropy was increased by NC alone. However, as stated in the previous discussion, the accelerator (A) reduces the thixotropy of SP-NC based cementitious materials. This suggests that A creates a layer around the NC at the outset, causing it to act differently in the mixtures. The VMA resulted in an average of 30% enhancements in thixotropy, and nearly 95% enhancement occurred with X. The polymer from VMA interacts with the NC, making it easier to disperse the NC. This contributes to the increase in thixotropy, especially at low shear rates. On the other hand, X, because of its high surface area and propensity to nucleate cement hydration provides the early directed formation of the microstructure of the cement matrix due to the seeding and packing effect (28). The combined effect of X and VMA with SP-NC based cementitious materials results in a very high degree of thixotropy. With SP-X-VMA-NC, 340% higher thixotropy was noticed when compared to SP. Fig 8c presents the influence of blended admixtures on VMA-SP based cementitious materials on shear thinning potential. Thixotropy increases (55%) with VMA content, mainly due to its polymer chains that entangle with SP-based cementitious materials. This is further influenced by the addition of X. The maximum thixotropy was observed for SP-X-VMA. Approximately 390% of rise in thixotropy was observed for SP-X-VMA when compared with SP alone. As anticipated the thixotropy value decreases drastically with the addition of A. Interestingly, with the addition of NC, the thixotropy of the cementitious materials decrease when compared with SP-VMA based cementitious materials. A similar phenomenon was also noted in SP-X-VMA-NC. The SP-X-VMA-NC exhibited lower thixotropy than the SP-A-X-VMA. As NC was added to the cementitious materials in the presence of VMA, more "free water" could be released for the "filler effect" of NC. This free water increases the water film thickness, which is an important factor for governing the workability of cementitious materials (29). This excess free water might help to break the flocculation structure without great difficulty. Fig. 8d summarizes the effect of different admixtures on X-SP based cementitious materials. The addition of X increases the hysteresis area by 63% when compared to SP alone because of its high surface area and seeding behavior. Thixotropy is further enhanced with the addition of NC to X-SP system.

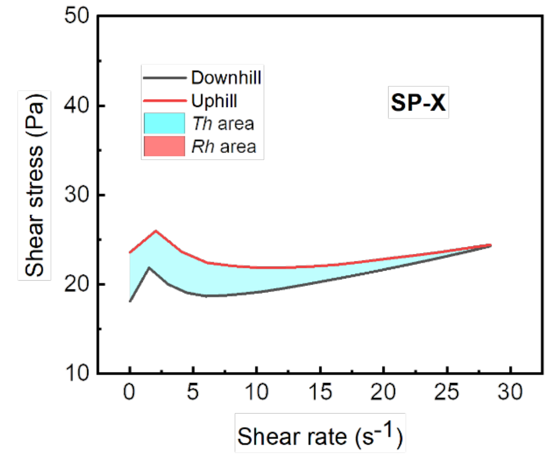

SP
SP-A
SP-NC
SP-VMA
SP-VMA-NC
SP-A-VMA
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
a)
b)
c)
d)
e)
f)


SP-A-NC
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
0
10
20
30
40
50
0
5
10
15
20
25
30

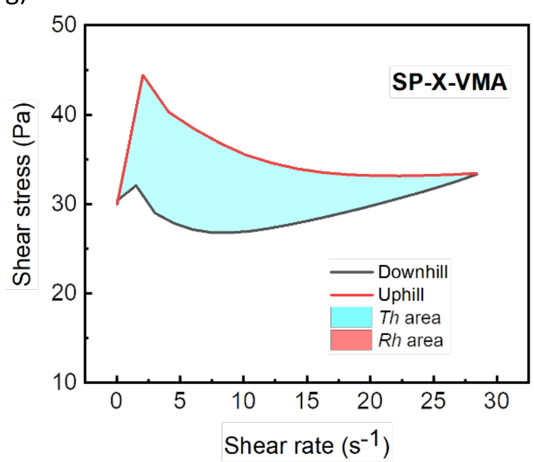
g)


SP-A-VMA-NC
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
10
20
30
40
50
0
5
10
15
20
25
30

h)


SP-X
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
10
20
30
40
50
0
5
10
15
20
25
30

i)


SP-X-VMA
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
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30
40
50
0
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10
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25
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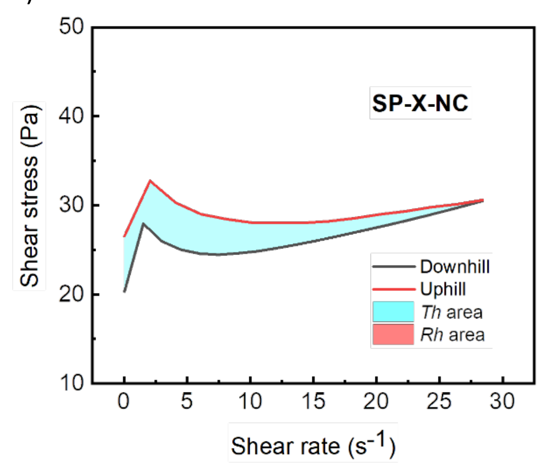
j)


SP-X-NC
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
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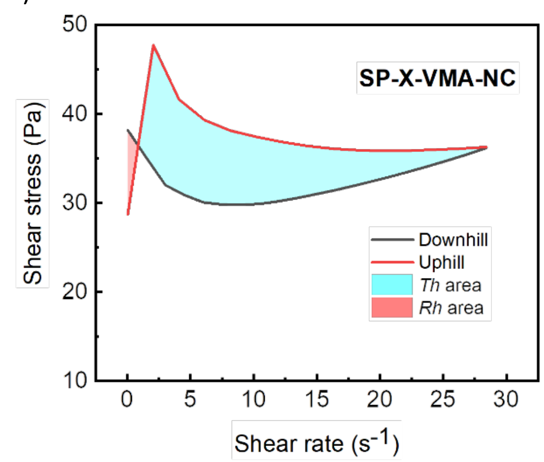
k)


SP-X-VMA-NC
Downhill
Uphill
Th area
Rh area
Shear stress (Pa)
Shear rate (s-1)
10
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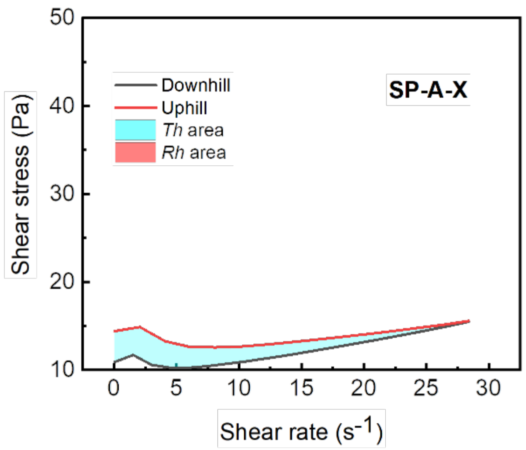
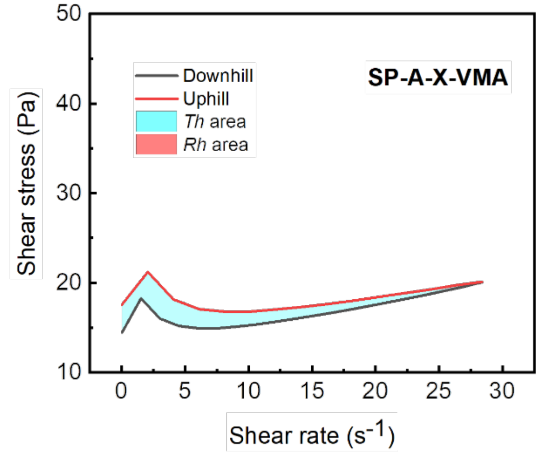
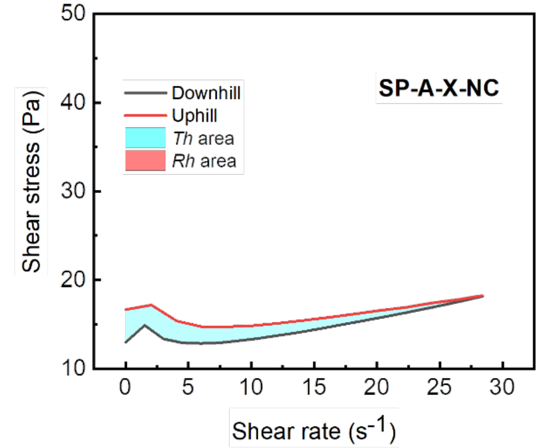
l)



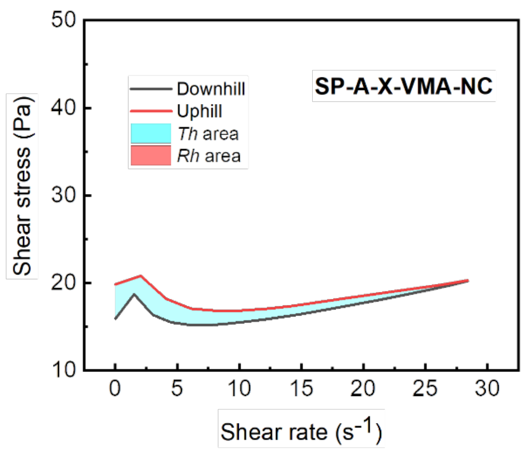
m)



n)



o)



p)

Figure 7. Hysteresis loop of the concrete mixes (Uphill – Increasing shear speed; Downhill – Decreasing shear speed).

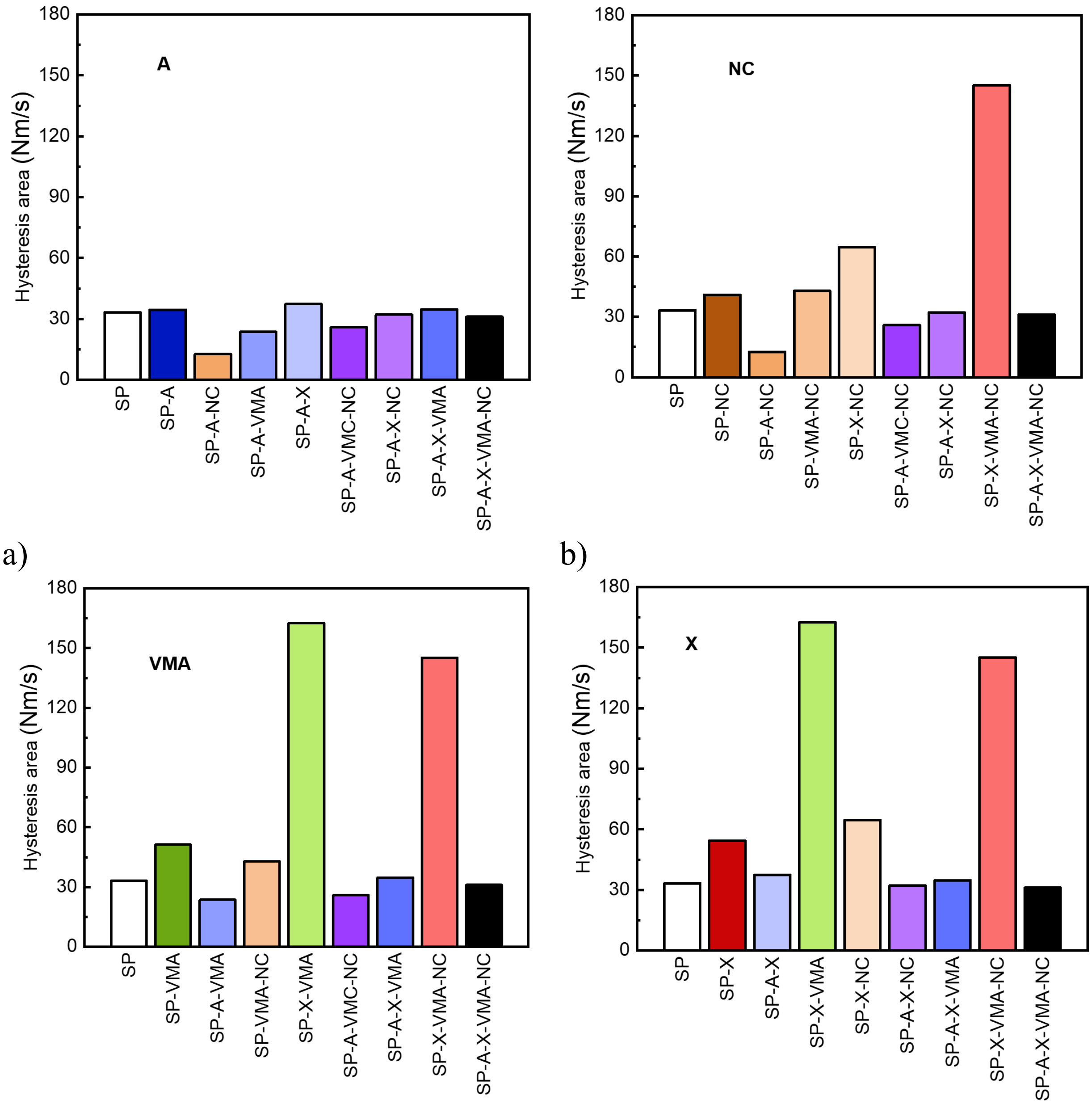
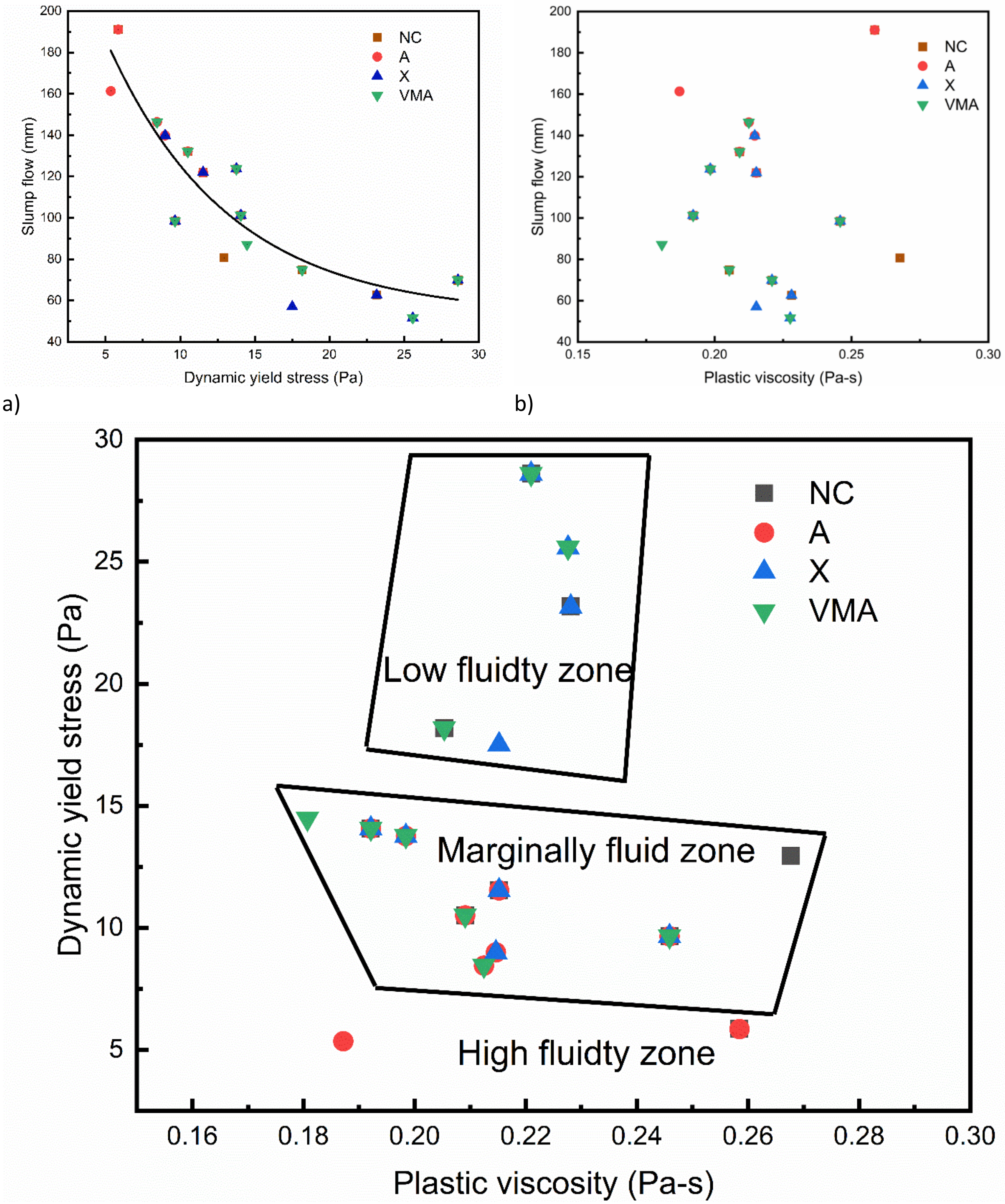


Fig 8. Hysteresis loop area for cementitious materials modified with different admixtures a) combinations with accelerators b) Nanoclay c) VMA d) CSH-seed

For assessing the relationship between the mini-slump and the Bingham constants, i.e. the yield stress and the plastic viscosity, the yield stress values for all mixtures were plotted versus the corresponding slump in Fig. 9(a,b). The mini-slump is inversely related to the yield stress with a curvilinear correlation and the data was fitted using an exponential trendline with a correlation coefficient of R^2 = 0.86. Several previously published empirical studies have demonstrated a correlation between yield stress and slump. For instance, Ferraris and DeLarrard presented a linear relationship between slump and yield stress (30). However, a negative curvilinear correlation for slump to dynamic yield stress has also been suggested (31, 32). A similar trend is also noted in the current investigation.

The highly scattered of data points in Fig. 9(b) demonstrate the independence of slump and plastic viscosity for the various admixture modified cementitious mixtures. The slump and the yield stress can be correlated, whereas no correlation was observed between the slump and the plastic viscosity (31, 33). They also observed that the loss of workability was directly reflected by the increase in the yield stress. However, the plastic viscosity remained nearly constant. This is expected since the slump is a static characteristic of fresh cementitious, whereas viscosity is a dynamic flow property. After the yield stress has been overcome, the flow behavior of concrete is governed by the plastic viscosity. Thus, the different behaviors of two concretes having the same slump is likely due to the different values of plastic viscosity between the two cementitious materials. The Bingham constants (yield stress and plastic viscosity) of various admixture-modified cementitious materials, as well as their slump measurements and visual observations, suggest the creation of bands as shown in Fig. 9c. In Fig. 9c., the yield stress was expressed as a function of the plastic viscosity for all the mixtures incorporated. The cementitious materials were classified as too fluid, marginally fluid, or low fluidity based on mini slump values and visual observations.



c)

Fig. 9 Relationship between: (a) yield stress and slump; and (b) plastic viscosity and slump (c) Plot of plastic viscosity versus yield stress for all concrete mixtures tested, showing suggested suitability bands

Conclusions

The assessment of the workability of fresh cementitious mixtures in terms of the Bingham parameters, namely, the dynamic yield stress, the plastic viscosity and the static yield stress can provide a good insight into the effect of blended additives on cement-based materials. The effect of time period on continuously agitated cementitious mixtures containing superplasticizer and a combination of water reducing accelerator, viscosity modifying admixture, CSH seeds and nanoclay were investigated in this study. The following conclusions can be drawn based on the comprehensive set of data presented in this investigation:

1. The maximum slump flow was noticed for cementitious materials containing admixtures SP-A-NC, and the low amount of slump flow was observed for SP-X-VMA followed by SP-X-NC.
2. High yield stress was observed for cementitious materials containing SP-X, which would have a positive effect on the structural build-up of the paste. It was further enhanced with the addition VMA. However, the shear stress value of SP-X decreases drastically with the addition of accelerator (A).
3. Mixes with the formulated CSH-seeds product and the VMA, without the accelerator, increase the thixotropy, which might have adverse effect when applying subsequent layers.
4. The accelerator tested lowered the static and dynamic yield stress of cementitious materials with different blended admixture, which would be beneficial for the extrusion and pumping step of the extrusion.
5. To measure the static yield stress, the constant speed method allowed to better differentiate the effect of the admixtures over time.
6. Plastic viscosity did not show any evident trend with the change in admixture dosage.

7. The slump had an inverse correlation with the yield stress in a logarithmic curvilinear trend, whereas no such correlation was found between a slump and plastic viscosity.
8. The change of the yield stress with plastic viscosity for all cementitious mixtures investigated was used to establish a control chart for 3D printing. These charts could provide a means for objective assessment of flowability, for 3D printing and these are merely judged based on visual inspection, and/or empirical tests such as the slump test.
9. It should be emphasized that the present results are applicable only for the particular admixtures and materials used in this study and need to be extended for other admixtures. Further investigation is needed to consider the temperature, structuration rate and other measurement methods such as the small amplitude oscillatory shear (SAOS) method.

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References

1. Roussel N, "Rheological requirements for printable concretes," Cement and Concrete Research, V. 112, 2018/10/01/. 2018, pp. 76-85.
2. Nerella VN, Beigh MAB, Fataei S, Mechtcherine V, "Strain-based approach for measuring structural build-up of cement pastes in the context of digital construction," Cement and Concrete Research, V. 115, 2019/01/01/. 2019, pp. 530-44.
3. Perrot A, Lecompte T, Khelifi H, Brumaud C, Hot J, Roussel N, "Yield stress and bleeding of fresh cement pastes," Cement and Concrete Research, V. 42, No. 7, 7//. 2012, pp. 937-44.
4. Yuan Q, Zhou D, Khayat KH, Feys D, Shi C, "On the measurement of evolution of structural build-up of cement paste with time by static yield stress test vs. small amplitude oscillatory shear test," Cement and Concrete Research, V. 99, 2017/09/01/. 2017, pp. 183-9.
5. Saak AW, Jennings HM, Shah SP, "A generalized approach for the determination of yield stress by slump and slump flow," Cement and Concrete Research, V. 34, No. 3, 2004/03/01/. 2004, pp. 363-71.
6. Gao J, Fourie A, "Spread is better: An investigation of the mini-slump test," Minerals Engineering, V. 71, 2015/02/01/. 2015, pp. 120-32.

7. Mahaut F, Mokéddem S, Chateau X, Roussel N, Ovarlez G, "Effect of coarse particle volume fraction on the yield stress and thixotropy of cementitious materials," Cement and Concrete Research, V. 38, No. 11. 2008, pp. 1276-85.
8. Benaicha M, Roguiez X, Jalbaud O, Burtschell Y, Alaoui AH, "Influence of silica fume and viscosity modifying agent on the mechanical and rheological behavior of self compacting concrete," Construction and Building Materials, V. 84, 2015/06/01/. 2015, pp. 103-10.
9. Qian Y, Kawashima S, "Distinguishing dynamic and static yield stress of fresh cement mortars through thixotropy," Cement and Concrete Composites, V. 86, 2018/02/01/. 2018, pp. 288-96.
10. Roussel N, "A thixotropy model for fresh fluid concretes: Theory, validation and applications," Cement and Concrete Research, V. 36, No. 10. 2006, pp. 1797-806.
11. Zhang Y, Zhang Y, Liu G, Yang Y, Wu M, Pang B, "Fresh properties of a novel 3D printing concrete ink," Construction and Building Materials, V. 174, 2018/06/20/. 2018, pp. 263-71.
12. Tan Z, Bernal SA, Provis JL, "Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes," Materials and Structures, V. 50, No. 6, 2017/10/19. 2017, pp. 235.
13. Roussel N, Stefani C, Leroy R, "From mini-cone test to Abrams cone test: measurement of cement-based materials yield stress using slump tests," Cement and Concrete Research, V. 35, No. 5, 2005/05/01/. 2005, pp. 817-22.
14. Olivas A, Helsel MA, Martys N, Ferraris CF, George WL, Ferron R, "NIST Technical Note 1946 Rheological Measurement of Suspensions Without Slippage: Experimental and Model," Book NIST Technical Note 1946 Rheological Measurement of Suspensions Without Slippage: Experimental and Model, Editor, ed.^eds., National Institute of Standards and Technology (NIST), City, 2016, pp. 45.
15. Charrier M, Ouellet-Plamondon C, "Testing Procedures on Materials to Formulate the Ink for 3D Printing," Transportation Research Record, V. 2674, No. 2. 2020, pp. 21-32.
16. Pan W, Ding Z, Chen Y, "Effects of TEA·HCl hardening accelerator on the workability of cement-based materials," IOP Conference Series: Materials Science and Engineering, V. 182, 2017/03. 2017, pp. 012046.
17. Li C, Miao L, You Q, Hu S, Fang H, "Effects of viscosity modifying admixture (VMA) on workability and compressive strength of structural EPS concrete," Construction and Building Materials, V. 175, 2018/06/30/. 2018, pp. 342-50.
18. Murray HH, "Traditional and new applications for kaolin, smectite, and palygorskite: a general overview," Applied Clay Science, V. 17, No. 5, 2000/11/01/. 2000, pp. 207-21.
19. Qian Y, De Schutter G, "Enhancing thixotropy of fresh cement pastes with nanoclay in presence of polycarboxylate ether superplasticizer (PCE)," Cement and Concrete Research, V. 111, 2018/09/01/. 2018, pp. 15-22.
20. Qian Y, Kawashima S, "Use of creep recovery protocol to measure static yield stress and structural rebuilding of fresh cement pastes," Cement and Concrete Research, V. 90, 2016/12/01/. 2016, pp. 73-9.
21. Zongo K, Charrier M, Duval C, Ouellet-Plamondon CM, "Dynamic and Static Yield Stress Determination of Cementitious Paste with Admixtures," Book Dynamic and Static Yield Stress Determination of Cementitious Paste with Admixtures, 28, Editor, ed.^eds., Springer, Cham, City, 2020, pp. 370-8.
22. Wallevik JE, "Rheology of particle suspensions: fresh concrete, mortar and cement paste with various types of lignosulfonates." Fakultet for ingeniørvitenskap og teknologi; 2003.
23. Van Der Vurst F, Grünewald S, De Schutter G, "The impact of VMA on the Rheology, thixotropy and robustness of self-compacting mortars," Calcined Clays for Sustainable Concrete, Springer, 2015, pp. 159-67.
24. Lachemi M, Hossain KMA, Lambros V, Nkinamubanzi PC, Bouzoubaâ N, "Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste," Cement and Concrete Research, V. 34, No. 2, 2004/02/01/. 2004, pp. 185-93.

25. Kropyvnytska T, Rucinska T, Ivashchyshyn H, Kotiv R, "Development of Eco-Efficient Composite Cements with High Early Strength," Book Development of Eco-Efficient Composite Cements with High Early Strength, Editor, ed.^eds., Springer, City, 2019, pp. 211-8.
26. Nan J, Yao M, Li Q, Zhan D, Chen T, Wang Z, et al., "The role of shear conditions on floc characteristics and membrane fouling in coagulation/ultrafiltration hybrid process – the effect of flocculation duration and slow shear force," RSC Advances, V. 6, No. 1. 2016, pp. 163-73.
27. Kim B-G, Jiang S, Jolicoeur C, Aïtcin P-C, "The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste," Cement and Concrete Research, V. 30, No. 6. 2000, pp. 887-93.
28. Sanytsky M, Marushchak U, Olevych Y, Novytskyi Y, "Nano-modified ultra-rapid hardening Portland cement compositions for high strength concretes," Book Nano-modified ultra-rapid hardening Portland cement compositions for high strength concretes, Editor, ed.^eds., Springer, City, 2019, pp. 392-9.
29. Wong H, Kwan AK, "Rheology of cement paste: role of excess water to solid surface area ratio," Journal of materials in civil engineering, V. 20, No. 2. 2008, pp. 189-97.
30. Ferraris CF, DeLarrard F, "Testing and modeling of fresh concrete rheology." 1998.
31. Nehdi M, Al-Martini S, "Coupled effects of high temperature, prolonged mixing time, and chemical admixtures on rheology of fresh concrete," ACI materials Journal, V. 106, No. 3. 2009, pp. 231.
32. Struble LJ, Chen C-T, "Effect of continuous agitation on concrete rheology," Journal of ASTM International, V. 2, No. 9. 2005, pp. 1-19.
33. Mori H, Tanigawa Y, "Flow simulation of fresh concrete subjected to vibration," Magazine of Concrete Research, V. 42, No. 153. 1990, pp. 223-32.