Rheological characterization of the viscoelastic solid-like properties of fresh cement pastes with nanoclay addition

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Abstract:

At sufficiently low applied shear deformation or shear stress, fresh cement paste exhibits viscoelastic solid-like behavior. This solid-like state is particularly important for some applications, such as self-consolidating concrete formwork pressure and 3D concrete printing. In this study, the viscoelastic solid-like behavior of fresh cement pastes is probed using a rheometer. Static yield stress, storage modulus, and cohesion are measured by creep recovery and constant shear rate test, small amplitude oscillatory sweep (SAOS) test and tack test, respectively. The effect of nanoclay addition is studied in various aspects of viscoelastic performance of fresh cement pastes. It is found that nanoclay addition not only enhances yield stress and cohesion, but also stiffness in terms of storage and tangent modulus.

Keywords: *static yield stress, storage modulus, tangent shear modulus, cohesion, nanoclay.*

1. Introduction

Rheology is a field of study on the deformation of materials – not only liquids, but also solids. Cementitious materials in the fresh state (i.e. before set) show both liquid and solid state properties. In particular, the viscoelastic solid properties are closely related to many engineering challenges. Since the invention of self-consolidating concrete (SCC), the study of solid state properties in fresh state has generated significant interest. Compared with conventional vibrated concrete, SCC is more flowable and designed to be easier to operate and cast. However, because of its high flowability SCC also induces higher formwork pressure, which makes formwork construction more costly. Experience and studies conclude that the solid state property after casting is related to formwork pressure [1]. In addition, while at rest, SCC builds up strength and the formwork pressure goes down further [2]. For extrusion based 3D concrete printing, fresh mixes are pumped through the pipe to the nozzle head, then extruded and deposited layer by layer. To build up to a certain height, the fresh material must exhibit sufficiently high strength and stiffness [3, 4]. Meanwhile, the rate of structural build-up should be carefully controlled to balance buildability and interlayer bonding [4, 5]. Cohesion is related to formwork pressure of SCC [6], but also to multi-layer bonding [7]. Higher magnitude and rate of increase of cohesion of SCC could lower formwork pressure [2, 8]. In concrete 3D printing applications, shape retention is also related to material cohesion.

Stability and homogenization of granular particles and fibers in the fresh cement paste matrix is also a big challenge in concrete technology, especially in modern flowable concrete. After casting, the granular particles in concrete could be stable if the fresh cement paste is strong enough to sustain gravity or creep [9].

Compared to dynamic flow properties, the solid-like state of fresh cementitious materials is not as well studied, especially stiffness of cement materials in terms of modulus. Slump tests by cone, mini-cone, Abrams cone, etc, which are widely used in concrete construction industry, could probe the solid state and it has been shown that the slump value follows a trendline correlated to yield stress [10-14]. In the next sections, it will be discussed how shear rheological methods can be used to measure parameters to describe the solid state of fresh cement pastes.

1.1. Rheological properties in solid-like state

Yield stress is a basic term to describe the flowability of cementitious materials. Depending on the shear history, cementitious materials exhibit different yield stresses. One simple example is explained below. In a typical response, under an intermediate shear rate, the shear stress increases to a peak value, then decays to an equilibrium value. The peak shear stress is related to the static yield stress before structural breakdown, while the equilibrium shear stress is related to the dynamic yield stress. The structural breakdown process corresponds to the change of microstructure in terms of flocculation states [15]. Various flocculation states correspond to various yield stresses [16].

Recently, thixotropy has been extensively studied. Thixotropy is defined as the ability of a material to flow at high shear rates but build up strength at low shear rates or resting [17]. Roussel et al. [18] concluded that the thixotropy of cement paste originates from colloidal bonding and CSH bridges and determines various flocculation states. Further, the authors confirmed that thixotropy is related to the discrepancy between static and dynamic yield stress [19].

The attractive forces, including CSH bridges and flocculation bonding in cement pastes, not only give cement paste yield stress, but also stiffness to retain its shape. Modulus is another term describing the stiffness in the solid state. Shear modulus, or modulus of rigidity, is a measure of response in shear stress corresponding to shear strain at low stress/strain range. It could be measured as storage modulus under oscillatory shear or tangent shear modulus under direct shearing.

Cohesion is a bonding property of cementitious materials under extension. It is not only related to liquid properties to wet the surface and form bonding, but also related to solid properties to sustain a certain debonding stress [20].

1.2. Nanoclay enhancing solid state properties

Nanoclays, namely attapulgite or palygorskite clay, have been used as a viscosity modifying agent (VMA) in concrete and has been demonstrated to be effective in various applications, such as decreasing SCC formwork pressure [21]. This can be attributed to the high initial value and rate of increase of static yield stress over resting time by nanoclay addition [22]. High thixotropy can enable low dynamic yield stress under flow while maintaining high static yield stress under rest. Nanoclay is extensively studied and demonstrated to increase thixotropy, even with PCE addition [23]. As thixotropy is desired to balance pumpability and buildability, nanoclay has been very popularly used in developing 3D printing cementitious materials [24-28]. Nanoclay has also been found to increase green strength and shape stability in slip-form pavement [29], which is beneficial for the buildability of 3D printing [30].

This study probes the rheological properties of fresh cement pastes in the solid-like state. Investigated properties include static yield stress via creep recovery test, storage modulus via oscillatory strain amplitude sweep, tangent shear modulus via low constant shear rate, and cohesion via tack test. In particular, the effect and underlying mechanisms of nanoclay on these solid-like properties are studied.

2. Theoretical background of approach

2.1. Creep recovery test

Creep recovery test has long been applied to probe the viscoelastic properties of materials, where constant stress is applied for a set time period, then the stress is released for another set time period. The response in terms of strain development is different for an elastic solid, a viscous liquid, a viscoelastic solid and a viscoelastic liquid material. Detailed description can be found in [22, 31]. Fresh cement pastes exhibit viscoelastic solid or viscoelastic liquid properties depending on the creep stress applied. When the applied creep stress is lower than a critical stress, the strain increases and approaches an equilibrium value, indicating no continuous flow. When the applied stress is higher than the critical stress, the strain keeps increasing, indicating the flow continues. Therefore, the critical creep stress when solid liquid transition occurs is the static yield stress. Before the onset of flow, at stresses lower than the static yield stress, the cement paste exhibits viscoelastic solid-like behavior [22].

2.2. Small amplitude oscillatory sweep (SAOS)

The oscillatory shear approach has been popularly applied to study the viscoelastic properties of fresh cement pastes. Small amplitude oscillatory sweep (SAOS) could be used to obtain storage modulus and critical strain [16, 32]. The theory is briefly explained here, while further reference for more details is given in [22].

An oscillatory strain is applied as a sine function and the measured stress is a combination of sine and cosine function due to the elastic and viscous response of the material. The storage modulus G' represents the elastic or in-phase response and the loss modulus G" represents the viscous or out-of-phase response. They are related to the viscoelastic solid and liquid properties, respectively.

Within a critical oscillatory strain, the particle colloidal system could recover elastically and the structural integrity is maintained. Within the critical strain, G' (and also G") is independent of applied frequency and strain, so this region is called the linear viscoelastic region (LVR). Above the critical strain, particle colloidal system is destructured and not able to recover elastically, so the storage modulus decreases.

We implement strain oscillatory sweep from 10^{-5} to 0.1 on fresh cement pastes. Constant frequency, 1 Hz, is set for SAOS, which is also commonly applied in other studies [32-34]. The corresponding storage modulus G' vs. strain curve exhibits two main regions: an initial plateau and a subsequent decrease indicating that the sample is experiencing a shear-induced breakdown. The strain at which there is an apparent drop in stiffness is considered to be the critical strain. Both the plateau storage modulus and critical strain are measured. For plain cement pastes, the critical oscillatory strain marking the end of LVR is in the range of 10^{-4} for plain cement pastes [18, 32, 35]. It could be much higher than 10^{-4} with PCE or other superplasticizer addition [36].

2.3. Constant shear rate

The typical response of cement-based materials under constant shear rate is an initial increase to a peak value and subsequent decrease to an equilibrium value. The increase in stress is related to the gradual deformation of the material.

2.3.1. Peak value and tangent shear modulus: low constant shear rate

The peak stress marks the yield stress of the suspension that must be overcome to initiate flow in a material. Therefore, the peak strain value has also been used to measure static yield stress before the structure breaks down [37, 38]. However, it has been concluded that the static yield stress by this method is shear rate dependent [39, 40].

The increasing rate of stress over strain corresponds to the stiffness and modulus of the materials. It is generally found that the shear stress increases rapidly in the beginning, then slows until reaching peak stress. It could be reasoned that continuous shearing breaks the microstructure, thus the stiffness or modulus decreases. The tangent shear modulus, which is the slope of a line tangent to the stress-strain curve, in the beginning is higher and considered to correspond to the solid-like properties.

2.3.2. Stress decay: high constant shear rate

At high shear rate, the stress increment process occurs too fast to be captured by rheometer, but high shear rate allow materials to obtain stable flow, thus the stress decay process under flow can be measured accurately in this case [41]. The authors have used exponential curve fitting for the stress decay process and used it to calculate a thixotropic index [15, 42]. They also used stress decay process to model the sand migration process during continuous shearing of fresh mortars [43]. The characteristic time calculated by the model indicates the rate of structural breakdown. The stiffer the microstructure, the lower the characteristic strain [17]. Details can be found in [15].

2.4. Probe tack test

Traditionally, cohesion of cement-based materials is measured by the washout test (CRD C 61 standard) [44], where an open bucket of concrete is dipped into water and taken out. The mass change is measured and taken as a measure of how cohesive the material is. However, the test is empirical and could be subjective and affected by many factors. Meanwhile, the probe tack test has been used to characterize debonding properties of different types of soft materials [45-47]. However, the cohesion of cementitious materials has not been extensively studied. Several studies (Kawashima et al. [6], Ma et al. [48] and Kaci et al. [20, 49]) adopted probe tack test to measure cohesion of cement materialssystems.

2.4.1. Normal force evolution at various pulling velocities

Probe tack test is performed on two parallel plates at an initial gap. The material is filled in between the two plates. The upper plate is lifted up at a constant pulling velocity. Correspondingly, the normal force increases to a peak value, then decreases until almost zero when the two plates are separated.

At the very beginning of pulling, the sample deforms elastically and the normal force increases with the gap. Beyond a critical tensile strain, the normal force reaches a peak value and starts to decrease, indicating that the sample starts undergoing a failure process, as shown in Figure 1. The value of the peak force may be composed of at least two contributions: resistance to flow or viscous dissipation (dynamic property) and resistance to elastic failure (static property) due to the intrinsic cohesion of the material [49]. The physical origin of cohesion may include intermolecular forces and capillary effects. The higher the pulling velocity is, the higher the viscous dissipation is [20]. To eliminate the effect of dynamic hydraulic forces on peak force, cohesion is considered to correspond to the value of the peak force for a vanishingly low pulling velocity. We first study the effect of pulling velocity on peak value F_{max}, which has been presented in the PhD thesis of the first author [50].

The peak value vs. pulling velocity for plain cement paste with w/c at 0.36 is summarized in Figure 2. The behavior of normal force can be categorized into two regimes by a certain pulling velocity criterion. If the pulling velocity exceeds a certain criterion, higher pulling velocity leads to higher peak normal force due to viscous dissipation [20]. At high pulling velocities, during the stress decay and failure process, the entire material sample progressively flows inward and separates as two peaks, as shown in Figure 3 (a).

Below the velocity criteria, lower pulling velocity leads to higher peak normal force. At relatively low pulling velocities, it takes a longer time for the stretching force to reach the peak value. Therefore, the higher peak normal force could be related to the elastic response and structural rebuilding over resting time. At low pulling velocity (1 $\mu m/s$), the sample shows heterogeneous cavitation and fingering failure mode [45] – this is shown in Figure 3 (b) where several inward flows are observed, which is a combination of moderate inwards flow and internal growth of voids. It is reasoned that at low pulling velocity, it takes a longer time for the material to fail and separate completely, and due to structural rebuilding [22] the paste stiffens. So instead of one moderate inward flow, it shows several inward flows and fingering features.

Thus, as shown in Figure 2, normal force at the critical pulling velocity, 10 $\mu m/s$, shows the smallest value. To mitigate the effect of viscous dissipation and structural rebuilding on the measured cohesion, the criterion value of 10 $\mu m/s$ is selected and used in the remainder of the study.

3. Materials and procedures

3.1. Materials and experimental setup

Type I Portland cement is used in all mixtures. According to ASTM C150 [51], its compressive strength at 28 days is 44.8 MPa, the Blaine fineness is 420 m^2/kg and the chemical constituents are summarized in Table 1. Samples are prepared with tap water. Highly purified attapulgite clay is also added to replace cement at small amounts. The nanoclay is a highly purified magnesium alumino-silicate, which is chemically exfoliated from bulk attapulgite to remove all impurities. When dispersed, it is needle-like with an average length of 1.75 μm and diameter of 30 nm, so it will be referred to as nanoclay herein. In this study, no chemical admixtures are used.

Mixtures have a water-to-cement ratio (W/C) of 0.36 by mass. As a parameter, the amount of nanoclay replacing cement varies from 0, 0.1, 0.3 and 0.5% by mass of binder including both cement and nanoclay.

Nanoclay powder is blended with the mixing water in a Waring blender for 2 minutes to produce a clay suspension, which remains stable after 24 hours at rest. Immediately after preparing the suspension, it is poured into a beaker. Cement powder is slowly added to the suspension and mixed by hand for 1 min. Then, it is mixed with a small egg mixer at a speed of 1100 rpm for 3 min. The fresh cement paste is loaded into the cup of the rheometer with a syringe to ensure each sample has the same volume.

3.2. Shear rheological protocols

We perform all tests on a HAAKE MARS III rotational rheometer. Rotational tests such as creep recovery, small amplitude oscillatory sweep (SAOS), and constant shear rate tests are run using a coaxial cylinder geometer – the radius of the bob is 12.54 mm and the gap between the bob and cup is 1.06 mm. As cementitious materials are thixotropic, the flow behavior is greatly dependent on the flocculation state. It must be consistent before each test to guarantee repeatability. Each sample is presheared at 600 s^{-1} for 4 min until the shear stress reaches equilibrium, after which the material is allowed to rest for 1 min for stress relaxation and to reach a stable state. Then, either the creep recovery test, oscillatory test, or constant shear rate is applied. In the creep recovery protocol, we apply the creep step for 60 s at each applied stress level and monitor its recovery for another 60 s. In SAOS, we apply strains from 10^{-5} to 10^{-1} at a fixed frequency of 1 Hz. For the constant shear rate, either 0.01 s^{-1} or 50 s^{-1} is applied.

For the tack test, parallel plates with a diameter of 60 mm are used. The lower plate is fixed, while the upper plate could rotate or move up and down. After loading a set volume of cement paste, the upper plate is lowered and squeezes the material until it reaches the target gap (2 mm). Once the top plate is in position, the sample is trimmed to match the diameter of the plates. The gap (2 mm) is the initial sample height. To prevent slip, the plates are covered by sand paper with an ISO/FEPA grit designation of P150.

During the test, each sample is presheared at 50 s^{-1} for 1 min until the shear stress reaches equilibrium, after which the material is allowed to rest for 1 min for stress relaxation and to reach a stable state. After preshear and resting, the top plate moves up vertically at a low pulling velocity at 10 $\mu m/s$. The normal force experienced by the top plate is recorded over time until the sample reaches complete separation.

For each test protocol with any mixture, a new sample is prepared. At least three measurements are conducted for each mixture and testing protocol.

4. Results and discussion

4.1. Static yield stress by creep recovery test

Static yield stress by creep recovery test has been measured and presented in a previous study [22] and briefly presented here. We implement the creep recovery protocol to measure the static yield stress of cement pastes modified with highly purified attapulgite clays, which exhibit high rate of thixotropic rebuilding at short time scales [52]. The results are shown in Figure 4. There is a linear increase of static yield stress with nanoclay addition. With 0.5% of nanoclay addition over cement, the static yield stress increases from 19 Pa to 58.2 Pa.

4.2. Cohesion by probe tack test

As shown in Figure 5, the cohesive strength of cement paste increases with nanoclay addition. It is noted here that the preshear rate is much lower for parallel plates geometry than bob-cup geometry (50 v.s. 600 s^{-1}). Because in parallel plates, high shearing rate might make the material distribute inhomogeneous in between the two plates, and make the material flow out of the plates. In a study by Kawashima et al. [6], preshear at 50 or 300 s^{-1} makes little difference to the first peak value compared with the second peak. In this study, only the first peak is measured and used.

4.2.1. Comparison of cohesion by tack test and static yield stress by creep recovery test

To explore the effects of nanoclay, the normalized values of cohesion measured by tack test and static yield stress measured by creep recovery test are compared in Figure 6. It could be seen that the normalized values show the same trend and similar rates. Thus, cohesion corresponds well with static yield stress in the case of nanoclay addition. It could be reasoned that nanoclay has similar effects on extension and shear loading directions. Possible mechanisms of nanoclay strengthening the microstructure are filling effect and interparticle linkage [23], and these bonding mechanisms are not expected to have a directional bias.

4.3. Storage modulus by small Amplitude Oscillatory Sweep (SAOS)

The storage modulus of cement pastes within linear viscoelastic region (LVR) with nanoclay addition is shown in Figure 7. The storage modulus G' with nanoclay addition increases from 2.96×10^{4} to 1.72×10^{5} Pa. Separate studies have shown differing effects of nanoclay on storage modulus, i.e. very similar to control or decrease over time [52, 53], which may be attributed to differences in dispersion methods and pre-shear conditions.

More investigation is needed to better understand the relationship between processing and shear conditions and the resultant effect of nanoclay on stiffness.

4.4. Peak stress and tangent shear modulus by low constant shear rate

4.4.1. Peak stress

The stress development of fresh cement pastes under 0.01 s^{-1} is shown in Figure 8 (a). It could be seen that the stress increases faster in the beginning and then slows until reaching a stress plateau value. The peak value is associated with static yield stress before the flow onset. From 0 to 0.5% of nanoclay addition, the plateau stress increases from 25.57 Pa to 58.43 Pa, as shown in Figure 9.

Using creep recovery test, the static yield stresses are 19 Pa and 58.2 Pa for plain cement and 0.5% of nanoclay addition, respectively. The plateau stress measured by low constant shear rate is higher than static yield stress measured by creep recovery test. It could be reasoned that the longer resting time and compaction effect could be contributing to the higher values. The solid-liquid transition in creep recovery test is abrupt, as viscosity bifurcation process occurs within 0.5 s (Figure 4 in [22]). In contrast, it takes more than 50 s to reach plateau values for low shear rate tests. The longer resting time could possibly increase the yield stress measured. It has been studied that under rest, the high stress applied could increase the yield stress due to compaction effect [53]. Similarly, the longer time before flowing also compacts the microstructure and increases the yield stress.

4.4.2. Tangent shear modulus

Meanwhile, the tangent shear modulus is measured as the slope of the tangent line of the stress-strain curve at low strains. It is related to the term "elastic shear modulus G" as the ratio between critical stress over critical strain at flow onset defined by Roussel [4]. It could be seen in Figure 8 that the shear stress increases more rapidly and linearly in the beginning at low strains. It could be assumed that the microstructure is more intact and stiffer at low strains. Further shear breaks down the microstructure, thus slowing the rate of stress increase over strain. Since we are more interested in the solid-like behavior, the tangent shear modulus is measured as the slope of the shear stress-strain curve at low strains: when the stress is between 5 and 10 Pa for plain cement paste and when stress is between 10 and 15 Pa for nanoclay 0.5%, as shown in the inset of Figure 8. It is found that with 0.5% of nanoclay addition, the tangent shear modulus increases from 2.27×10^{4} Pa to 1.09×10^{5} Pa, as shown in Figure 9.

Using SAOS, the average value of storage modulus are 2.96×10^{4} to 1.72×10^{5} Pa for mixtures with no clay and 0.5% clay. It could be seen that the tangent shear modulus measured by low constant shear rate is lower than the storage modulus measured by SAOS. It could be hypothesized that continuous shearing a low constant shear rate is more destructive than SAOS.

Studies show that strength and modulus could be a bottleneck of concrete 3D printing. As the height of the structure increases, the gravity-induced stress to the bottom layer increases linearly, while required modulus increases even faster [4]. Studies by Salet et al. [30] found that 3D printed structures tend to fail under buckling because of insufficient modulus rather than strength. Meanwhile, as the height increases, the structure becomes a slender body. Typical failure mode like loss of stability or buckling could occur [30]. Currently, many 3D printed structures are assembled from various sections after concrete materials become hardened. Findings that indicate nanoclay enhances modulus as well as yield stress provide promising support for the application of nanoclay in concrete 3D printing.

4.5. Critical strain: indication of connectivity of the microstructure

4.5.1. Characteristic time during deflocculation measured by constant shear rate

Using intermediate constant shear rate (50 s^{-1}), the stress decay process is captured, as shown in Figure 10. According to thixotropy theory, the stress decay curve depicts the destructuration process [17], which can be fitted with an exponential model. The characteristic time indicates the rate of destruction, and is calculated as when the stress decreases to $1/e$ of the initial stress value [15].

The result in Figure 10 shows that the characteristic time of plain cement paste decreases significantly with 0.5% of nanoclay addition, from 3.65 to 1.55 s. Another study by the authors using a different setup also found the same conclusion (refer to Figure 6 (a) in [23]). Under the same constant shear rate, results indicate that nanoclay addition decreases the characteristic strain.

4.5.2. Critical strain measured by SAOS

Meanwhile, the critical strain, associated with the modulus when it exhibits a significant decrease, is measured by SAOS and has been presented in [22]. With 0.5% nanoclay addition, the critical strain decreases from 7.68×10^{-4} to 1.69×10^{-4}.

4.5.3. Rigid bonding mechanism with nanoclay addition

Both the characteristic time/strain by constant shear rate and critical strain by SAOS decrease with nanoclay addition, indicating higher interconnectivity and bonding. Compared with cement particles used in this studywith an mean size of 18 μm, the dispersed nanoclay could fill the voids between particles/agglomerates and enhance interparticle bonding. Alternatively, nanoclays themselves can form an interconnected structure at high electrolyte concentrations [54].

In the study of polycarboxylate ether superplasticizer (PCE) of cement paste, the authors found that both yield stress and critical strain increase with low dosages of PCE [15]. This phenomena is further confirmed in another study [36]. Comparatively, nanoclay addition increases static yield stress, yet decreases both critical strain by SAOS and the characteristic strain in stress decay at 50 s^{-1}. The authors found that small amounts (0.05%) of PCE addition in plain cement pastes provided a possible bonding mechanism with slightly higher increases in dynamic yield stress, characteristic time, or characteristic strain (refer to Figure 12 in [15]). In comparison, a previous study by the authors found that nanoclay in plain cement paste does not change the size distribution of the colloidal paste system, but increases the inter-particle/agglomerate bonding [23]. A possible mechanism is that compared with soft bonding mechanisms by PCE addition, nanoclay addition provides a comparatively rigid bonding, thus increasing the storage modulus [52] and decreasing the critical strain. This indicates that nanoclay addition enhances the connectivity of the microstructure of the cement paste, which corresponds well with the possible strengthening mechanisms of nanoclay addition summarized by the authors [23]: filler effect and interparticle linkage. It also corresponds to the findings by Tregger et al. [55] and Kawashima et al. [56]: nanoclay addition decreases the packing density of the cement paste system.

5. Conclusions

This study summarized and implemented various protocols to probe the viscoelastic solid-like behavior of fresh cement pastes. Static yield stress, storage modulus and cohesion are measured by the creep recovery test, small amplitude oscillatory sweep and tack test, respectively. Under creep, the flow stops when the applied stress is lower than the static yield stress. Under small amplitude oscillatory sweep, the material exhibits viscoelastic solid behavior at sufficiently small strains where the integrity of the flocculated network is maintained. Beyond a critical strain, the modulus decreases and the material shows liquid-like behavior. Cohesion is taken to be the peak normal force at vanishingly small pulling velocities and the resistance of the material to extension.

It is found that a small nanoclay addition increases these three parameters. Cohesion and static yield stress increases with increasing nanoclay addition. Possible mechanisms of the nanoclay strengthening the fresh microstructure include filling effect and interparticle linkage, where there is no bias in loading direction: extension or shearing. Both the critical strain measured by SAOS and characteristic strain of stress decay decrease with nanoclay addition, which indicates higher connectivity of the microstructure with nanoclay.

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Reference

[1] N. Gardner, Pressure of concrete on formwork-A review, ACI Journal Proceedings, ACI, 1985.

[2] J. Assaad, K.H. Khayat, H. Mesbah, Variation of formwork pressure with thixotropy of self-consolidating concrete, ACI Materials Journal, 100 (2003).

[3] A. Perrot, D. Rangeard, A. Pierre, Structural built-up of cement-based materials used for 3D-printing extrusion techniques, Mater Struct, 49 (2016) 1213-1220.

[4] N. Roussel, Rheological requirements for printable concretes, Cement and Concrete Research, (2018).

[5] L. Reiter, T. Wangler, N. Roussel, R.J. Flatt, The role of early age structural build-up in digital fabrication with concrete, Cement and Concrete Research, (2018).

[6] S. Kawashima, M. Chaouche, D.J. Corr, S.P. Shah, Influence of purified attapulgite clays on the adhesive properties of cement pastes as measured by the tack test, Cement and Concrete Composites, 48 (2014) 35-41.

[7] N. Roussel, F. Cussigh, Distinct-layer casting of SCC: The mechanical consequences of thixotropy, Cement and Concrete Research, 38 (2008) 624-632.

[8] K. Khayat, J. Assaad, H. Mesbah, M. Lessard, Effect of section width and casting rate on variations of formwork pressure of self-consolidating concrete, Mater Struct, 38 (2005) 73-78.

[9] N. Roussel, A theoretical frame to study stability of fresh concrete, Mater Struct, 39 (2006) 81-91.

[10] N. Roussel, P. Coussot, "Fifty-cent rheometer" for yield stress measurements: from slump to spreading flow, Journal of Rheology (1978-present), 49 (2005) 705-718.

[11] N. Roussel, C. Stefani, R. Leroy, From mini-cone test to Abrams cone test: measurement of cement-based materials yield stress using slump tests, Cement and Concrete Research, 35 (2005) 817-822.

[12] N. Roussel, Correlation between yield stress and slump: comparison between numerical simulations and concrete rheometers results, Mater Struct, 39 (2006) 501-509.

[13] J.E. Wallevik, Relationship between the Bingham parameters and slump, Cement and Concrete Research, 36 (2006) 1214-1221.

[14] Z. Tan, S.A. Bernal, J.L. Provis, Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes, Mater Struct, 50 (2017) 235.

[15] Y. Qian, K. Lesage, K. El Cheikh, G. De Schutter, Effect of polycarboxylate ether superplasticizer (PCE) on dynamic yield stress, thixotropy and flocculation state of fresh cement pastes in consideration of the Critical Micelle Concentration (CMC), Cement and Concrete Research, 107 (2018) 75-84.

[16] N. Roussel, A. Lemaître, R.J. Flatt, P. Coussot, Steady state flow of cement suspensions: a micromechanical state of the art, Cement and Concrete Research, 40 (2010) 77-84.

[17] N. Roussel, A thixotropy model for fresh fluid concretes: theory, validation and applications, Cement and Concrete Research, 36 (2006) 1797-1806.

[18] N. Roussel, G. Ovarlez, S. Garrault, C. Brumaud, The origins of thixotropy of fresh cement pastes, Cement and Concrete Research, 42 (2012) 148-157.

[19] Y. Qian, S. Kawashima, Distinguishing dynamic and static yield stress of fresh cement mortars through thixotropy, Cement and Concrete Composites, 86 (2018) 288-296.
[20] A. Kaci, R. Bouras, V. Phan, P. Andréani, M. Chaouche, H. Brossas, Adhesive and rheological properties of fresh fibre-reinforced mortars, Cement and Concrete Composites, 33 (2011) 218-224.
[21] J.H. Kim, M. Beacraft, S.P. Shah, Effect of mineral admixtures on formwork pressure of self-consolidating concrete, Cement and Concrete Composites, 32 (2010) 665-671.
[22] Y. Qian, S. Kawashima, Use of creep recovery protocol to measure static yield stress and structural rebuilding of fresh cement pastes, Cement and Concrete Research, 90 (2016) 73-79.
[23] Y. Qian, G.D. Schutter, Enhancing thixotropy of fresh cement pastes with nanoclay in presence of Polycarboxylate ether superplasticizer (PCE), Cement and Concrete Research, 111 (2018) 15-22.
[24] A. Kazemian, X. Yuan, E. Cochran, B. Khoshnevis, Cementitious materials for construction-scale 3D printing: Laboratory testing of fresh printing mixture, Construction and Building Materials, 145 (2017) 639-647.
[25] M. Rubio, M. Sonebi, S. Amziane, 3D PRINTING OF FIBRE CEMENT-BASED MATERIALS: FRESH AND RHEOLOGICAL PERFORMANCES, ICBBM 2017, 2nd International Conference On Bio-Based Building Materials, RILEM, 2017.
[26] Y. Zhang, Y. Zhang, G. Liu, Y. Yang, M. Wu, B. Pang, Fresh properties of a novel 3D printing concrete ink, Construction and Building Materials, 174 (2018) 263-271.
[27] B. Panda, S. Ruan, C. Unluer, M.J. Tan, Improving the 3D printability of high volume fly ash mixtures via the use of nano attapulgite clay, Composites Part B: Engineering, 165 (2019) 75-83.
[28] A. Rahul, M. Santhanam, H. Meena, Z. Ghani, 3D printable concrete: Mixture design and test methods, Cement and Concrete Composites, (2018).
[29] T. Voigt, J.-J. Mbele, K. Wang, S.P. Shah, Using fly ash, clay, and fibers for simultaneous improvement of concrete green strength and consolidatability for slip-form pavement, Journal of Materials in Civil Engineering, 22 (2010) 196-206.
[30] R. Wolfs, F. Bos, T. Salet, Early age mechanical behaviour of 3D printed concrete: Numerical modelling and experimental testing, Cement and Concrete Research, 106 (2018) 103-116.
[31] L.J. Struble, M.A. Schultz, Using creep and recovery to study flow behavior of fresh cement paste, Cement and concrete research, 23 (1993) 1369-1379.
[32] M.A. Schultz, L.J. Struble, Use of oscillatory shear to study flow behavior of fresh cement paste, Cement and Concrete Research, 23 (1993) 273-282.
[33] Z. Sun, T. Voigt, S.P. Shah, Rheometric and ultrasonic investigations of viscoelastic properties of fresh Portland cement pastes, Cement and Concrete Research, 36 (2006) 278-287.
[34] A. Betioli, P. Gleize, D. Silva, V. John, R. Pileggi, Effect of HMEC on the consolidation of cement pastes: Isothermal calorimetry versus oscillatory rheometry, Cement and concrete Research, 39 (2009) 440-445.

[35] L. Nachbaur, J. Mutin, A. Nonat, L. Choplin, Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting, Cement and Concrete Research, 31 (2001) 183-192.
[36] Y. Qian, Flocculation bonding of polycarboxylate ether superplaticizer (PCE) in fresh cement pastes and its effect on rheological parameters over time at early age, Cement and Concrete Composites, submitted (2019).
[37] F. Mahaut, S. Mokeddem, X. Chateau, N. Roussel, G. Ovarlez, Effect of coarse particle volume fraction on the yield stress and thixotropy of cementitious materials, Cement and concrete research, 38 (2008) 1276-1285.
[38] G. Ovarlez, X. Chateau, Influence of shear stress applied during flow stoppage and rest period on the mechanical properties of thixotropic suspensions, Physical Review E, 77 (2008) 061403.
[39] A.W. Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement paste, Cement and concrete research, 31 (2001) 205-212.
[40] Q. Yuan, D. Zhou, K.H. Khayat, D. Feys, C. Shi, 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, 99 (2017) 183-189.
[41] S. Jarny, N. Roussel, S. Rodts, F. Bertrand, R. Le Roy, P. Coussot, Rheological behavior of cement pastes from MRI velocimetry, Cement and Concrete Research, 35 (2005) 1873-1881.
[42] Y. Qian, G. De Schutter, Different Effects of NSF and PCE Superplasticizer on Adsorption, Dynamic Yield Stress and Thixotropy of Cement Pastes, Materials, 11 (2018).
[43] Y. Qian, S. Kawashima, Flow onset of fresh mortars in rheometers: contribution of paste deflocculation and sand particle migration, Cement and Concrete Research, 90 (2016) 97-103.
[44] C. CRD, Test Method for Determining the Resistance of Freshly-Mixed Concrete to Washing Out in Water, US Army Experiment Station, Handbook for Concrete, Vicksburg, Mississippi, (1989).
[45] Y.M. Abdelhaye, M. Chaouche, J. Chapuis, E. Charlaix, J. Hinch, S. Roux, H. Van Damme, Tackiness and cohesive failure of granular pastes: Mechanistic aspects, The European Physical Journal E, 35 (2012) 1-8.
[46] Q. Barral, G. Ovarlez, X. Chateau, J. Boujlel, B. Rabideau, P. Coussot, Adhesion of yield stress fluids, Soft Matter, 6 (2010) 1343-1351.
[47] Y.M. Abdelhaye, M. Chaouche, H. Van Damme, The tackiness of smectite muds. 1. The dilute regime, Applied Clay Science, 42 (2008) 163-167.
[48] S. Ma, Y. Qian, S. Kawashima, Performance-based study on the rheological and hardened properties of blended cement mortars incorporating palygorskite clays and carbon nanotubes, Construction and Building Materials, 171 (2018) 663-671.
[49] A. Kaci, R. Bouras, M. Chaouche, P. ani, H. Brossas, Adhesive and rheological properties of mortar joints, Applied rheology, 19 (2009) 51970.
[50] Y. Qian, Characterization of Structural Rebuilding and Shear Migration in Cementitious Materials in Consideration of Thixotropy, Department of Civil Engineering and Engineering Mechanics, Columbia University, 2017.

[51] A. C150, Standard Specification for Portland Cement, ASTM International, West Conshohocken, PA, 2015.
[52] S. Kawashima, M. Chaouche, D.J. Corr, S.P. Shah, Rate of thixotropic rebuilding of cement pastes modified with highly purified attapulgite clays, Cement and Concrete Research, 53 (2013) 112-118.
[53] S. Ma, Y. Qian, S. Kawashima, Experimental and modeling study on the non-linear structural build-up of fresh cement pastes incorporating viscosity modifying admixtures, Cement and Concrete Research, 108 (2018) 1-9.
[54] A. Neaman, A. Singer, Rheological properties of aqueous suspensions of palygorskite, (2000).
[55] N.A. Tregger, M.E. Pakula, S.P. Shah, Influence of clays on the rheology of cement pastes, Cement and concrete research, 40 (2010) 384-391.
[56] S. Kawashima, J.H. Kim, D.J. Corr, S.P. Shah, Study of the mechanisms underlying the fresh-state response of cementitious materials modified with nanoclays, Construction and Building Materials, 36 (2012) 749-757.

List of Tables

Table 1 Cement chemical constituents

Constituents	% by mass
SiO_2	19.22
Al_2O_3	4.98
Fe_2O_3	3.42
CaO	62.42
MgO	3.87
SO_3	2.72

List of Figures