



Rheological properties of cement pastes: A discussion of structure formation and mechanical property development

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ARTICLE INFO

Article history:

Received 22 August 2007

Accepted 26 June 2008

Keywords:

Rheology

Characterization

Reaction

Physical properties

Workability

ABSTRACT

The objective of this paper is to examine the evolution of rheological properties (e.g. yield stress) and to evaluate the use of these properties as a method to monitor structure formation and mechanical property development (i.e. setting) in cementitious materials. The authors utilize the stress growth technique to assess the development of a solid structure in cement pastes. An increase in the yield strength of the system due to cement hydration is identified to occur near the end of the dormant period as identified by chemical shrinkage. The transition from a fluid to a solid state and the development of elastic properties in the material are both noted to occur prior to the time of initial set as identified by the Vicat needle.

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1. Introduction and background

The rheological properties of fresh concrete are related to cement hydration and chemical interactions in the cement paste system [1]. In addition, the rheological properties of concrete are also dependent on the shape and gradation of the aggregates (coarse and fine) contained in the mixture. But the evolution of the rheological properties at early ages depends almost entirely on the cement paste. The properties of fresh concrete evolve, starting from the time the water and the cement are in contact, from a fluid to a solid. The most common test that is performed to determine property development is the Vicat needle test, performed to assess the setting time. The setting time is typically measured according to a standard procedure where the depth of penetration of a weighed needle into a fresh sample is monitored. The time at which the needle penetrates to a specific depth in a cement paste is used as an indication of setting (ASTM C191 [2]). Other techniques which have been used to assess early-age properties include acoustic wave propagation [3,4], electrical conductivity [5,6], hydraulic pressure variation [7–9], and the evolution of rheological properties [10,11].

The research presented in this paper is part of a larger project aimed at the development of experimental techniques to characterize cementitious material behavior at early ages [12]. The main goal of this

project is identification of the interval of occurrence of the fluid–solid transition and evaluation of material property development in cementitious materials at early ages. With this objective, a set of cementitious materials and mineral and chemical admixtures were selected to be used in performance of a wide range of measurements. In this paper, three techniques were evaluated to determine the setting time of cement pastes; rheological properties, chemical shrinkage, and the Vicat needle.

1.1. Rheological properties

The rheological behavior of non-Newtonian fluids such as cement paste, mortar, or concrete is often characterized by two parameters, yield stress, τ_0 , and plastic viscosity, μ , as defined by the Bingham equation (Eq. (1)).

$$\tau = \tau_0 + \mu \dot{\gamma} \quad (1)$$

where: τ is the shear stress (Pa) and $\dot{\gamma}$ is the shear strain rate (s^{-1}).

Amziane et al. [8] showed that the Bingham relationship becomes complex when the cement paste is close to setting, resulting in aberrations such as a negative plastic viscosity calculated using Eq. (1). Consequently, an improved method to monitor the evolution of the yield stress at early ages was determined to be stress growth measurements [10]. These measurements are designed to apply a constant shear rate to the material while measuring the resulting shear stress. A plot of the shear stress versus time shows a linear portion, below the yield stress, followed by a peak and a stable flow region. In the pre-peak region, a linear-elastic response is typically

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displayed by the cement paste. The true yield stress is determined at the end of this linear portion, but due to the low shear resistance of the material at early ages (in the fluid state), and the low measurement resolution in this region, the true yield stress is almost impossible to measure. Therefore, the value of the peak shear stress is frequently identified as the yield stress [10,13], since it is easier to quantify. The duration of a stress growth measurement is short enough that the yield stress obtained could be plotted versus the age of the specimen.

When the yield stress obtained by stress growth is plotted versus the time since water and cement were in contact (Fig. 1), three points, A, B and C, can be determined. Point A identifies the initial yield stress a few minutes after first contact with water; Point B identifies the time interval at which the yield stress dramatically increases and Point C is the last measurement possible within the torque limit of the available rheometer ($\tau_{\max} = 19$ kPa in this case). Section AB identifies the period during which the paste is a viscous fluid exerting little resistance to the shearing action of the rheometer. Section BC of the curve identifies a dramatic increase in the yield stress as a solid structure begins to develop in the system. At this stage, the flow ability of the mixture is restricted and material placement is no longer possible. Consequently, point B is considered to be the time of initial set as identified by rheological property measurements.

This methodology could be applied using any rheometer geometry. However, for measurements of cement paste Ferraris and Gaidis [14] argued that a parallel plate geometry offers the most flexibility. This geometry is the only rotational rheometer configuration that allows for continuous variation of the distance between the two shear planes, which facilitates the measurement of the cement paste in the same shearing conditions that occur in concrete. In concrete, the shearing surfaces for cement paste are the sides of aggregates, either fine or coarse aggregates. The lower the cement paste content in a mortar or concrete, the smaller the distance between the aggregates, and thus the smaller the gap in the rheometer should be when measuring the cement paste alone. The ability to adjust the gap is paramount if rheological measurements of a cement paste or mortar are used to predict or to make a comparison with measurements obtained on mortar or concrete, respectively.

In addition to measurements of the shear stress, rheological property measurements can be used to determine the dynamic viscosity of a material sheared at a known shear rate. Eq. (2) may be used to describe the viscosity of pastes at early ages.

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2)$$

where η describes the viscosity (Pa s) of a material subject to a shear stress at a known shear strain rate, $\dot{\gamma}$ (s^{-1}), and τ is the shear stress applied by the rheometer on the material (Pa).

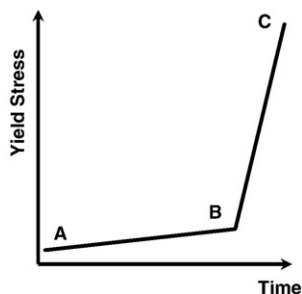


Fig. 1. Yield stress from stress growth measurement versus time since water and cement were in contact. Point A is the initial yield stress, Point B is the time of initial setting, and C is the maximum torque measurable with the rheometer used.

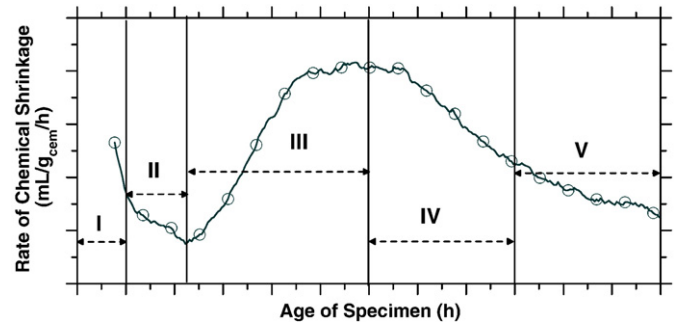


Fig. 2. A representative illustration of the rate of chemical shrinkage as a function of time representing the various stages in cement hydration for a cementitious material.

1.2. Chemical shrinkage

Chemical shrinkage was first observed in the early 1900s by Le Chatelier [15] who noticed an absolute volume reduction due to the hydration reactions in a cement paste. Later Powers [16] used measurements of chemical shrinkage to indicate the progress of hydration reactions in cementitious materials, considering an ultimate value of 6.4 ml of chemical shrinkage per 100 g of cement reacted. Knudsen and Geiker [17,18] used chemical shrinkage to determine the rate of strength development in concrete.

The objective of chemical shrinkage testing is to quantify the total reduction in sample volume due to the hydration reactions occurring in cementitious materials. The reduction in the sample volume can be used to infer the extent of reaction (assuming ultimate chemical shrinkage experienced of 0.064 mL/g of cement completely reacted [16,18]).

The rate of reaction inferred from chemical shrinkage can be plotted to delineate the stages in cement hydration: stage I – the initial wetting peak (partially observed), stage II – the dormant period, stage III – the acceleration period, stage IV – the deceleration period and stage V – the steady state period (Fig. 2) [19]. Chemical shrinkage is quantified by measuring the amount of water absorbed by a saturated cement paste [20]. Two test methods have been reported in the literature, tests that measure the volume change of a liquid in contact with the cement paste and tests that measure the change in mass of an immersed paste specimen using a buoyancy based technique. The density/buoyancy procedure works on the principle of a mass change that occurs when water is absorbed in the hydrating specimen. This paper will utilize a buoyancy measurement procedure as described in detail in Section 4.2 [23].

1.3. Vicat set-time tests

A standard method to estimate the setting time of a cement paste is the Vicat test described in ASTM C191 [2]. A needle weighing 300 g and diameter of $1 \text{ mm} \pm 0.05 \text{ mm}$ is lowered into a specimen of fresh cement paste and the penetration depth is recorded. The cement paste is kept in a standard frustum 40 mm in height. Initial setting time is when the needle penetration is $25 \text{ mm} \pm 0.5 \text{ mm}$ and the final setting time corresponds to less than 0.5 mm penetration. In the standard method, the cement paste is required conform with normal consistency. In this paper, the procedure was modified by using the same Vicat device while the cement paste was prepared according to the composition described in Table 1 without attempting to achieve normal consistency. The reason being, the Vicat test is used here to measure setting time of the cement paste as prepared for other testing methods and not to determine the standard setting time.

2. Research significance

Conventional methods of assessing setting (Vicat needle) in cementitious mixtures are overly simplistic and arbitrary in their

Table 1
Mixture proportions by mass fraction (grams)

	Plain paste	Paste with 5% SRA	Paste with 20% SF	Paste with 20% SF+5% SRA
Water	0.3000	0.2850	0.3000	0.2850
Cement	1.0000	1.0000	1.0000	1.0000
Silica Fume	–	–	0.2000	0.2000
HRWRA-1	0.0050	0.0050	–	–
HRWRA-2	–	–	0.0083	0.0083
SRA	–	0.0150	–	0.0150

interpretation. A need exists to identify methodologies which relate setting to the development of fundamental properties (yield stress, elastic and shear moduli, etc.) in the material. In this paper, the authors use a fundamental approach, applying rheological properties and chemical shrinkage to interpret setting in cementitious mixtures. For the mixtures evaluated, the time of set (and the development of mechanical properties) assessed using rheology corresponds to the end of the dormant period in cement hydration, and occurs significantly prior to setting assessed using the Vicat needle.

3. Materials and mixing procedures

3.1. Cementitious materials and admixtures used in testing

Four different cement paste mixtures were prepared according to the mixture proportions shown in Table 1. The mixture compositions were selected to span a wide variety of cement and admixture (chemical and mineral) combinations allowing a wide variety of mixtures to be characterized [12].

Type I ordinary portland cement was used with a Blaine fineness of 360 m²/kg and a potential Bogue phase composition (mass fraction) of 60% C₃S, 12% C₂S, 12% C₃A, 7% C₄AF and a Na₂O equivalent of 0.72%. An undensified silica fume was added at 20% addition by mass of cement. The phase composition of the silica fume used (mass percent) was 93.0% SiO₂, 0.5% Fe₂O₃, 0.7% Al₂O₃, 0.7% CaO, 0.7% MgO, 0.9% K₂O and a Na₂O equivalent of 0.4%. The silica fume used had a density of 2200 kg/m³. To enhance the workability of the paste mixtures, two high range water reducing admixtures were added, labeled HRWRA-1 and HRWRA-2. A shrinkage reducing admixture (SRA) was added at a 5% concentration of the initial water-SRA solution by replacement (by mass) of the initial mixing water.

3.2. Cement paste mixing procedures

The mixtures used for the rheological measurements and for the chemical shrinkage were prepared in two different laboratories at different times, but using the same materials. The Vicat needle measurements were used to ensure that no significant changes in the setting time had occurred between the two different locations and mixing procedures.

The cement paste prepared for rheological measurements was mixed using the methodology [21] developed by the Portland Cement Association (PCA). This methodology utilizes a blender mixer with a capacity of 1 L connected to a speed controller and a temperature controlled water bath. The speed controller allows the speed of the blades in the mixer to be held at a preset speed regardless of the load. The controlled temperature bath was set to 15 °C ± 1 °C in this study. This allows the paste temperature to be at ~20 °C to 23 °C at the end of the mixing cycle. Without the temperature controller, the temperature of the cement paste would be much higher due to friction from mixing and this would affect the hydration of the paste as well as its rheological behavior. The cooled base of the mixer plays the role normally filled by the aggregates in concrete, which is that of a heat sink. The mixing regime adopted for the cement paste was as follows. After adding water to the mixer, the mixer blades rotated at a speed of

about 419 rad/s (4000 rpm) while the cement was introduced in a period of 30 s. The speed of the blades was increased to 1047 rad/s (10,000 rpm) and kept constant for another 30 s. The mixer was stopped and the walls of the mixer scraped. After 2.5 min, the mixer was turned on at a speed of 1047 rad/s (10000 rpm) for 30 s. The paste temperature at the end of this cycle was in the range of 20 °C to 23 °C.

The cement paste that was prepared for measurement of chemical shrinkage was mixed using de-aired, de-ionized water. The water was de-aired by boiling and then cooled to room temperature (20 °C to 23 °C) before mixing. The dry constituent materials were placed in a special mixing chamber [22,23]. The chamber was sealed, air was evacuated from the chamber using a vacuum pump, and the solution of water and the chemical admixtures was introduced into the chamber under the same evacuated condition. The chamber was then placed in a commercial paint shaker and shaken for 5 min to uniformly mix the constituents and obtain a consistent cement paste mixture. After mixing, the chamber was opened and the de-aired cement paste slurry was placed in the molds using external vibration [23].

4. Experimental procedures

4.1. Rheological property measurement

A parallel plate rheometer was used in experimental testing (Fig. 3). The rheometer was equipped with serrated test plates (35 mm diameter) to measure the rheological properties of the cement paste [24]. The gap between the plates was fixed at 1 mm. Previous experience [24] showed that this gap is adequate for characterizing the cement paste behavior if direct comparison with a specific concrete mixture is not a goal. To limit the evaporation of water from the sample, the specimen was enclosed in a chamber surrounded by a wet sponge (Fig. 3c). The mixing operation lasted 5 min and another minute was needed to transfer the material from the mixer to the rheometer and begin measurements. Consequently, the first test was started approximately 6 min after the first contact of water with cement. Between rheological measurements, the mixture was stored in a hermetically sealed vacuum flask.

The test protocol includes the following steps and was similar to a procedure described earlier [10]. Except the first test, which was conducted immediately after mixing, for each subsequent test the cement paste was homogenized in a sealed vacuum bottle using a blender plunged into the bottle. The remixing was performed to ensure that a representative sample was used for the rheology test. Fresh cement paste (~2 mL) was placed on the lower plate of the rheometer using a disposable syringe. The two plates were then set to a gap of 1 mm. The test was carried out at a controlled temperature (23 °C ± 0.2 °C), which is the average cement paste temperature during the setting period. The fresh cement paste was then subjected to the stress growth test. The stress growth test is characterized by the material being sheared at the lowest shear rate (0.18 s⁻¹) possible with the available rheometer. The shear stress is then recorded as a function of time. The results obtained display an uncertainty of approximately 10% [10].

4.2. Chemical shrinkage measurements

Measurement of chemical shrinkage on cement pastes was performed by monitoring the change in buoyancy that occurs for samples suspended in paraffin oil [23]. The theory of this technique can be briefly explained as follows: initially, while the cement paste is a fluid, the only type of volume change experienced by the material is external volume change. However, as a solid structure forms, vapor spaces can evolve in the material, leading to a decrease in the internal solid-volume of the system. This results in an under-pressure which promotes absorption (suction) of surface water, to fill the vapor spaces that have formed in the material. This results in a change in material

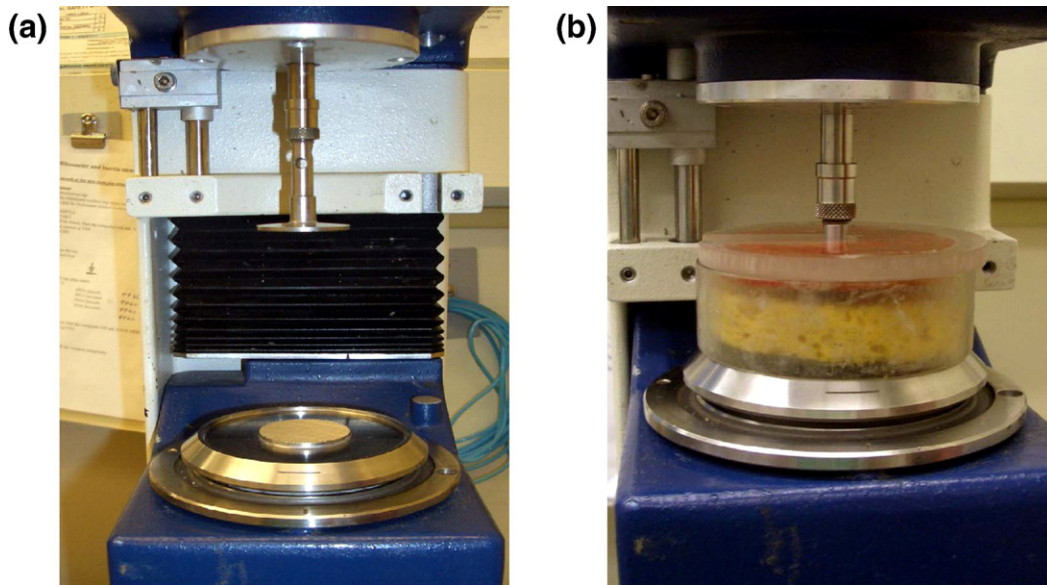


Fig. 3. (a) The serrated parallel plate rheometer used in the stress growth test, (b) The environmental chamber used to contain the sample for the duration of the test.

density (buoyancy), and consequently the submerged mass of the specimen, as it hydrates. The change in density (mass) can be related to the volume of water absorbed, and hence the extent of volume reduction experienced by the sample.

Each chemical shrinkage test consists of de-aired freshly mixed cement paste that was placed in a cylindrical glass crystallization dish (70 mm in diameter and 50 mm tall). A 25 g sample is the typical sample size used in this measurement. After the cement paste was placed in the glass crystallization dish (Fig. 4a) the specimens were vibrated until a uniform amount of paste was spread over the bottom of the dish. After vibration was complete, a layer of de-aired and de-ionized water was applied to the surface of the paste with an eyedropper until a continuous film of fluid was formed. For normal tests, 10 g of surface water were used. After the addition of water to the surface of the paste, paraffin oil was applied drop by drop, until it covered the entire surface of the water in the beaker. More paraffin oil was added until the crystallization dish was nearly completely filled. The crystallization dish was positioned on a stainless steel mesh

platform that was then suspended with a monofilament line from a balance plate (Fig. 4b). To ensure thermal regulation, the container of paraffin oil was submerged in a water bath maintained at $23\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$.

The submerged mass of the sample was recorded automatically every 5 min from the time the specimen was placed in the bath (30 min after the addition of water to the dry cement during mixing). Eq. (3) describes how the chemical shrinkage was calculated:

$$V_{CS} = \frac{\Delta V_{\text{paste}}(t)}{g_{\text{cem}}} = \frac{W_{\text{sub}}(t) - W_{\text{sub}}(30)}{\rho_{\text{par}} \cdot g_{\text{cem}}} \quad (3)$$

where ΔV_{paste} (mL) is the volume change of the paste, g_{cem} (g) is cement content by mass of the cement paste, $W_{\text{sub}}(t)$ (g) is the submerged weight of the paste at time t , $W_{\text{sub}}(30)$ (g) is the initial submerged mass of the paste 30 min after water addition, and ρ_{par} (g/mL) is the density of the paraffin oil in the buoyancy bath (i.e., measured to be 850 kg/m^3 at $23\text{ }^{\circ}\text{C}$). Chemical shrinkage measurements will be generally presented

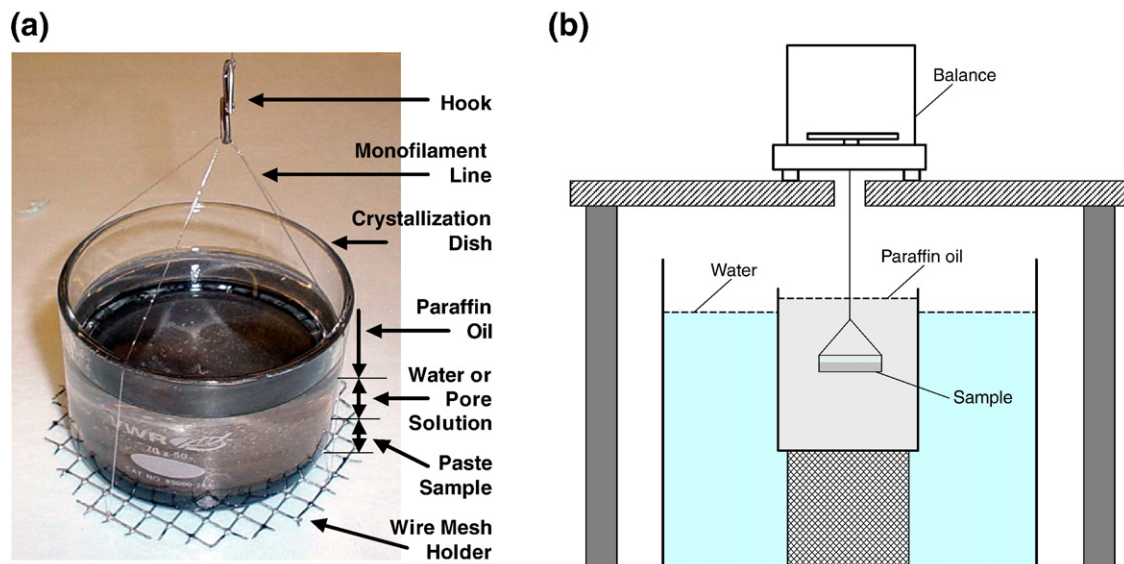


Fig. 4. An illustration of the setup used to measure chemical shrinkage (a) a photo of the chemical shrinkage test specimen (b) an illustration of the buoyancy method.

Table 2

Initial set times determined using the Vicat test

Mixture ID	Initial set (h) – NIST	Initial set (h) – Purdue University
W/C=0.30	6.2	6.0
W/C=0.30+5% SRA	7.5	7.5
W/C=0.30+20% SF	5.2	5.5
W/C=0.30+20%SF+5% SRA	6.5	6.8

The uncertainty in setting times is estimated to be ± 0.5 h (30 min).

in this paper as volume change per mass of cement in the mixture (mL/g_{cem}) or V_{cs} (Eq. (3)). In addition, the rate of chemical shrinkage will be presented as volume change per mass of cement per time unit ($\text{mL}/(g \text{ h})$) and used to describe the progress of the hydration reaction. The uncertainty is estimated to be 5%, based on tests conducted between 1 h and 24 h.

4.3. Vicat set-time tests

Initial and final set times for all the cement paste mixtures were measured using a Vicat apparatus as described in ASTM C191. Cement pastes were prepared using the PCA procedure [21] at NIST and the vacuum mixing procedure at Purdue University. Similar initial and final set times were obtained for the paste mixtures mixed using both mixing procedures. The initial setting results are detailed in Table 2 below. The variation in the time of initial set between the two locations and mixing procedures was less than 5% or 20 min and so not

considered to be significant. These results ensured that the cement paste could be considered identical whether prepared at NIST or at Purdue University, allowing comparison of the rheological measurements and the chemical shrinkage.

5. Experimental results

5.1. Rheological property measurements

Initially, rheological measurements were performed approximately every 30 min, and every 15 min as the paste started to set in order to capture point B (Fig. 1) with reasonable accuracy. Time t_0 is defined as the time at which water and cement were first in contact.

The time-dependent shear response is shown in Fig. 5. At early ages, the post-peak shear stress reduces to an equilibrium value shortly after the test begins. This response is significantly different from the response noted as the cement mixtures begin to set (at later ages). At later ages, the yield stress increases considerably and the measured shear stress shows a saw-tooth response. The saw-tooth response indicates spontaneous loss and recovery of interparticle forces in the material, under application of an applied shear stress. The shear thinning response is consistent with microstructural breakdown in the material under applied shear. This is similar to the behavior observed by Amziane et al. [8].

Rheological measurements were programmed to be performed under a constant strain rate set at 0.1 s^{-1} , but the device was not always able to maintain that low of a shear rate. Nevertheless, the true

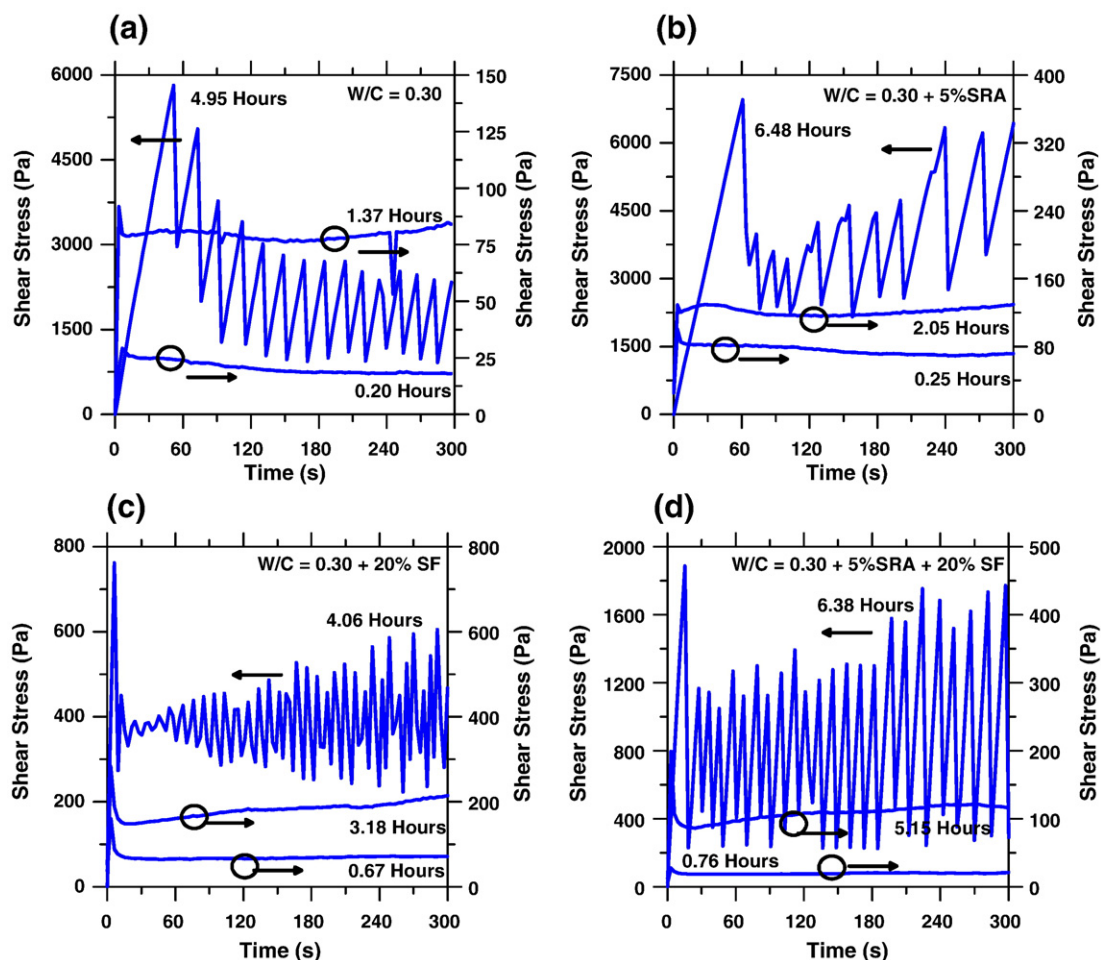


Fig. 5. The evolution of the shear stress as a function of time (a) W/C=0.30, (b) W/C=0.30+5%SRA, (c) W/C=0.30+20% SF, and (d) W/C=0.30+5%SRA+20% SF. The curves on each plot are identified by the time after t_0 , the time when the cement first came into contact with the water. The uncertainty in measurements is $\sim 5\%$.

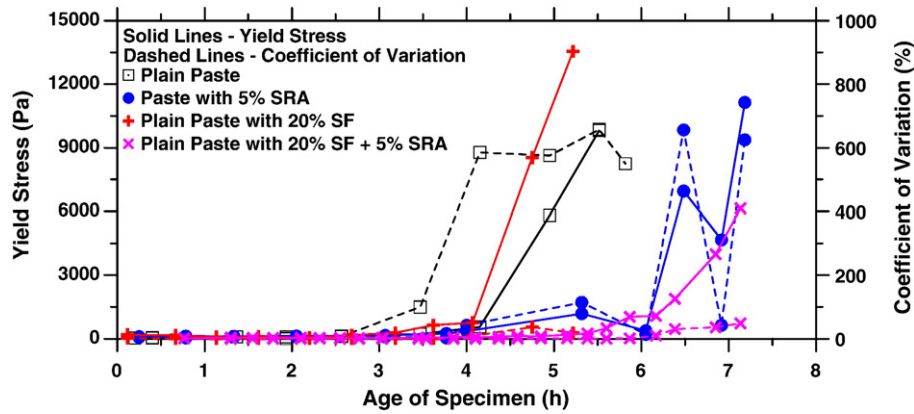


Fig. 6. The yield stress and coefficient of variation of the shear strain rate as a function of time for the cementitious mixtures used in this project.

shear rate experienced by the materials was recorded. The average shear rate as well as the inter-measurement standard deviation of the shear rate was determined. From these the coefficient of variation (COV), defined as the ratio between the standard deviation and the average, was calculated. Fig. 6 shows the results obtained as a function of specimen age. The yield stress is shown to highlight the similarity in the evolution of the two properties (yield stress and COV). It is noticed until initial set (as identified by rheological property measurement or point B in the yield stress versus time curve) the COV is less than 10%

but it increases dramatically after initial set. This variability can be attributed to two factors: 1) slippage of the plate on a cement paste that is too stiff to be sheared; 2) the breakdown and rebuilding of the cement paste microstructure during the shearing regime. The second factor is also observed in the saw-tooth stress measured as shown in Fig. 5. This variability in the shear strain rate impacted measures of the shear and yield stress and the dynamic viscosity, measured for the cement paste mixtures after the time of initial set as identified by rheological properties or point B in the yield stress versus time curve.

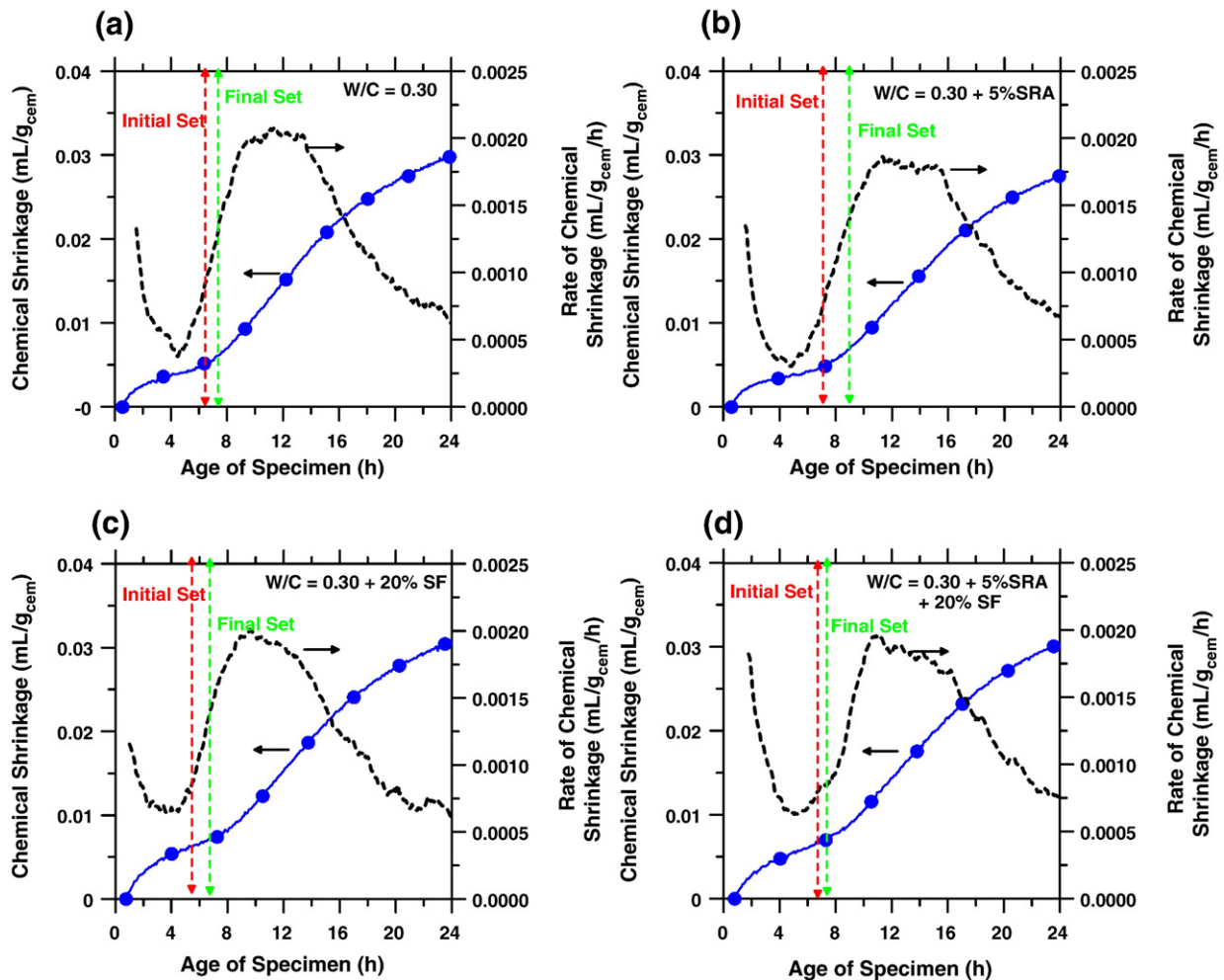


Fig. 7. Chemical shrinkage, rate of chemical shrinkage measurements and the Vicat initial and final setting time as a function of age of the specimen (a) $W/C=0.30$, (b) $W/C=0.30+5\%SRA$, (c) $W/C=0.30+20\%SF$, and (d) $W/C=0.30+5\%SRA+20\%SF$. The uncertainty in measurements is about 5%.

5.2. Chemical shrinkage measurements

The measured chemical shrinkage, rate of chemical shrinkage and the Vicat initial and final setting time are shown in Fig. 7 as a function of specimen age. Chemical shrinkage measures may be used to identify the extent of hydration and the rate of reaction of cementitious materials [25,26]. The rate of chemical shrinkage denoted on each figure may be used to identify the evolution of cement hydration in these mixtures. Consequently, each rate curve may be used to delineate the various stages in cement hydration as demonstrated in Section 1.2. Using such an interpretation, it is noted that the end of stage II in cement hydration correlates to the point of time that the chemical shrinkage experienced by each mixture begins to increase. This would correspond to the initiation of the acceleration period and an increasing extent and rate of chemical shrinkage evolution in the system.

6. Discussion of experimental results

6.1. Determination of the setting process in cementitious systems

Fig. 8 shows the evolution of the yield stress, the rate of chemical shrinkage and set as identified by the Vicat test as a function of time. Considering that the scope of the paper was to evaluate the ability of chemical shrinkage, rheological and Vicat techniques to characterize setting, certain observations can be made.

While this project does not aim to specifically compare rheological and Vicat techniques, for the materials tested it was noted initial set as identified by rheological measurements (Point B) occurs at approximately 70% of the time of initial set for the plain mixtures and at approximately 80% of the time of initial set for the silica fume mixtures as identified by the Vicat test. The setting time identified by rheological measurements (Point B) also corresponds to a sharp increase in chemical shrinkage or the end of the dormant period in cement hydration (stage II), as shown in Fig. 8. This can be explained as follows; the development of an increasing rim of hydration products around the cement particles, combined with a reduction in the overall system volume (chemical shrinkage); would result in decreasing interparticle distances, increasing solid–solid attractive forces and consequently the yield stress of the material [27,30].

The difference between the time of set determined by the Vicat test and the rheological measurements (point B) may be approximately explained by a simplified analysis of the Vicat test. The Vicat test is based on the extent (depth) a weighed needle penetrates into a hydrating cement paste. The Vicat needle applies an axial force of 2.94 N through a 300 g needle, having a 1 mm² cross-sectional area. Two other forces are exerted by the paste on the needle, and need to be accounted for to satisfy force equilibrium; a skin resistance exerted on the 'penetrated' surface of the needle which is dictated by the shear resistance (shear strength – τ_0) of the material and a compressive resistance (compressive strength – σ) exerted on the tip of needle (1 mm²). The shear stress on the surface of the needle nearly equals

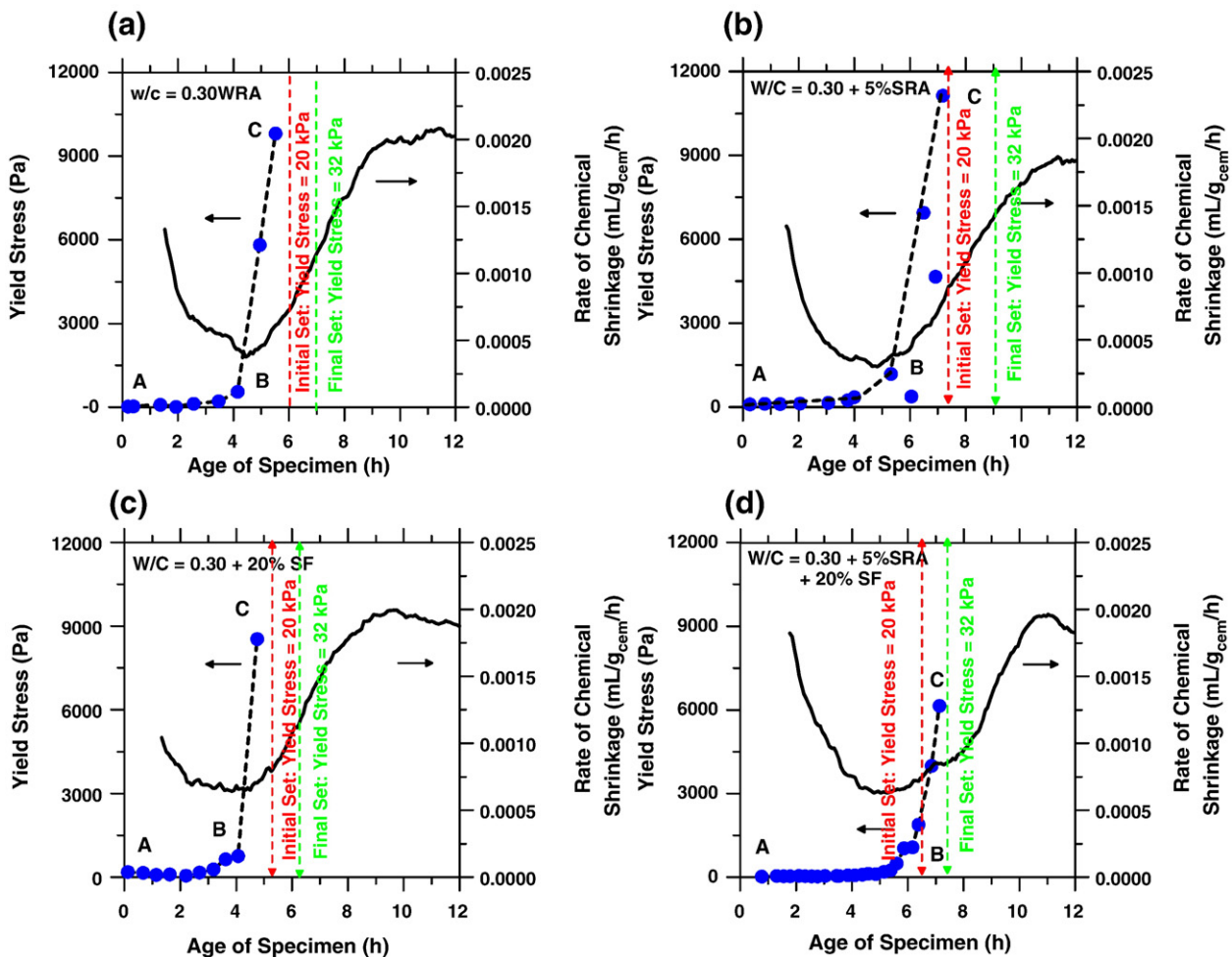


Fig. 8. The yield stress as a function of time (a) W/C=0.30 (b) W/C=0.30+5% SRA (c) W/C=0.30+20% SF (d) W/C=0.30+5% SRA+20% SF. The experimental uncertainty is about 5% for the chemical shrinkage and 10% for the yield stress.

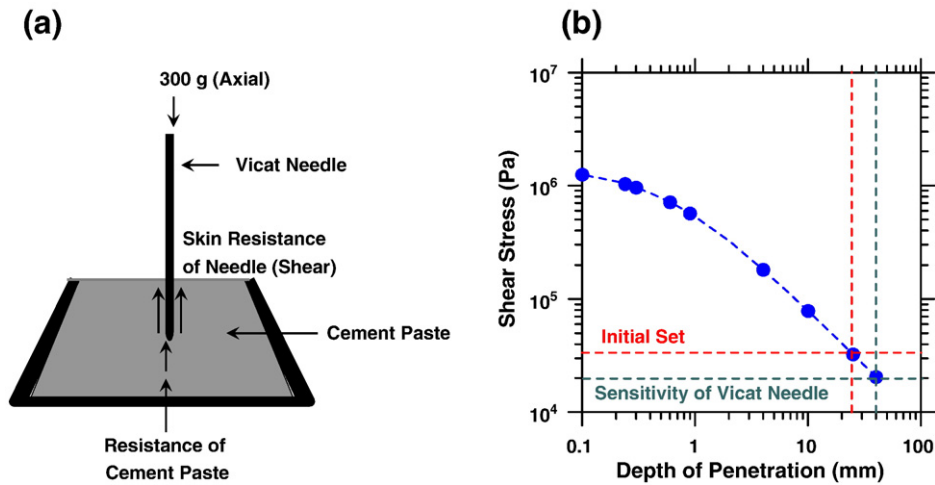


Fig. 9. (a) A schematic illustration of the Vicat Test (b) Shear stress as a function of penetration depth for the Vicat test (Initial set, $h=25$ mm. Final set, $h=0.5$ mm).

the shear strength of the material. The compressive resistance can be approximated by assuming a plastic failure criterion in which case the compressive strength is equal to twice the shear strength ($\sigma=2\tau_0$). A force equilibrium analysis of this nature can be illustrated as shown in Eq. (4).

$$\tau_0 = \left(\frac{2.94}{(2 \cdot \pi \cdot r \cdot h) + (2 \cdot \pi \cdot r^2)} \right) \quad (4)$$

where: 2.94 (MPa) is the axial force exerted by the needle, and r and h (mm) are the radius and depth of penetration of the needle respectively.

Fig. 9b shows the shear resistance offered by the material as a function of varying penetration depths, according to Eq. (4). This information may be related to the ‘yield capacity’ of the material. An increasing extent of solid formation results in increasing shear resistance until finally the needle is no longer able to penetrate the material. Fig. 9b estimates the shear stress exerted by the Vicat needle at the maximum penetration depth (40 mm), and the penetration depth corresponding to initial set (25 mm). The shear stresses exerted at these depths of penetration are 20 kPa and 32 kPa respectively. The Vicat needle is unable to detect material property development until the shear resistance of the material is at least 20 kPa which is slightly higher than the maximum shearing capacity of the rheometer, which is 19 kPa. Therefore, the stress growth method is able to detect changes in the material response well before the Vicat needle. This

response was also observed by Amziane et al. [8]. Consequently, setting identified by rheology occurs earlier than the Vicat test because the rheometer used, was unable to measure stresses higher than 19 kPa.

Another representation of the results is shown in Fig. 10 which examines the shear stress evolution as a function of time for rheological and Vicat techniques. This is additionally compared to the rate of chemical shrinkage, indicative of the rate and extent of reaction experienced by the material. The Vicat stress is calculated using Eq. (4) (Fig. 9b). Fig. 10 shows the results for one mixture (plain cement paste) as an example. The initial setting time for this mixture is 4.2 h as per the yield stress measurement. The Vicat stress response is measurable at the end of the rheological measurements and is a continuation of the data obtained from rheological tests. As seen in Fig. 10, the time of initial set as identified by rheology corresponds to the end of the dormant period in cement hydration, as identified by the rate of chemical shrinkage. However, Vicat measurements identify initial set approximately 1.8 h later, for reasons previously explained. The Vicat test results are consistent with rheological measurements, but fail to capture the early stress response of the material (Fig. 10).

6.2. The development of mechanical properties – the shear modulus

Cement paste at early ages is a suspension that can be modeled to demonstrate a viscoelastic response. The viscoelastic response can be explained by interparticle forces among the suspended solids [19]. The

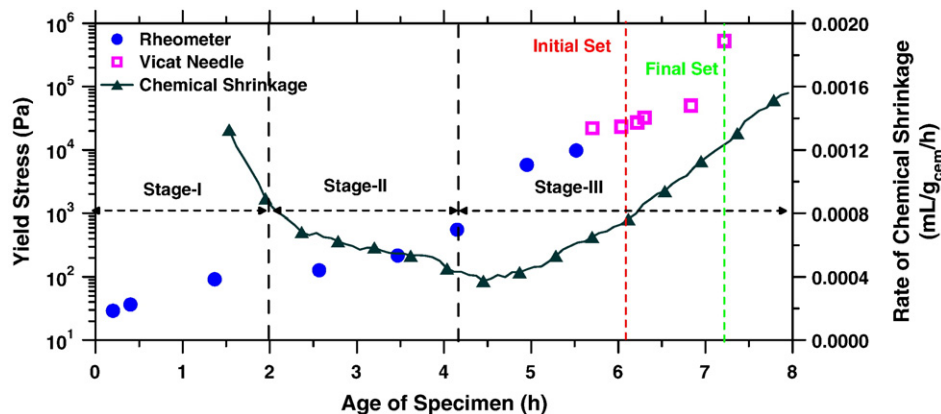


Fig. 10. The combined rheological and Vicat setting response for the plain cement paste mixture ($W/C=0.30$). The uncertainty is about 5% for the chemical shrinkage and 10% for the yield stress.

shear modulus that would characterize the mixture behavior before initial setting can be determined using rheology measurements of the shear stress and shear strain as defined by Eqs. (5) and (6)):

$$\gamma = \int_0^t \dot{\gamma} \cdot dt \quad (5)$$

where γ is the shear strain ($\mu\text{m/m}$), $\dot{\gamma}$ is the shear strain rate (s^{-1}), and t is the time interval over which the shear strain is applied (s).

Eq. (6) can be used to determine a shear modulus (G) (Pa) for the cementitious mixtures, within the linear-elastic shear regime for each measurement interval, where γ is the shear strain ($\mu\text{m/m}$) and τ is the shear stress applied on the material (Pa):

$$G = \frac{\tau}{\gamma} \quad (6)$$

During the hydration process the shear modulus should increase as the yield stress increases, denoting the development of hydration products, that build a rigid skeleton in the material [19]. Fig. 11 shows the development of the shear modulus, which develops before the mixture attains initial set (Vicat). The increase in the development of the shear modulus is seen to correspond to the time of initial set as identified by rheological measurements, and the end of the dormant period (stage II) in hydration.

Fig. 11 would suggest that the development of the shear modulus is better related to small scale microstructural changes identified by rheology that correspond with hydration states (as identified by

chemical shrinkage) rather than the Vicat response. Consequently, though an increase in the shear stress is identified (Point B), it may not correspond to the material having attained a degree of stress resistance (as defined by the Vicat needle). The increase in the shear resistance (modulus) identified here would correlate to an increasing rate and extent of hydration in the system [28] as the dormant period concludes and the acceleration period initiates, as shown in Fig. 11.

6.3. Early age property assessment – implications on setting time

From Section 6.1, it has been ascertained rheological measurements identify a sharp increase in the shear stress of the material with increasing age (and hydration). The Vicat test defines initial set at the duration when the needle penetrates 25 mm into the sample. This depth of penetration is somewhat arbitrary and does not correspond to a specific characteristic of structure evolution or the extent of reaction experienced. However, in contrast chemical shrinkage and rheological measurements monitor the material response a few minutes after contact with water, and relate to the fundamental behavior (yield stress or extent of reaction as determined by volume change) of the material. While chemical shrinkage measures do not specifically identify the setting process, this technique tracks the progress of the hydration reaction in the material. At this point it is important to note, while chemical shrinkage is indicative of reaction kinetics, the use of measures such as chemical shrinkage and isothermal calorimetry is inappropriate in determining set since if sufficient water is available (as during the first several hours of

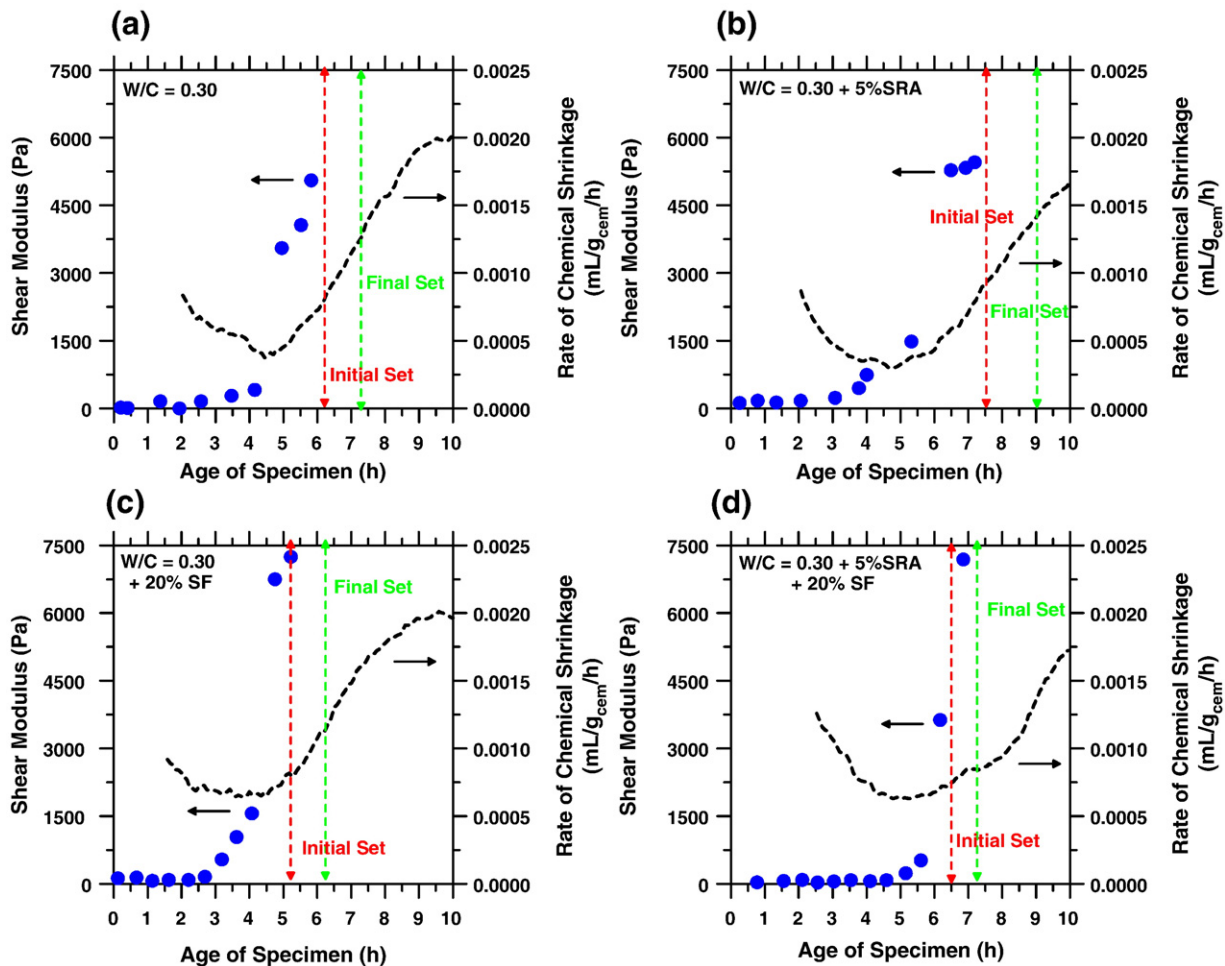


Fig. 11. The shear modulus and Vicat time of set as a function of time (a) W/C=0.30 (b) W/C=0.30+5%SRA (c) W/C=0.30+20% SF (d) W/C=0.30+5%SRA+20% SF. The uncertainty is about 5% for the chemical shrinkage.

hydration), the chemical shrinkage (or isothermal calorimetry) response is similar, independent of W/C (water content) [29,31]. However, for similar mixtures (as considered in this paper) it is possible to correlate set as identified by rheology to a particular extent of reaction (in this case the end of the dormant period (stage II) in cement hydration), provided the W/C is kept constant. The increase in the yield stress identified by rheology corresponds to the development of a solid network in the material. The development of this network is dependent on particle size, W/C ratio, solid–solid spacing and corresponds to a specific volume fraction of percolated solids in the system [30]. This percolated network is capable of resisting an applied stress. The development of a solid network causes the dramatic increase in yield stress identified by rheology and corresponds to an acceleration in hydration identified by chemical shrinkage. It is important to indicate that while this response is consistent for a single water–cement ratio, the effect of initial water content on solid percolation and extent of reaction at the time of percolation (solid) is considerable. This can be illustrated as follows: if we consider mixtures having varying initial water contents (W/C=0.3, 0.4, and 0.5) the initial porosity of these mixtures varies from 48% to 62%. Consequently, initial solid–solid distances in these mixtures are significantly different. Under these conditions, the extent of hydration product development (and reaction) needed to percolate the solid phase is greater in the case of a higher W/C (dispersed) system as compared to a low W/C system (smaller interparticle bridging distances). Consequently, it is inappropriate to relate setting to a technique such as chemical shrinkage (and similar techniques such as isothermal calorimetry) which identifies the extent of reaction experienced, as this parameter is dependent upon the initial porosity (W/C) and to the development of a percolated structure in the system.

These considerations highlight the importance in differentiating physical and chemical material behavior during the development of a solid structure from engineering properties of the material (flowability, finish-ability, etc). While the Vicat test assesses shear resistance, rheological measurements identify small microstructural changes, dictated by reaction kinetics. Consequently, rheological measures directly relate yield stress evolution to the progress of the hydration reaction in the material. For the Vicat needle setting time to match the rheological yield stress, the needle mass, diameter or depth of penetration need to be redefined. In summary, setting time needs to be better defined and probably should be linked to the application of interest, i.e., the end of the placement period (material cannot flow or be placed) or when the compressive or penetration strength is higher than a predetermined value (sustain the weight of a person to walk on the concrete). Either definition would be acceptable, but it cannot be expected that the setting time value would be similar for techniques that track a physical response (Vicat) and a change in reaction kinetics (rheology or chemical shrinkage). Therefore, setting time should be redefined to reliably relate to both the application of interest and fundamental material parameters, such as the yield stress of the system.

7. Summary and conclusions

This project has used two methods to monitor the setting process in cementitious materials, specifically rheological property development (assessing yield stress evolution), and the Vicat penetration test. In addition, measures of chemical shrinkage have been used to relate setting to the extent of reaction experienced by the material. From experimental results for the mixtures evaluated at constant W/C, it has been inferred that setting time as assessed by rheological measurements corresponds to the end of the dormant period in hydration as identified by chemical shrinkage. In addition, the evolution of the shear modulus in the material has been related to small scale microstructural changes, dictated by the progress of the hydration reaction.

Further, this paper has highlighted the need to differentiate between chemical and physical material behavior as a basis of identifying setting in cementitious systems. This is significant as while W/C has little influence on cement hydration at early ages it exerts a significant influence on the physical properties. While rheological techniques identify structural changes dictated by the hydration reaction, the Vicat needle tracks the development of the shear resistance of the material until a given point (25 mm of penetration), and then defines the material as having achieved 'initial set'. To obtain a correlation between early age property assessment techniques it would be necessary to correlate structure development to the evolution of fundamental material properties in the system. It is then essential to define setting in terms of the application of interest and the concrete composition, such as ability to flow or from a more fundamental point in terms of having the true material response of a fluid, or a rigid solid.

Acknowledgements

The authors gratefully acknowledge the support received from the Center for Advanced Cement Based Materials (ACBM). This work was conducted in the Material Characterization and Sensing Laboratory at Purdue University and the Building and Fire Research Laboratory (BFRL) at the National Institute of Standards and Technology (NIST). The authors gratefully acknowledge the support from these laboratories that has made this research possible. In addition, the authors would also like to acknowledge the assistance of John Winpiger (NIST) in experimental testing and Edward Garboczi and Nicos Martys for their valuable review of this paper.

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