EFFECT OF MIXING METHOD ON MICROSTRUCTURE AND RHEOLOGY OF CEMENT PASTE

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ABSTRACT

Mixing is one of the most important processes for producing concrete. The influence of different mixing methods on the rheological properties and fresh state microstructure of cement pastes were evaluated. In this work, the mixing process of cement paste was based on two different sample preparation methods: ASTM C305 and ASTM C1738. ASTM C1738 uses a high shear mixer, whereas ASTM C305 uses a planetary mixer to homogenize cement paste. A considerable increase in the rheological properties was seen in pastes prepared using the ASTM C1738 protocol versus those prepared according to ASTM C305, especially when a superplasticizer was incorporated. Not only were the rheological properties affected, but differences in hydration kinetics and fresh state microstructure was also observed, with mixtures prepared with ASTM C1738 generally displaying more flocculated microstructural features and accelerated hydration kinetics than mixtures prepared with ASTM C305.

Keywords: mixing; microstructure; high shear mixer; rheology; flocculation,

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28 **1 INTRODUCTION**

29 The mixing process is one of the most significant factors governing the properties of concrete [1].
30 Mixing not only homogenizes the composition of concrete; it also plays a significant role on the
31 rheological properties of fresh concrete [2]. Numerous studies have been published regarding the
32 influence of mixing intensity on the rheological properties of cement-based mixes [2–5];
33 generally as the mixing intensity increases, the viscosity and yield stress of concrete decreases.
34 In addition, the shear forces generated during mixing also influence the agglomeration strength
35 amongst cement particles [6] and the morphology of the hydration products on the surface of
36 cement particles [7]. Mixing intensity is affected by many factors, including, but not limited to
37 the type of mixer, mixing speed, and mixing time. In the lab, concrete is often mixed for
38 approximately 8 minutes [8], however the mixing time of concrete in the field differs drastically.
39 For example, in a central-mixed batch plant, concrete may be mixed in a stationary mixer for as
40 little as 60 seconds prior to being discharged into a concrete truck agitator [9,10]. Thus, the
41 concrete undergoes additional mixing after it is mixed in the plant due to the mixing that occurs
42 in the concrete truck as it is being transported from the plant to the site. The length of mixing and
43 degree of agitation that the concrete is subjected to during the delivery process can vary, while
44 90 minutes is a common limit for the maximum mixing time; allowable mixing times can range
45 from 30 to 120 minutes and can be dependent on temperature [11]. The length of the mixing is
46 an important factor to consider as this can influence microstructure and rheological properties of
47 cement paste in concrete [12–14]. Prasittisopin and Trejo [11] observed an increased 28-day
48 porosity and saw changes in the hardened state microstructure of mortars that were subjected to
49 increased mixing time and increased mixer revolutions. Furthermore, with the increasing

incorporation of various admixtures into concrete, additional mixing time is often needed to aid with admixture dispersion. For example, self-consolidating concrete may require an additional 30 to 90 seconds more of mixing versus conventional concrete [15].

All concrete, whether it is for the field or the lab, must be mixed; yet the mixing process is probably one of the least areas studied with respect to the life cycle of concrete. Ideally the sample preparation technique used in the experimental test should simulate the processing conditions that would occur in the field. ASTM C305 [16] is a popular standard used to prepare cement paste samples in the lab. This preparation technique uses a planetary mixer to prepare the samples, but studies have shown that the shear rates generated in this mixer are not representative of the shear rates that the cement paste matrix experiences during the mixing of concrete [2,17,18]. Cement paste in concrete is subjected to higher shear rates than that imparted by the ASTM C305 procedure because of the ball-milling action of the aggregates in concrete [19]. Williams et al. evaluated the effects of hand mixing, mixing with a Hobart planetary mixer, and mixing with a Ross high shear mixer on the rheology of cement paste, and determined that the shear rate experienced by cement paste in concrete mixture is most similar to the shear rate experienced by cement paste mixed with the Ross high shear mixer [3]. Recently, another standard, ASTM C1738 [20], has been introduced for preparation of cement pastes. Different from ASTM C305, this standard uses a high shear mixer for preparation of cement pastes. Although ASTM C1738 was introduced as a method to prepare pastes for rheological evaluation, since it is a sample preparation technique, in theory it can be used for preparing samples for other evaluations (e.g. setting time, calorimetry, etc.) in which simulating the conditions of the paste in concrete is important [2,18,20].

Limited studies have been conducted to examine how mixing variables affect early-age characteristics of cement-based mixtures as summarized in Table 1. The objective of the research presented in this manuscript was to compare how ASTM C305 and ASTM C1738 procedures influence the microstructure, hydration and rheological properties of cement paste. In addition, the influence of additional mixing time on the rheological properties was also taken into consideration. The evaluation of the rheological properties and the microstructure of cement pastes were conducted using a rheometer and a focused beam reflectance measurement (FBRM) probe, respectively. The FBRM probe uses backscatter light principles to measure the chord length of particles in a suspension [6,21,22]. The FBRM technique enables the user to conduct the test without diluting the cement paste suspension [6] and provides a way to indirectly observe the dynamic microstructure of cement paste during mixing.

2 EXPERIMENTAL PLAN

2.1 Materials and mix proportions

A commercially available Type I/II cement, conforming to ASTM C150 [23], was used in all of the mixtures, and according to the manufacturer of the cement, the cement had a Blaine fineness of $401 \text{ m}^2/\text{kg}$, an initial setting time of 100 minutes, and a specific gravity of 3.15. The oxide composition of the cement is given in Table 2. A commercially available Type F polycarboxylate superplasticizer (SP), conforming to ASTM C494 [24], was used in most of the mixtures. The solid concentration of the admixture was reported by the manufacturer to range between 29 -36%. All of the mixtures were prepared using deionized water.

The mixture proportions were based off of a neat paste that was proportioned to have a solid volume content (vol. % solid) of 0.45, which corresponds to a water-to-cement ratio (w/c)

of 0.39. This paste was considered the “control” mixture. Three additional mixtures with different vol. % solid and containing SP were also prepared (see Table 3). For the mixtures incorporating SP, the SP dosage was set to 0.20% by mass of cement, and the water content of these mixtures were corrected to take into account the water added due to using the SP.

2.2 Sample Preparation

Samples were prepared according to two methods: ASTM C305 and ASTM C1738. An additional 2 minutes were added onto each of the protocols (herein called ASTM C305_2m, and ASTM C1738_2m) to evaluate the influence of extending the mixing time on the samples. The mixing sequences for ASTM C305 and ASTM C1738, and the modified sequences of ASTM C1738_2m and ASTM C305_2m are provided in Figures 1 and 2, respectively.

For the ASTM C1738 protocol, the mixtures were prepared using a Chandler 3060 high shear mixer (see Figure 3(a)). The mixing speeds were controlled by a control unit; therefore during the mixing process the mixing speeds were maintained at the pre-set speeds. The Chandler high shear mixer was equipped with a water bath. This water bath circulated water around the mixing container and allowed for the temperature of the cement paste to be controlled during mixing. The unit was set to maintain a temperature of $23 \pm 2.0^{\circ}\text{C}$. However, even with the water bath system, a 10.0°C temperature increase in the paste may occur from mixing with the high shear mixer[25], therefore additional treatments were taken to counteract the temperature increases due to the high shear mixing. Specifically, the temperature of the water in the bath unit was set to circulate at a temperature of $15 \pm 1.0^{\circ}\text{C}$ and the mixing water was also chilled to $15 \pm 2.0^{\circ}\text{C}$ prior to mixing. With these treatments, the temperature of the cement pastes after mixing was approximately $24 \pm 2.0^{\circ}\text{C}$ (see Table 4).

For the ASTM C305 protocol, a Hobart planetary mixer with a standard designated paddle was used to prepare the samples (see Figure 3(b)). The planetary mixer had three fixed speeds: speed 1, speed 2 and speed 3. According to the manufacturer's specification [26], speed levels 1, 2 and 3 corresponds to a maximum agitator speed of 136, 281, and 580 rpm, respectively. Unlike the high shear mixer, the mixing speed for the planetary mixer was not controlled by a control unit; thus the agitator speed during mixing may be lower than the maximum agitator speed. The planetary mixer was not equipped with a temperature control set-up. When mixing water with an initial temperature of $23 \pm 1.0^{\circ}\text{C}$ was used, on average only a $1 \pm 0.5^{\circ}\text{C}$ increase was seen in the temperature of the paste after mixing (data not shown). Table 4 displays the initial and final temperature of the pastes prepared using the Hobart planetary mixer (see samples prepared using the ASTM C305 and ASTM C305_2m mixing methods in Table 4); the final temperatures of mixtures prepared using the Hobart mixer were within $24 \pm 1.0^{\circ}\text{C}$.

2.3 Experimental Methods

Flow Rheology: Flow curve tests were conducted with a commercially available rotational rheometer, Anton Paar MCR 301. For the flow curve tests, the rheometer was configured with a concentric cylinder geometer (see Figure 4(a)). The gap between the inner and outer cylinder was 2.3 mm, and the temperature of the outer cylinder was maintained at $23 \pm 1.0^{\circ}\text{C}$ with a peltier setting. A solvent trap was used to prevent the sample from extreme evaporation during the tests. Each cement paste sample was pre-conditioned with a pre-shear of 50 s^{-1} until an equilibrium state was achieved (typically within 120 seconds), followed by a 30 s rest period. Then, the flow curve test was performed by increasing the shear rate using a step-up approach from 0 s^{-1} to 50 s^{-1} in increments of 10 s^{-1} . The shear rate during each period was maintained

until an equilibrium shear stress was measured. Typically, the equilibrium stress was obtained within 1 minute after reaching a given shear rate. The data were fitted to a linear equation using ordinary least squares regression to determine a slope and an intercept so that the Bingham model parameters could be determined (see Equation 1):

$$\tau = \tau_y + \eta \dot{\gamma} \quad (1)$$

Equation 1 represents the Bingham model; τ is the (resultant) shear stress, τ_y is the yield stress, η is plastic viscosity and $\dot{\gamma}$ is (applied) shear rate. The flow curve measurement was performed at least twice with a new specimen each time in order to check the repeatability, averaged values are provided for the Bingham parameters. However, to show the behavior of materials, only a representative flow curve from one of the samples is shown. Rheological material functions is a term that is used to convey that the rheological parameters (e.g. viscosity, storage modulus, etc.) are not constants, but are dependent on other parameter(s) such as shear rate, shear stress, etc. (such as is the case for a Bingham material in which the plastic viscosity approaches infinity when the shear stress is less than the yield stress, but at stresses higher than the yield stress the plastic viscosity is a function of the shear stress and shear rate) [27].

Small angle oscillatory shear (SAOS) rheology: SAOS rheology experiments SAOS was used in order to gain insight on how the material functions changed over time without damaging the structure of the paste [28]. The SAOS tests were also conducted using the Anton Paar MCR 301 rheometer. Even though both the SAOS and flow rheology tests use a rheometer, the SAOS tests examine a different behavior and was meant as a complementary test to the flow rheology test

(similar to the particle size measurement tests and the calorimetry tests) to identify trends in the material behavior. The SAOS test should be performed within the linear viscoelastic range (LVER), and this range is bounded by the critical strain and critical frequency of the sample. In this study, the LVER was determined by conducting a strain sweep test and a frequency test on the cement paste with the lowest viscosity (045_SP). For the strain sweep test, the frequency was fixed at 1 Hz and the strain varied from 0.001% to 1%. A critical strain of 0.6% was determined, and thus a strain less than this was selected for the frequency sweep test. For frequency sweep test, the strain was fixed at 0.03% obtained from the strain sweep test and the frequency was changed from 0.01 Hz to 10 Hz. The critical frequency was determined to be 8 Hz. As a result, strain of 0.03% and frequency of 1 Hz were used as they were found to be within the LVER of the examined pastes. The SAOS test was performed by imposing a sinusoidal strain and the stress response was monitored. For viscoelastic materials, such as cement paste, the resultant stress can be decomposed into the portion of the shear stress that is in-phase with the applied shear strain and into the portion of the shear stress out of phase with the applied shear strain. The storage modulus (G') of a viscoelastic material is obtained from the stress in-phase, and represents the solid-like property of the samples. The loss modulus (G'') of a viscoelastic material is obtained from the stress out-of-phase, and represents the liquid-like property of the samples. Each modulus is expressed as follows:

$$G'(\omega) = \frac{\tau_0}{\gamma_0} \cos \delta \quad (2)$$

$$G''(\omega) = \frac{\tau_0}{\gamma_0} \sin \delta \quad (3)$$

where, γ_0 is maximum strain amplitude (in this case 0.3), τ_0 is maximum resultant stress

amplitude and δ is angle of delay depending on the viscoelastic properties of the samples and it ranges within 0 to $\frac{\pi}{2}$. For the SAOS test, the rheometer was configured with a parallel plate geometry (see Figure 4(b)). Because of the longer test time duration of the SAOS test, the geometry was changed from coaxial cylinder to parallel plate due to concerns about the stiffening/setting of the cement paste making it difficult to clean the concentric cylinder geometry measurement system. A 1.0 mm gap was maintained between the plates, and the temperature of the lower plate was maintained at $23 \pm 1.0^\circ\text{C}$ with a peltier setting. The upper plate of the parallel plate was serrated to minimize slippage during the tests, and a solvent trap was used to prevent the sample from extreme evaporation during the tests. The shear stress was calculated using the torque on the rim of the upper plate as an approximation. Unlike the flow curve tests, a pre-shear was not applied in order to prevent damaging the microstructure of the cement paste.

Particle size measurements: Focused beam reflectance measurement (FBRM) [22] testing was conducted to examine the influence of the sample preparation methods on the fresh state microstructure. FBRM provides particle conditions, such as chord length distributions (CLD) and evolution of particle sizes and counts, by measuring the chord length and numbers of the particles. In the FBRM operating process, a focused laser beam scans agglomerates in the suspension and measures the time duration of backscatter of the laser from the one edge of the agglomerate to other edge (see Figure 5). The laser beams scans at a fixed velocity (2 m/s in this study), and the chord length of the various agglomerates can be calculated based on a series of algorithms (once the velocity of the beam and the time duration for the backscatter light to reach the detector is known. A unique feature with the FBRM device is that samples can be agitated

during measurement. Thus, insight about the aggregation kinetics, as well as disaggregation kinetics can be obtained. The FBRM tests were performed by monitoring the samples for 30 minutes under a constant agitation of 300 rpm. The FBRM test was performed after the cement paste was prepared using the planetary or high-shear mixer. For each mix that was evaluated using the FBRM technique, at least two independent cement pastes were tested.

Calorimetry: In order to evaluate the whether the sample preparation technique had an effect on hydration kinetics, calorimetry experiments were conducted. After preparing the cement pastes according to different sample preparation protocols, a sample of cement paste was placed in a 3114/3236 TAM Air Thermal, Thermometric AB Isothermal Calorimeter for 20 hours. For each mix, at least two replicates were tested; Figures 14 and 15 present the results of a representative sample from each mix while the data in Table 6 are based on the average of the samples.

3 RESULTS AND DISCUSSION

3.1 Flow Rheology

The viscosity and yield stress values were calculated according to the Bingham model, however, the flow curves from the high mixing intensity (ASTM C1738, and ASTM C1738_2m) prepared cement pastes showed slightly non-linear behavior (see Figure 6). The Bingham model is only valid for linear flow curve behavior; since the coefficient of determination (R^2) values were over 0.95, thus the Bingham model was applied for all samples. Figure 7 shows the effect of the sample preparation method on the rheological properties of each of the mixtures. For the control mixture (i.e. 045 mixture), changes in mixing intensity did not have a considerable effect on the yield stress, whereas the viscosity was slightly more affected. The effect of mixing intensity on

the rheological properties of cement paste depends on many variables including, but not limited to, mixture composition and aggregation mechanisms. There appears to be a synergistic effect of solids content volume (solids content has been shown to be linked to mixture viscosity [29], initial fluidity level, and the incorporation of polymeric additives that is governing the behavior of the mixtures. It can be seen that as the initial fluidity level of the mixture increased (via decreasing the solids content and/or through incorporation of a superplasticizer), the sensitivity of the mixtures to changes in the mixing protocol increased. This can be considered that plastic viscosity is the property of resistance to flowing while yield stress is the property of resistance to start flowing. Hence, viscosity can be influenced continuously by the microstructure, while yield stress can be influenced by one-time resistance of the microstructure. Therefore, for 045 mixture of relatively low vol. % of mixture can have a weak microstructural energy, and thus yield stress did not influenced by microstructure of high mixing speed mixed cement paste rather than other mixtures with higher vol. %. As the mixing time increased, the viscosity of the 045 mixture increased by 8.8% when the ASTM C305_2m protocol was used versus the ASTM C305 protocol; the viscosity increased by 45.9% when the ASTM C1738_2m protocol was used versus the ASTM C1738 protocol. However, incorporation of SP (i.e. the 045_SP mixture in Figure 6) resulted in a system that was more sensitive to variations in mixing intensity, and this became more apparent as the solid content of the plasticized mixtures increased. All mixtures that contained SP and were prepared using the ASTM C1738 protocol displayed higher yield stresses than their counterpart pastes prepared according to ASTM C305, and in some cases as much as a four-fold increase was seen in the yield stress values when ASTM C 1738 was used versus ASTM C 305 (e.g. see Figure 7b and compare the yield stress of 045_SP prepared according to ASTM C305 versus the yield stress of 045_SP prepared according to ASTM

C1738). In general increasing the mixing time of the ASTM C305 protocol had a minor effect on the viscosity of most of the mixtures containing SP. When a high shear mixer was used, the effects of extending the mixing time were more apparent in all the mixtures. As the mixing time of the mixtures prepared according to the ASTM C1738 protocol increased, the viscosity also increased. It was expected that as the mixing intensity increased that the plastic viscosity and yield stress would decrease, and this has often been reported in the literature [2–4,7]. However, much of the reported results were based on mixtures that were examined using shearing conditions that were lower than those examined in this work. The increase in the plastic viscosity and yield stress that occurred when samples were prepared using a high shear mixer suggests that the fresh microstructural state tend towards a more agglomerated state as the mixing time or mixing speed is increased. Although this type of behavior has not been reported by many, Lowke et al. [30] reported increasing viscosity due to “over mixing.” Similarly, the behavior does not appear to be unique to the cement-HRWR combination used in this research, since similar behavior was observed with different cement-HRWR combinations when high shear mixers were used [25]. In the work presented in this paper, increases in the rheological functions were more significant in the mixtures containing SP, which could be due to the high mixing intensity affecting the adsorption of the polymers on the cement particles or the high mixing intensity inducing polymer entanglement. Papo and Piani [31] observed shear thickening behavior in superplasticized pastes and it was suggested that the shear-thickening behavior was due to non-adsorbed segments of the polymer chain interacting with each other. The pastes in the work conducted by Papo et al. were prepared with a vane stirrer and were mixed according to ASTM C305. Cyr et al. [32] observed shear thickening behavior in cement pastes containing various types of superplasticizers and postulated that the shear thickening behavior was due to parts of

the adsorbed polymers being locally torn off by shear. No information was provided about the type of mixer or mixing speed that was used to prepare the pastes in the work conducted by Cyr et al; however it was stated that the pastes were mechanically mixed for 8.5 minutes and a two-step process was used to introduce the superplasticizer (1/3 of the superplasticizer was added with the initial water and the remaining 2/3 of the superplasticizer was added halfway through the mixing process).

3.2 Small Angle Oscillatory Shear (SAOS)

SAOS experiments were conducted on the mixtures prepared with the modified ASTM protocols in order to examine in further detail the fresh state microstructural development of these cement paste under resting conditions. Figures 8, 9, 10, and 11 present the results of the SAOS experiments for the *045*, *045_SP*, *047_SP*, and *050_SP* samples, respectively. Regardless of the vol. % solid or whether the paste contained SP, the magnitude of the storage and loss moduli of cement pastes prepared using the ASTM C1738_2m approach was higher than their counterpart pastes prepared using the ASTM C305_2m approach. This indicates that although the composition of the sample did not change, that changing the mixing process affected the microstructural arrangement of the pastes. Furthermore, a greater difference between the storage modulus of the paste prepared with ASTM C305_2m and the storage modulus of the paste prepared with ASTM C1738_2m was seen when the paste contained SP versus when it did not contain SP (i.e. compare the difference between the ASTM C1738_2m (G') and ASTM C305_2m (G') lines in Figure 8 to the difference ASTM C1738_2m (G') and ASTM C305_2m (G') in Figure 9). These increased differences between the two storage moduli suggests a

stronger microstructural network was induced in pastes prepared with the ASTM C1738_2m approach versus those prepared with the ASTM C305_2m approach.

The average rate of change of the storage modulus ($\Delta G' / \Delta t$) increased over time (see Table 5 for the actual values since visual inspection of the slopes of the curves in figure 8-11 may be misleading due to the y-axis being based on a logarithmic scale). This increase is attributed to increases in the rigidity of the system due to the hydration [33] and other phenomena such as thixotropy [6,34]. Microstructural rebuilding forms a network that contributes to the rigidity of the system [35]. The modulus of the system will increase as the network densifies and/or the links between the flocs increases. For example, densification of the microstructural network can occur from an increase in the solids concentration (e.g. reducing w/c) or formation of hydrates (due to the hydration process). The storage modulus increased faster for the cement paste prepared according to the ASTM C1738_2m protocol than for the cement paste prepared with ASTM C305_2m protocol. This suggests that the microstructural reconstruction is shear-history sensitive and in this research it was seen that as the mixing intensity increased so did the rate of microstructural rebuilding [33]. Even after 60 minutes the rate of change of the storage modulus was higher when the cement pastes were prepared with the ASTM C1738_2m protocol than with the ASTM C305_2m protocol, thus showing that the effects of the sample preparation method on the rheological properties persisted long after the cessation of the mixing process. In addition, from Table 5, it can be seen that for a given mixing protocol, that the rate of change of the storage modulus was higher in the cement paste not containing SP (i.e. 045 mixture) than the cement paste with SP (i.e. 045_SP mixture). This is to be expected due to the repulsion mechanism of the superplasticizer hindering the cement particles from agglomerating. Furthermore, it has been found that polycarboxylate-based superplasticizers often have a

retarding effect on early-age cement hydration [36,37]. However, when a high shear mixer was used to prepare the pastes, the magnitude of the average rate of change of the storage modulus of the cement paste containing SP was greater than the cement paste without SP during the 0 – 30 minute time frame; furthermore, smaller differences between the $\Delta G'/\Delta t$ values of these two pastes at other time frames were observed. Therefore, the high mixing intensity of ASTM C1738_2m is considered to have compensating or a preventive effect against the dispersion effect of SP.

3.3 Focused Beam Reflectance Measurement (FBRM)

FBRM tests were performed on a paste containing SP (i.e. the *045* cement paste) and a paste not containing SP (i.e. the *045_SP* cement paste). Figures 12 and 13 display the effect of sample preparation method on the number of agglomerate counts and average chord length measurement for the *045* and *045_SP* cement pastes, respectively. For the cement paste without SP, regardless of the sample preparation method used to prepare the paste, this research confirmed a trend towards an aggregated condition (exhibited by decreasing agglomerate counts and increasing mean chord length [6]) (see Figure 12). The sample prepared according to ASTM C1738_2m displayed the largest chord length sizes (see Figure 12(b)) and fewest number of agglomerate counts (see Figure 12(a)) which suggests that its fresh state microstructure is in a condition that is more agglomerated than the samples prepared with ASTM C305, ASTM C305_2m, and ASTM C1738. This is consistent with the general trends that were seen in the flow rheology and the SAOS experiments, and is in agreement with the work of Yim et. al. [38] who observed an increase in the viscosity of a cement paste suspension as its packing density increased.

The paste mixture containing SP showed different behavior than the paste not containing SP when prepared according to the different mixing methods. As shown in Figure 13, the *045_SP* paste prepared using ASTM C305 protocol (or a variation of it) displayed constant agglomerate conditions over the time of observation. This suggests that fresh state microstructure was in a state in which the rate of aggregation and rate of disaggregation was in equilibrium. Thus, it is considered that SP contributes to dispersing cement flocs in the suspension, while the high mixing conditions of ASTM C1738 serves to induce aggregation amongst the cement flocs. Similar to the results of the SAOS test, when samples were prepared according to ASTM C1738 and ASTM C1738_2m protocols the dispersing effectiveness of the SP appears to be hindered (compare storage moduli of *045* and *045_SP* for both protocols in Table 5)

3.4 Calorimetry

Figure 14 shows the influence of sample preparation methods on the rate of hydration of the cement pastes. It can be seen that pastes prepared according to ASTM C1738 displayed accelerated hydration kinetics compared to their companion mixtures that were prepared according to ASTM C305. The act of using a high shear mixer not only decreased the time (from the point that water and cement contacted) that it took for end of the induction period and acceleratory period to occur (see Table 6), but an increase in the cumulative amount of heat evolved also occurred. Increasing the mixing time to prepare the samples had a minor effect on samples prepared according using the planetary mixer (see curves for ASTM C305 and ASTM C305_2m samples in Figure 15), and the samples showed similar rates of hydration. Comparing cement paste containing SP (i.e., *045_SP* sample) and cement paste not containing SP (i.e., *045* sample), some delay in hydration kinetics was observed in the cement pastes containing SP

under the mixing intensity conditions of ASTM C305 and ASTM C305_2m protocols (see Figure 14 and the shift to the right of the curve representing the *045_SP* sample). This delay of hydration in the *045_SP* paste may be due to adsorption of the polymer molecules from the polycarboxylate based SP onto cement flocs hindering the dissolution of alite and delaying the formation of hydration products on the surface of cement particles [36,37,39]. However, interestingly, when cement pastes were mixed with the ASTM C1738 and ASTM C1738_2m methods, the degree of hydration of the *045_SP* cement paste increased and the end of acceleration period was similar to the *045* paste (see Figure 14). The slope of the heat flow curve during the acceleration period is an indicator of the rate of hydration products formation of cement paste [40], and pastes prepared with the ASTM C1738 and ASTM C1738_2m protocols displayed steeper slopes than those prepared with ASTM C305 and ASTM C305_2m (see Table 6). However, for a given paste composition, extending the mixing time did not greatly affect the slope of the heat flow during the acceleration period (e.g., compare the dashed curve with the solid curve of same color in Figure 15). The slope of the heat flow curve during the acceleration period is related with crystallization of hydration products (CH and C-S-H) [41,42]. Therefore, a steeper slope may suggest that increased CH and C-S-H crystallization occurred, even though the overall shape of the heat of hydration curve remained unchanged. Similarly, Juilland et al [40]. evaluated the effect of mixing on early hydration and observed that increasing the mixing speed from 200 rpm to 2000 rpm resulted in reducing the induction period and increasing the slope of the heat flow curve during the acceleration period. Since the shape of the calorimetry curve was not changed, it was suggested that the faster mixing speed contributed to accelerating the alite hydration and that the underlying mechanisms of hydration was not changed [40].

Table 6 summarizes the calorimetry results for the pastes. Comparing *045* pastes prepared with ASTM C305 and ASTM C1738 protocols, a negligible decrease (~ 6 minutes) was observed in the point at which the induction period ended when the ASTM C1738 protocol was used. However, the slope of acceleration period was increased by as much as 41%, and the end point of acceleration period was accelerated by about 50 minutes. At the end of acceleration period, the heat evolution rate of the cement paste prepared with ASTM C1738 protocol was 15% greater than the cement paste prepared with ASTM C305 protocol (compare *ASTM C305 045* paste to *ASTM C1738 045* paste). However, extending the mixing time resulted in a minor reduction in the cessation point of the induction period, the slope of the curve during the acceleration period and the amount of heat at the end of acceleration period for ASTM C305 protocol. In the case of ASTM C1739 protocol, when the mixing time was extended, a larger reduction was seen in the point at which the induction period ended and the magnitude of the slope of the curve during the acceleration period also increased. It was seen that hydration kinetics was more sensitive to variations in the sample preparation protocol when SP was added to the mixture. Compared to ASTM C305 mixing speed, when the *045_SP* was prepared with ASTM C1738, the end point of the induction period decreased by 33 minutes, however, the end point of acceleration period was reduced by as much as 163 minutes. Additionally, the slope of acceleration period was increased 59%, and the heat evolution rate at the end of acceleration period was increased by 22%. Thus it is confirmed that although the incorporation of SP resulted in delayed hydration kinetics in pastes prepared using ASTM C305, using the ASTM C1738 protocol almost compensated for the delay, and using the ASTM C1738_2m protocol overcame any retardation that would have been caused by the SP.

4 CONCLUSION

The effect of sample preparation method, primarily the role of mixing intensity, on the rheological behaviors and microstructural development of cement paste were evaluated using sample preparation approaches based on standardized methods: ASTM C305 and ASTM C1738. Variations on the standardized methods were also done in order to evaluate the effect of extending the mixing time on paste behavior. From the flow rheology evaluations, it was seen that when the ASTM C1738 protocol was used, an increase in plastic viscosity occurred when the mixing time of the protocol was extended; a similar effect was not seen when the cement paste was prepared using the ASTM C305 protocol or its variation (ASTM C305_2m). Furthermore, this increase in plastic viscosity was amplified with increased vol. % solid and/or existence of SP in cement paste. Therefore, it is considered that the high mixing intensity of the ASTM C1738 protocol can hinder the dispersing action of the SP. It was also observed that the ASTM C1738 and its variation, ASTM C1738_2m, affected the development of early age fresh state microstructure. From the SAOS test, the cement paste prepared with ASTM C1738_2m protocol showed a higher storage modulus and faster rate of change in the storage modulus values than the cement paste prepared with ASTM C305_2m protocol. Based on the FBRM testing, it was determined that pastes with SP showed flocculating conditions under both ASTM C1738 and ASTM C1738_2m protocol, while pastes prepared with ASTM C305 and ASTM C305_2m protocols appeared to be in an equilibrium state of aggregation/disaggregation. Finally from the calorimetry experiments, accelerated hydration kinetics were observed when the cement paste was prepared with ASTM C1738 protocol versus when the paste was prepared with the ASTM C305 protocol. It was found that extending the mixing time of the ASTM C1738 protocol contributed further to accelerating cement hydration, and compensated for the retardation effect

of the SP on hydration of cement paste. The present work illustrates that the sample preparation technique used to prepare cement pastes plays an important role on not only the rheological properties, but also on fresh state microstructural development and hydration kinetics, particularly in the case of plasticized pastes. As such, additional guidelines and specifications on sample preparation techniques for pastes containing chemical admixtures may need to be developed. Furthermore, additional research is needed to examine the effect of mixing variables on plasticized portland cement concrete in order to determine whether the differences in the behavior seen in the plasticized and non-plasticized pastes are manifested in the properties (both early age and hardened) of concrete.

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Table 1. Overview of research pertaining to the effect of mixing methods on rheology and fresh state microstructure

Researchers	Mixing Method	Rheological Properties Investigated	Fresh State Microstructure	Reference
Yang, et al.	Hand-mixed	Yes, shear stress	Yes, ESEM*	2
	Paddle mixer (300 rpm)			
	High shear blender (3000 rpm)			
Williams, et al.	Hand-mixed	Yes, viscosity, thixotropy	No	3
	Paddle mixer (140 to 285 rpm)			
	High shear blender (2500 rpm)			
Roy, et al.	Hand-mixed	Yes, viscosity, yield stress	No	4
	Spindle (100 rpm)			
	High shear blender (9000 to 17000 rpm)			
Dils, et al.	Concrete mixer (1.4 to 1.6 m/s)	Flow curve	No	5
Ferron, et al.	Hand blender (low speed)	No	Yes, FBRM	6
Rößler, et al.	Planetary mixer (140 to 285 rpm)	Yes, torque	Yes, ESEM	7
Prasittisopin, et al.	Planetary mixer (140 to 285 rpm)	No	No	11
Vandanjo, et al.	Concrete mixer (23.1 rpm)	No	No	14
Ferraris, et al.	High shear blender (4000 to 10000 rpm)	Yes, viscosity, yield stress	No	17
Juilland, et al.	Hand-mixed	No	Yes, ESEM	40
	High shear blender (200 to 2000 rpm)			
Vlachou, et al.	Propeller mixer (4000 to 12000 rpm)	No	Yes, ESEM (frozen sample)	43
Vlachou, et al.	Propeller mixer (4000 to 12000 rpm)	Yes, viscosity	Yes, ESEM (frozen sample)	44
Lei, et al.	Hand-mixed	Yes, yield stress	Yes, SEM**	45

*ESEM: Environmental scanning electron microscopy

**SEM: Scanning electron microscopy

Table 2. Oxide composition of the cement

Items	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
Amount (%)	20.70	4.50	3.30	65.10	1.40	2.60	0.18	0.48

Table 3. Mixing proportions

Sample Name	vol. % solid	w/c	SP included	Quantity for 1 liter paste		
				Cement (g)	Water (g)	SP (g)
<i>045</i>	0.45	0.39	No	1417.50	550.00	-
<i>045_SP</i>	0.45	0.39	Yes	1417.50	547.34	2.84
<i>047_SP</i>	0.47	0.36	Yes	1480.50	527.22	2.96
<i>050_SP</i>	0.50	0.32	Yes	1575.00	497.04	3.15

Table 4. Temperature of the mixing water before mixing (T_i) and cement paste after mixing (T_f)

Mixing methods	Sample Name	Temperature	
		T_i	T_f
ASTM C305	<i>045</i>	23.9	25.1
	<i>045_SP</i>	23.3	24.3
	<i>047_SP</i>	23.2	24.3
	<i>050_SP</i>	23.1	25.3
ASTM C305_2m	<i>045</i>	23.1	25.6
	<i>045_SP</i>	23.5	24.9
	<i>047_SP</i>	22.8	25.8
	<i>050_SP</i>	22.8	26.1
ASTM C1738	<i>045</i>	15.1	22.9
	<i>045_SP</i>	16.4	22.3
	<i>047_SP</i>	15.0	22.3
	<i>050_SP</i>	14.1	23.1
ASTM C1738_2m	<i>045</i>	15.6	22.7
	<i>045_SP</i>	16.5	25.1
	<i>047_SP</i>	17.0	24.8
	<i>050_SP</i>	18.6	24.7

Table 5. Effect of extended time mixing protocol on the rate of change of storage modulus ($\Delta G'/\Delta t$)

Time	ASTM C305_2m (KPa/h)				ASTM C1738_2m (KPa/h)			
	<i>045</i>	<i>045_SP</i>	<i>047_SP</i>	<i>050_SP</i>	<i>045</i>	<i>045_SP</i>	<i>047_SP</i>	<i>050_SP</i>
0 – 30	2.5	1.1	2.5	5.0	3.9	5.8	7.9	10.9
30 – 60	8.6	3.1	8.1	19.7	24.8	20.4	31.6	32.1
60 – 90	37.2	8.3	21.9	45.9	93.7	75.1	96.7	86.6

Table 6. Summary of the information of calorimetry for induction period and acceleration period: as increased mixing intensity (increasing speed and extended mixing time), the end point times were decreased and the slope of acceleration period was increased with increased evolution rate of heat at the end point of acceleration period

Pastes	Mixing protocols	Induction period	Acceleration period		
		End point* (min.)	End point* (min.)	Slope (J/h ² /g)	Rate of heat evolution at the end point (J/h/g)
045	ASTM C305	83 ± 6	443 ± 13	2.30 ± 0.00	12.43 ± 0.00
	ASTM C305_2m	76 ± 10	421 ± 1	2.43 ± 0.00	12.51 ± 0.03
	ASTM C1738	77 ± 4	393 ± 3	3.24 ± 0.01	14.25 ± 0.03
	ASTM C1738_2m	75 ± 7	340 ± 8	3.80 ± 0.02	14.79 ± 0.07
045_SP	ASTM C305	105 ± 12	516 ± 15	2.46 ± 0.01	13.25 ± 0.00
	ASTM C305_2m	101 ± 12	511 ± 9	2.64 ± 0.00	13.89 ± 0.01
	ASTM C1738	72 ± 6	353 ± 17	3.90 ± 0.03	16.23 ± 0.16
	ASTM C1738_2m	59 ± 5	297 ± 15	4.46 ± 0.01	17.44 ± 0.05

* The end point was based the time after water contact time

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(b) ASTM C305

Figure 1. Mixing protocols of original ASTM standards

(a) ASTM C1738_2m

(b) ASTM C305_2m

Figure 2. Mixing protocols of modified ASTM standards

(a) Chandler high shear mixer blade and setup (for ASTM C1738)

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Figure 12. Effect of sample preparation method on fresh state agglomerate condition for 045 cement paste

(a) Agglomerate counts per second

(b) Mean chord length

Figure 13. Effect of sample preparation method on fresh state agglomerate condition for 045_SP cement paste

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(b) 045_SP mixtures

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