Deformation capacity of fresh cement pastes

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Abstract

The deformation capacity conditions several processes in cement based-materials, including workability and structural build-up. However, the origins of this deformation capacity present some ambiguities. This paper aims to contribute to improving the comprehension of the deformation capacity of fresh cement pastes. For this, the effect of water to cement ratio (w/c) and superplasticizer (SP) dosage on the viscoelastic properties of cement paste is examined using oscillatory rheology and yield stress measurements. It appears that water to cement ratio affects slightly the critical strain at the end of the linear viscoelastic domain (LVED) and strongly the storage modulus. The addition of superplasticizer seems to have a strong effect on the critical strain. In addition, it was shown that the critical strain at the end of the LVED is associated with strong physical forces (colloidal forces enhanced by early hydrates formation), while the transition strain at the flow onset is due to large structural reorganizations.

Keywords: *yield stress, admixture, rheology, storage modulus, critical strain*

1 Introduction

The comprehension of the rheological behavior of fresh cement-based materials is essential to control certain processes such as pumping, multi-layer casting, and formwork pressure. This rheological behavior displays various complexities including yielding, structural build-up, non-linearity, and chemical evolution (dissolution of anhydrous cement and formation of hydrates). Under shear, fresh cement pastes generally display a viscoelastic behavior involving the deformation capacity.

The characterization of the viscoelastic properties of fresh cement paste can be performed by several procedures such as dynamic mode rheology (small amplitude oscillation strain) [1–6], and transient mode rheology (yield stress measurement [5,7–9] or creep/recovery technique [10]). These procedures can be used to understand different phenomena including the setting [11], the structural-build-up [2,3] and the effect of superplasticizer [1]. Dynamic mode rheology includes strain sweep, frequency sweep and time sweep procedures and seems suitable to probe the microstructure of fresh cement paste in order to investigate the deformation capacity. It consists on the measurement of the viscoelastic properties such as the storage (or elastic) modulus G', the loss (viscous) modulus G" and other relevant parameters (critical strain, phase angle, oscillation stress…). Frequency sweep mode is generally carried out to study the cement paste stability [12], while time sweep mode is more suitable to examine the structural build-up during the dormant period of the cement hydration [2,3,5]. Strain (or stress) sweep mode can be performed to examine the microstructure of cement paste and can give information concerning the network of cement particles and the forces acting inside this network. It allows the linear viscoelastic domain (LVED) to be determined. In this domain, the storage (G'**)** and loss (G") moduli remain almost constant as a function of strain. The end of the LVED is associated with a critical strain of the order of few hundredths (10^{-3} to 10^{-2} %) [1,6,8,11], while the transition solid/liquid (G'= G") at the flow onset is associated with a large strain (few %). Nachbaur et al. [11] used this procedure to examine the evolution of the structure of cement and pure tricalcium silicate (C_3S) pastes during the setting process. According to theses authors, the critical strain of the cement paste is very small and of

the order of 3.10^{-2} %, which suggests that the forces acting between cement particles are attractive physical forces associated with the formation of early-hydrates (calcium silicate hydrates C-S-H) at the contact points between particles.

Transient mode includes yield stress measurement and creep/recovery procedure and can be also used to examine the viscoelastic behavior of cement paste. The yield stress measurement is often carried out using the stress growth procedure which allows the static yield stress to be measured [7,9,13,14]. It consists on the application of a very low and constant shear rate ranging from 0.001 to 0.01 s^{-1} (depending on the rheometer sensitivity) and on the measurement of the shear stress evolution as a function of time (or strain). For cement paste, the rheological tool suitable for this experiment is Vane geometry. The typical curve consists of two domains. The first domain is related to the elastic behavior in which the shear stress increases linearly with time (or strain:$\tau = G\gamma$) until reached a peak followed by the second domain (viscous regime) corresponding to a plateau in which the shear stress remains almost constant with time (steady state flow). The peak defines the static yield stress corresponding to the flow onset. According to Roussel et al. [15], the yield stress originates from colloidal interactions and direct contacts between cement particles that contributes to form a network of interacting particles able to withstand the applied stress. The strain associated with the static yield stress is usually of the order of few percentages and is attributed to the soft colloidal network [8]. In addition, as reported by Roussel et al. [8] and Fourmentin et al. [16], the shear stress-shear strain curve can display an abrupt change of the slope in the very first stages of shearing process. In fact, for a very low shear strains, the shear stress increases very quickly with the shear strain which could characterize a very stiff material [8,16]. This slope change is associated with a rigid critical strain which could be associated to the breakage of early hydrates (C-S-H) bridges between cement particles [8,16], while the peak is attributed to the rupture of a soft colloidal network.

Moreover, the deformation capacity is affected by time. In fact, fresh cement paste exhibits a time-dependent behavior characteristic of flocculated suspensions. However, this behavior cannot be referred as thixotropic since it is not completely reversible due to chemical reactions. This is described by a structural build-up that affect the deformation capacity of the connections between

74 cement particles originating from flocculation and bridging effect [2,5,17–20]. In fact, the
75 structural build-up is originated from flocculation which leads to the formation of a percolated
76 network and from bridging effect induced by the formation of early hydrates at the surface of
77 cement particles [3,8,21–23]. Mostafa and Yahia [3] performed time sweep measurements to
78 quantify the structuration of cement pastes by monitoring the evolution of both storage modulus
79 and phase angle. They found that the structural changes at rest can be described by a percolation
80 time corresponding to the time needed to form colloidal percolated network, while the linear
81 increase at rest of the storage modulus within the dormant period can describe the chemical
82 rigidification rate of formed network. Otherwise, the structural build-up at rest can be described
83 by the increase of the static yield stress with resting time [5,17]. Recently, an interesting study
84 has been performed by Zhang et al. [21] to quantify the contribution of colloidal forces and early
85 hydrates (C-S-H) formation on the structural build-up using the evolution of the yield stress. They
86 showed that the interparticle force, which is the combination of colloidal force and interaction
87 force between C-S-H particles, is the driving force for the structural build-up. The contribution
88 of colloidal force appears to be greater in the early period (until 60 min), while the C-S-H force
89 determines the evolution trend from 30 min at rest [21]. This interparticle force strongly
90 influences the deformation capacity of the fresh cement paste.
91 Furthermore, the effect of several factors (water to cement (w/c) ratio, SP dosage, supplementary
92 cementitious materials, time…) on the deformation capacity has been investigated [1,4,5,8,11].
93 Jiao and De Schutter [1] examined the effect of w/c ratio and superplasticizer dosage on the
94 critical strain (at the end of the LVED), and found that this critical strain is strongly affected by
95 superplasticizer dosage, while the effect of w/c ratio is less significant. The critical strain increases
96 only at high w/c ratio. Jiao and De Schutter [1] explain the effect of w/c ratio by the increase of
97 the dissolution rate leading to the increase of early hydrates formation, which could also be more
98 fragile when w/c increases. The effect of superplasticizer on the critical strain is explained by the
99 entanglement of superplasticizer molecules with each other and the possible enhancement of the
100 C-S-H bridges. According to the authors, this leads to the improvement of the cohesive bonding

between cement, inducing an increase of the deformation capacity of the connections. So, the shear strain required to initiate the relative movement between particles thus increases [1].

Nevertheless, some ambiguities could be pointed out concerning the origins of the deformation capacity of fresh cement pastes. In fact, it is often assumed that the deformation capacity involves two mechanisms occurring at different strains. The critical strain at the end of the LVED (of the order of 10^{-2}%) is attributed to the breakage of early hydrates links between cement particles, while the transition strain at the flow onset is associated with colloidal network [8,10,11,16]. However, the bridging effect due to the formation of early hydrates at the contact points between particles remains unclear and depends on several factors (time, dispersion state, composition, etc…) [23–26]. In addition, a chemically inert materials such as calcite suspension, which have granular properties close to that of cement paste and sometimes used to mimic the fresh behavior of cement paste [27,28], display a critical strain at the end of the LVED of the same order of magnitude [29]. This critical strain cannot be associated with the bridging effect and is attributed to the inter-floc rupture associated with a weak-link structure, while the transition strain (where G'=G") of the order of few % is associated with the fragmentation of flocs [29]. Moreover, the effect of solid volume fraction and superplasticizer dosage on the yield stress and on the critical strain [1,13,15] suggests that the origins of the deformation capacity of fresh cement pastes is closely related to the interparticle distance.

The aim of this paper is to investigate the origins of the deformation capacity of fresh cement pastes. The first part is devoted to the description of the tests which make it possible to characterize the viscoelastic behavior of fresh cement pastes. Then, the effect of the water to cement ratio (w/c) and superplasticizer dosage (SP) is examined. Finally, the origins of deformation capacity of fresh cement pastes are discussed.

2 Materials and methods

2.1 Materials

An ordinary Portland cement (CEM I-52.5 R) and calcium carbonate (calcite) were used in this study. The particle size distributions (Fig. 1) were determined using laser granulometer (LS 13320-Beckman Coulter). The granular properties are summarized in Table 1.

A commercial polycarboxylate-based superplasticizer with dry extract of 19 wt% was used. Three dosages of this superplasticizer were used: 0.1, 0.2 and 0.5 wt% of dry substance (by mass of cement).

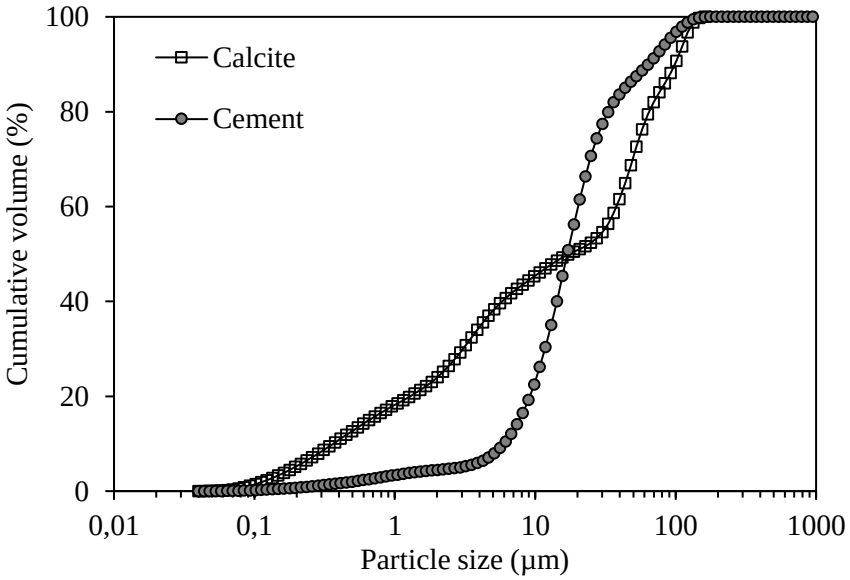


Fig. 1. Particle size distribution of cement and calcite

Table 1. Granular properties of cement and calcite

	Cement	Calcite
d_{10} (µm)	6.6	0.4
d_{50} (µm)	18.6	19.2
d_{90} (µm)	70.0	108.4
Density	3.14	2.70
Blaine fineness (m^2/g)	0.44	0.45

Cement pastes were prepared with water to cement (w/c) of 0.4, 0.45, 0.5 and 0.6 (Table 2). 200 g of cement was mixed with deionized water in a planetary agitator (Stuart SS30) for 5 minutes at 500 rpm, then the walls of the mixer were scraped to homogenize the mixture (30 seconds), and finally the paste was mixed for 1 minute at 1000 rpm. For cement pastes with superplasticizer, the cement was first mixed with 90% of water for 5 minutes at 500 rpm, followed by scraping the

walls of the mixer (30 seconds), and the required amount of superplasticizer was added to the remaining water (10%) and the paste was mixed for 1 minute at 1000 rpm.

Table 2. Water to cement ratio and the corresponding solid volume fraction

water to cement ratio w/c	solid volume fraction ϕ
0.40	0.44
0.45	0.41
0.50	0.39
0.60	0.35

2.2 Rheological measurements

The rheological measurements were performed using a rotational rheometer (AR2000Ex-TA Instruments) equipped with a four-blade vane geometry (internal diameter = 28 mm, outer cup diameter =30 mm, gap = 1 mm).

2.2.1 Oscillatory mode

The viscoelastic properties of cement paste can be assessed using oscillatory mode such as stress sweep procedure. After a pre-shear phase during 30 seconds at a shear rate of 100 s^{-1}, an oscillation stress sweep from 0.01 to 400 Pa is performed with a frequency of 1Hz. It can be noted that this type of experiment can provide information on the microstructure of the fresh cement paste [1,4,6]. The typical curve obtained with this oscillation sweep is shown in Fig. 2. The evolution of storage and loss moduli during this protocol reveals three different regimes: the linear viscoelastic domain (LVED), the transient yielding zone, and the flow domain. In the linear viscoelastic domain (LVED), the storage G' and loss G" modulus remains almost constant, which indicates that the microstructure of cement paste is maintained [4]. When G' is greater than G", cement paste displays a solid-like behavior, whereas when G' is lower than G", cement paste exhibits a liquid-like behavior. At the end of the LVED, the moduli begin to drop significantly. The critical strain at the end of the LVED of order of 10^{-2}% can be interpreted as a signature of the breaking of C-S-H links between cement particles [8,10,11]. The intersection of the storage modulus and the loss modulus curves (G'= G") defines the so-called gel point which characterizes a solid/liquid transition, i.e. the flow onset. This transition point is associated with a large strain noted transition strain in Fig. 2.

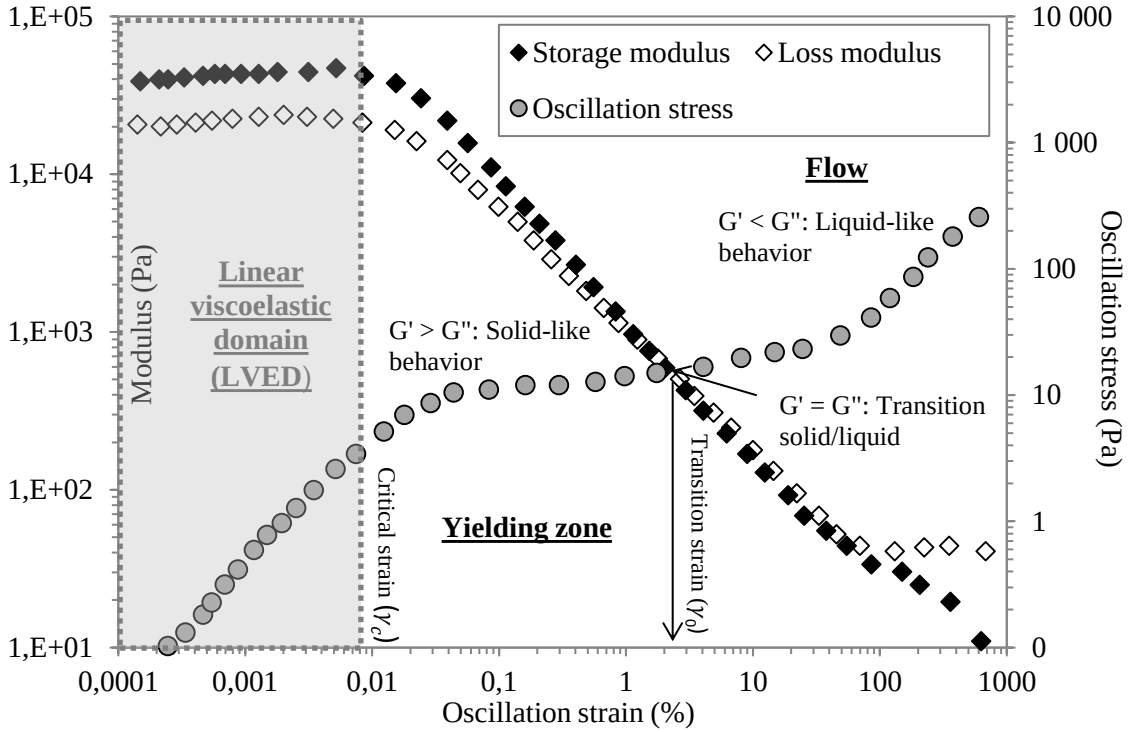
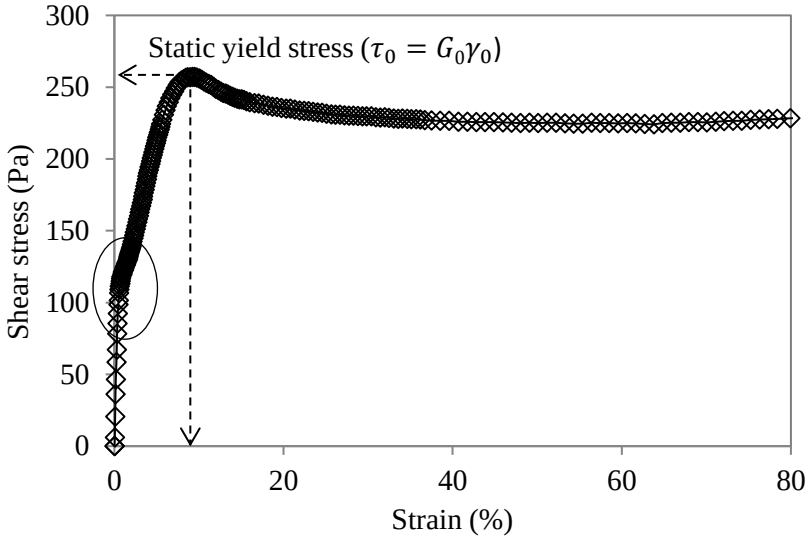


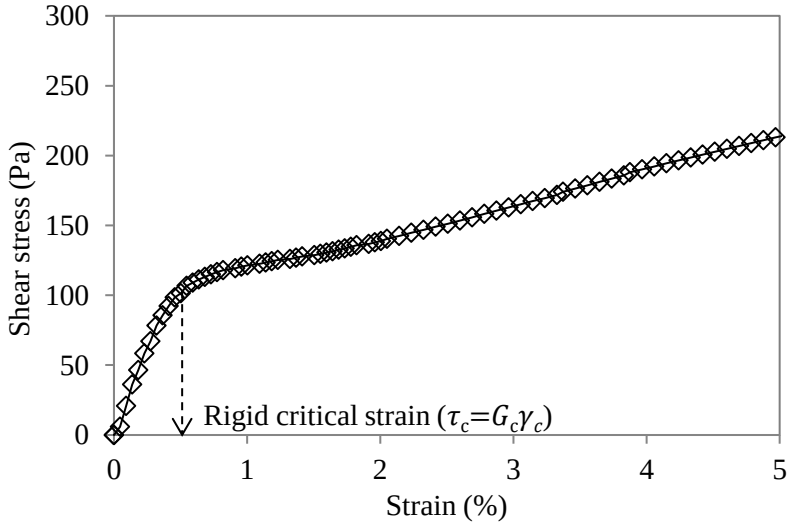
Fig. 2. Typical response to oscillatory stress (or strain) sweep of cement paste (w/c=0.4, 0%SP)

2.2.2 Stress growth protocol

The stress growth protocol allows the static yield stress to be measured. It consists of the application of a low and constant shear rate of $0.005 s^{-1}$ during 180 seconds after a strong pre-shear phase during 30 seconds at $100\ s^{-1}$ and a resting time. The typical response of cement paste is shown in Fig. 3, where the peak defines the static yield stress and the flow onset (Fig. 3-a). As reported by Roussel et al. [8] , the shear stress-shear strain curve can display an abrupt change of the slope in the very first stages of shearing process as shown in Fig. 3-b. This slope change is associated with a rigid critical strain (γ_c) due to the breakage of C-S-H bridges between particles [8,16]. The peak representing the static yield stress (γ_0), which characterizes the flow onset, can be the results of the breakage of a soft colloidal network and a rigid network formed by C-S-H bridges between cement particles that was not totally broken when the rigid critical strain was reached or that continuously broken and reformed all along the measurement [8].



(a)



(b)

178 **Fig. 3. Shear stress as a function of shear strain during a stress growth test on a cement paste with**
179 **a water to cement ratio of 0.4 after 25 min of resting (a) shear strain scale fron 0 to 100%, (b) shear**
180 **strain scale from 0 to 5%**

181 # 3 Results

182 ## 3.1 Effect of water to cement ratio

183 Fig. 4 shows the variation of the storage and loss moduli with the oscillation strain for different
184 water to cement ratios. In the linear viscoelastic domain (LVED), the storage and loss moduli
185 remain almost constant as a function of oscillation strain. The increase of water to cement ratio
186 leads to a decrease of both storage and loss modulus. The increase of the storage modulus with

water to cement ratio (and solid volume fraction) characterizes the increase of the cement paste stiffness and the formation of percolated network [1,30,31] (Fig. 5).

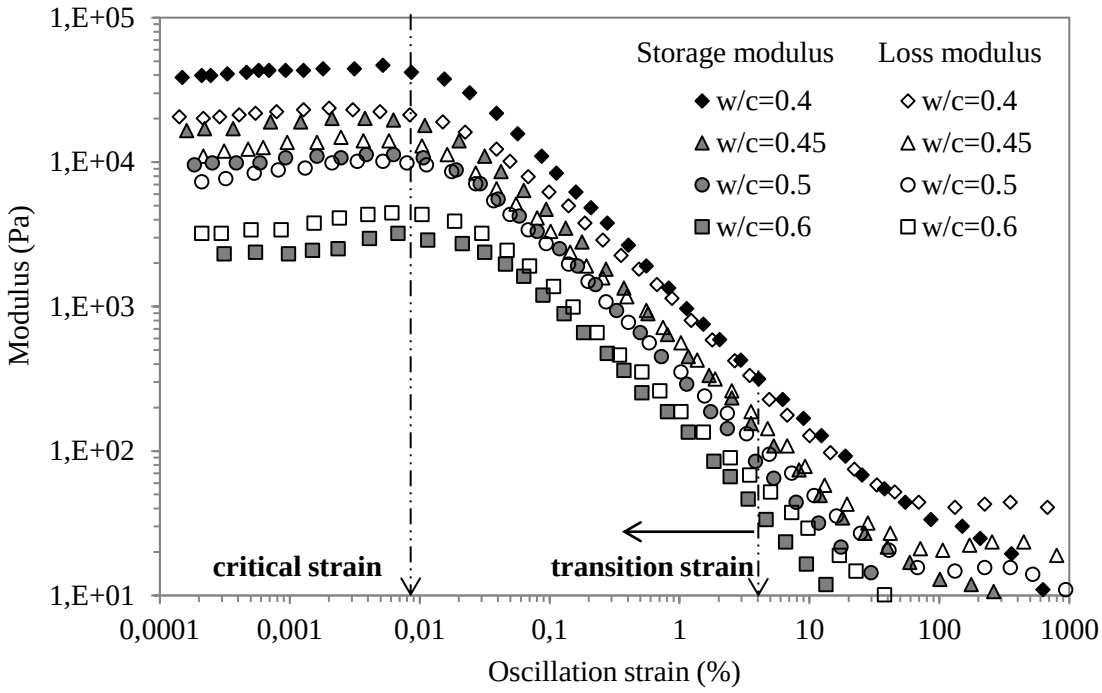


Fig. 4. Effect of water to cement ratio (w/c) on storage and loss modulus of cement paste

In addition, it can be noted that the cement paste displays a solid-like behavior in LVED for low w/c ratios, since the storage modulus is greater than the loss modulus. For high water to cement ratio, the cement paste can exhibit a liquid-like behavior in LVED.

This behavior change is related to the dependence of the storage modulus (and the yield stress) on solid volume fraction (Fig. 5). The storage modulus (or yield stress)-volume fraction relationship reflects the network of interacting particles which percolates under the effect of colloidal forces when the percolation volume is reached (Fig. 5) [15]. This particles network becomes frictional (direct contacts) with increasing solid volume fraction [15]. This suggests that the deformation capacity can be affected by the solid volume fraction which dictates the nature of the interaction network (colloidal and/or frictional). As shown in Fig. 4, the critical strain at the end of LVED depends slightly on water to cement ratio, but the transition strain seems to decrease. The critical strain, often interpreted as a signature of early hydrates (C-S-H) forming links between cement particles, corresponds to the shear strain (and the associated shear stress)

required to breakdown the contacts and to initiate the relative movement of neighboring cement particles [1,8,11,32]. The transition strain (γ_0) describes the transition solid/liquid. Its decrease with decreasing solid volume fraction may reflect the reduction in the strain required to induce flow as the number of solid particles decreases. This suggests that this strain would be linked to large rearrangements in the suspension.

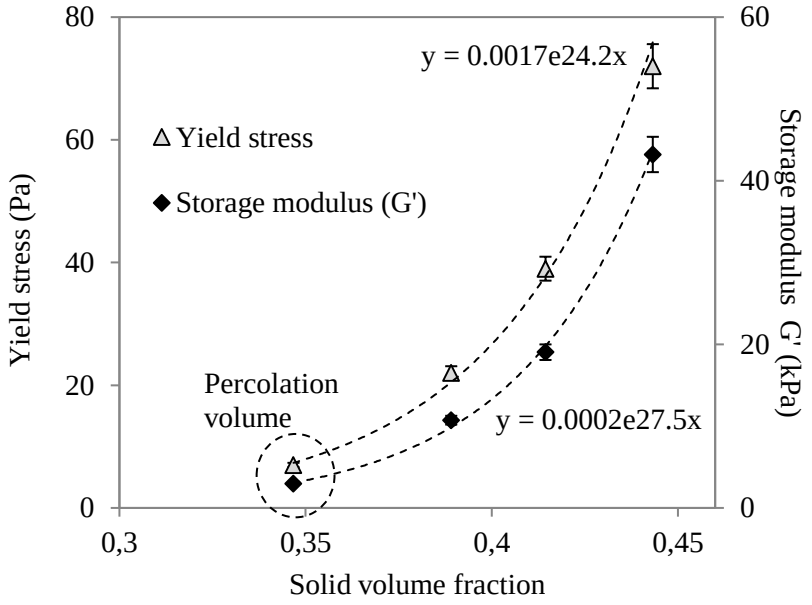


Fig. 5. Evolution of the yield stress and the storage modulus as a function of solid volume fraction

3.2 Effect of SP dosage

The effect of superplasticizer dosage on the storage and loss moduli of cement paste is presented in Fig. 6. It can be noted that the LVED is significantly affected by the addition of superplasticizer. The storage modulus decreases strongly with SP dosage. In fact, the addition of superplasticizer reduces the magnitude of colloidal interactions [33], and the stiffness of the network of interacting particles is thereby decreased.

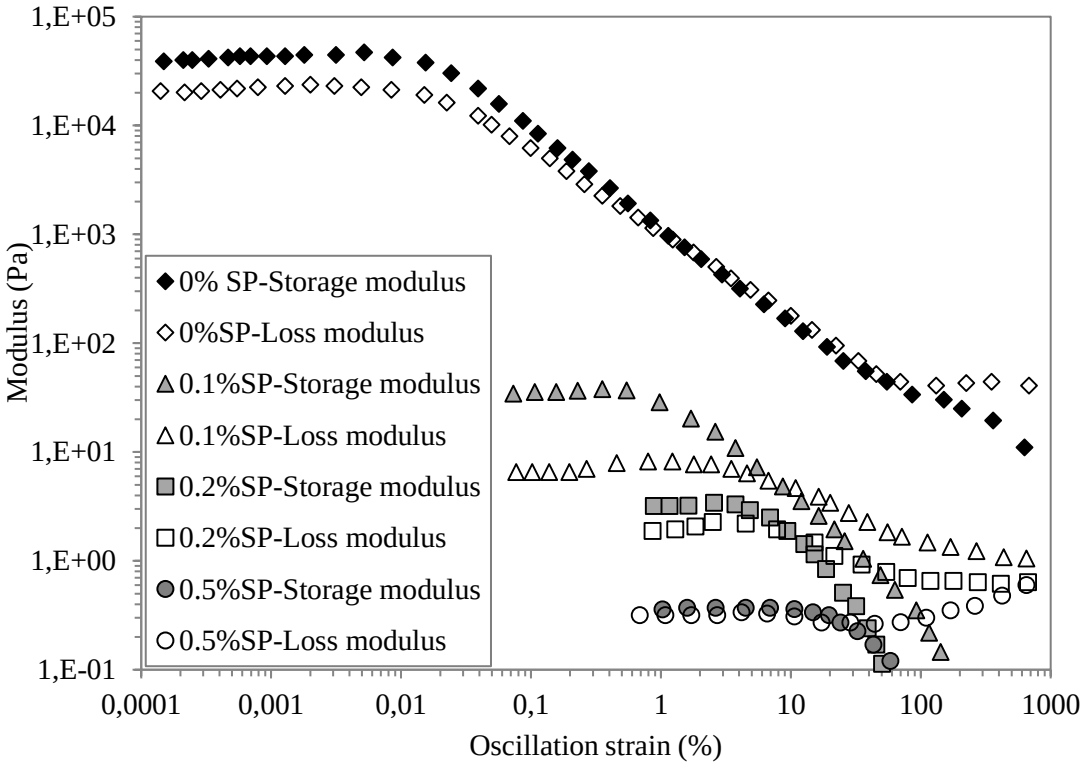


Fig. 6. Effect of superplasticizer dosage on storage and loss modulus of cement paste with w/c of 0.4

Moreover, the critical strain (γ_c), at the end of the LVED, is strongly affected by SP dosage as shown in Fig. 6 and Fig. 7. For cement paste without superplasticizer, the critical strain is of the order of few 10^{-2}%, while for cement paste with 0.5% SP, the critical strain is of the order of 10%. Others authors reported the same observations [1,3,5], indicating an increase in the deformation capacity with the addition of superplasticizer due to the enhanced dispersion of cement particles.

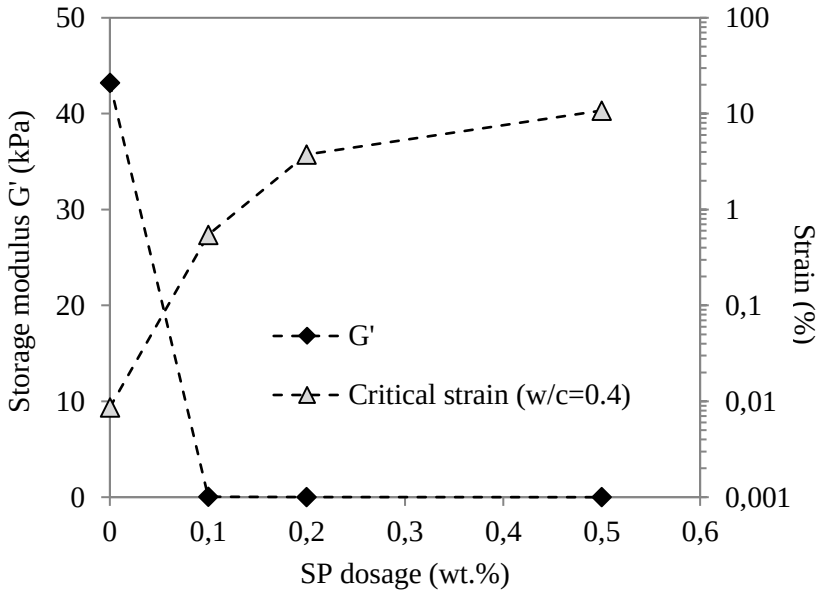
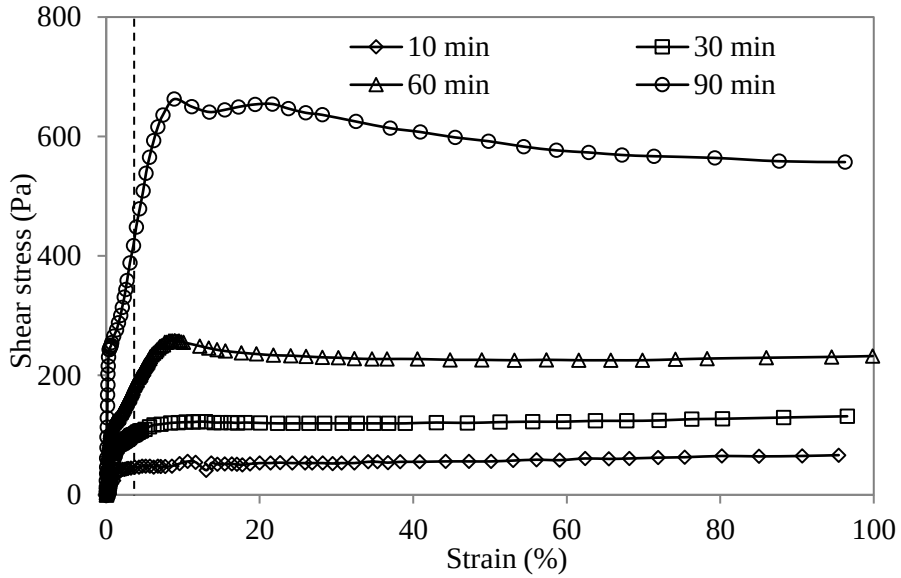


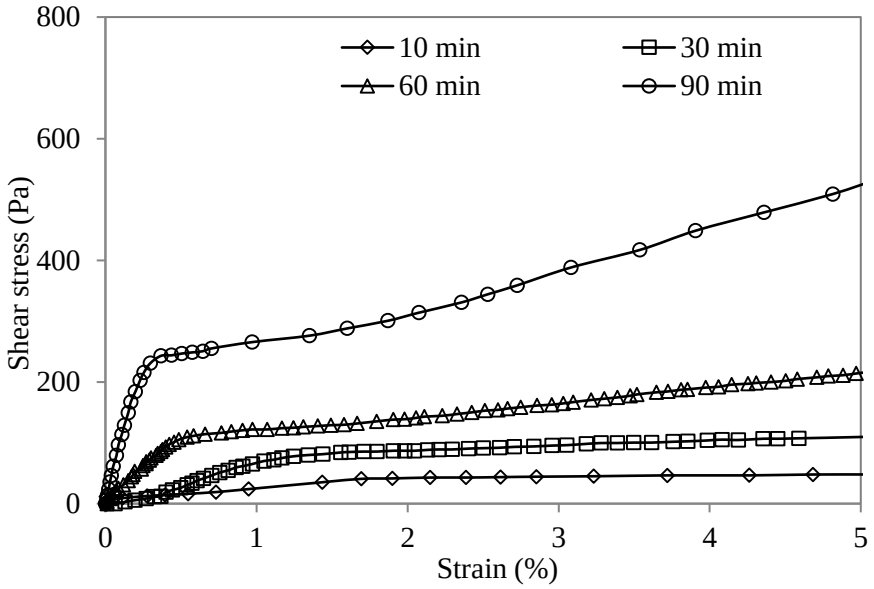
Fig. 7. Evolution of the storage modulus and the critical strain as a function of superplasticizer dosage

3.3 Discussion

As reported by Roussel et al. [8], there is an ambiguity in the literature concerning the origins of the deformation capacity of fresh cement pastes. The strain (γ_0) corresponding to the peak of the shear stress-strain curve obtained by yield stress measurement describes the flow onset (Fig. 8-a). This strain varies little with the hydration time as shown in Fig. 8-a. Roussel et al. [8] designate this strain as the largest strain or the soft colloidal strain associated to the colloidal network. In addition, Roussel et al. [8] and Fourmentin et al. [16] pointed out the existence of a small strain (γ_c) in the very first stages of the shearing process during yield stress measurement as shown in Fig. 8-b, which can be attributed to the rupture of C-S-H bridges between cement particles [8,16]. It can be noted that this small strain slightly decreases with hydration time, and the associated shear stress increases as shown in Fig. 8-b. This reflects a rigidification of the cement paste probably due to the formation of hydrates at the contact point between particles.



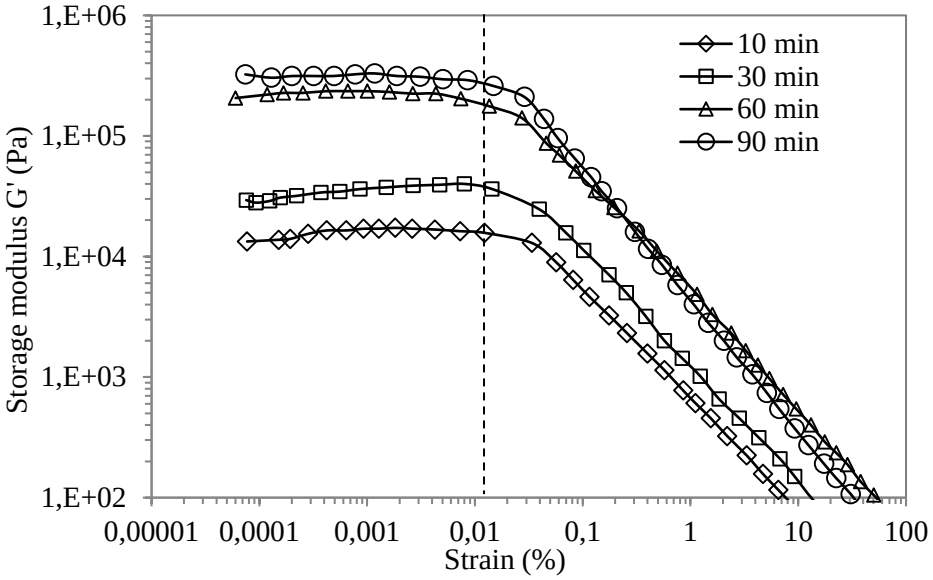
(a)



(b)

Fig. 8. Yield stress measurement performed at different times of hydration (cement paste with w/c of 0.5: (a) full linear scale, (b) zoom on the first 5% of strain

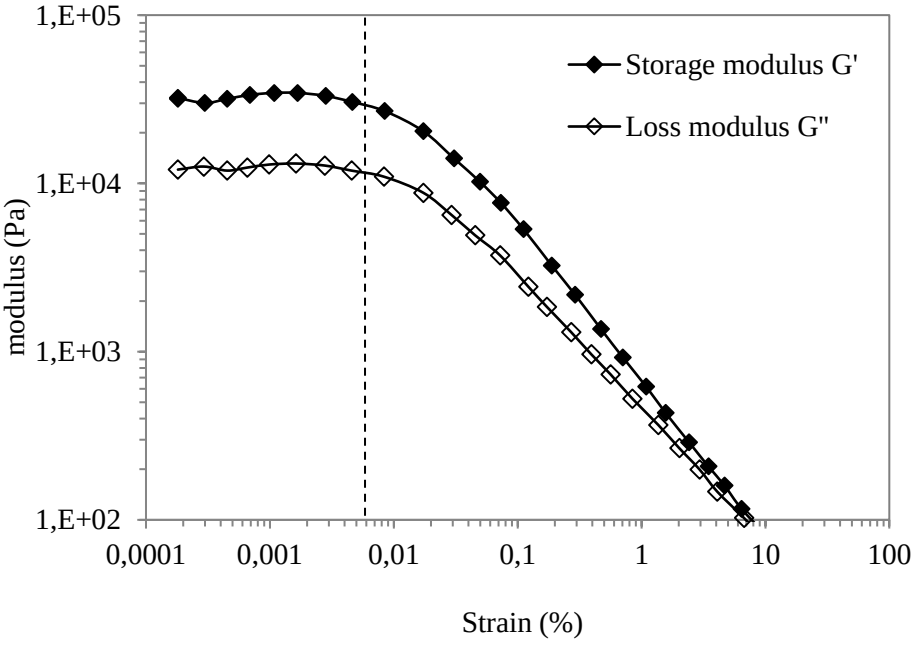
The critical strain in oscillatory tests (at the end of the LVED) is also associated to the breakage of C-S-H links between cement particles [8]. Nevertheless, the formation of early hydrates at the contact points between particles during the dormant period of the cement hydration is not clearly elucidated. According to Sujata and Jennings [24], after 10 min of hydration, C_3S gets covered by C-S-H, while Gauffinet et al. [25] rather reported 1 hour of hydration. Nachbaur et al. [11] reported that the critical strain remains the same from mixing to after setting suggesting that particles are held together by strong physical forces. Fig. 9 shows an example of the evolution of the storage modulus as a function of hydration time. It can be observed, as reported by Nachbaur et al. [11], that as the hydration progresses, the storage modulus increases but the critical strain remains constant. According to Nachbaur et al. [11], just after mixing, there are only a few contacts between cement particles, this small contact surface corresponds to low storage moduli. As the anhydrous cement particle are covered with hydrates, the contact surface increases and the storage modulus increases too.



254

255 **Fig. 9. Evolution of the storage modulus G' with hydration time (cement paste with w/c=0.45)**

256 Furthermore, as shown in Fig. 10, calcite suspension exhibits a linear viscoelastic domain with a
257 critical strain of the order of few hundredths (10^{-2} %), as in fresh cement paste. This critical strain
258 cannot be explained by the formation of hydrates, since calcite suspension is chemically inert.
259 The interacting particles network in such suspension is principally due to the colloidal attractive
260 forces and to direct contacts between particles [29].



261

262 **Fig. 10. Storage and loss moduli in calcite suspension with water to solid ratio of 0.35**

263 According to these observations, the effect of w/c ratio and SP dosage on the deformation capacity
264 of fresh cement pastes could be explained. In fact, as shown in Fig. 11-a, immediately after the

end of mixing, the cement paste is a concentrated suspension of more or less dispersed particles. The average spacing between cement particles (λ in Fig. 11-a) is of the order of µm [34,35]. Guo et al [34] found, through yield stress calculations, that the distance between cement particles is ranging from 2.5 to 5 µm, while Zhu et al. [35] obtained an average spacing between cement particles ranging from 0.9 to 1.4 µm. It is worth noting that this distance depends strongly on w/c ratio and particle size distribution.

After a few seconds, which corresponds to the characteristic time of flocculation [8], a flocculation occurs due to colloidal attractive forces which lead to the formation of a network of interacting particles that occupies the entire volume of the sample; i.e. there exist a continuous percolation path able to withstand a minimum stress (Fig. 11-b). The behavior of cement paste kept at rest tends towards a solid-like behavior. As the hydration progresses (after few minutes), the early hydrates (in red in Fig. 11), which preferentially form on the surface of the anhydrous phases, increase the contact between cement particles (Fig. 11-c). Zingg et al. [26] found that in the absence of superplasticizer, early hydrates tend to precipitate immediately after mixing on clinker surfaces forming hydration rims leading to agglomeration and interlocking bridges. However, in the presence of superplasticizer, the early hydrates precipitate in the pore solution and the agglomeration is limited. In addition, the thickness of hydration rims around the clinker grains is more greater in the absence of superplasticizer [26]. The separation distance between cement particles (h in Fig. 12) after agglomeration is of the order of nm [13,15,31]. Values ranging from 5 to 10 nm can be found in the literature. This separation distance depends on the conformation of superplasticizer [36,37]. It has to be kept in mind that as the hydration progresses, the dissolution of anhydrous cement increases and leads to an increase in the number of fine particles and an increase in ionic strength which enhances flocculation [38,39].

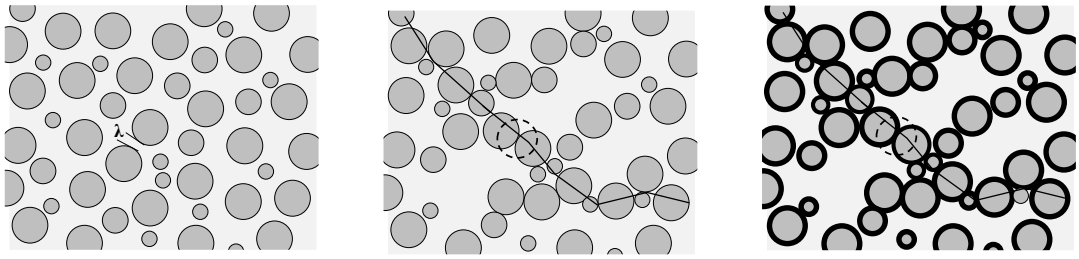


Fig. 11. Illustration of the formation of a percolation path: (a) cement paste immediately after the end of the mixing, (b) few seconds after the mixing, (c) few minutes after the mixing (in bold: early hydrates)

The application of shear stress, a few seconds or a few minutes after mixing, induces a macroscopic deformation that can be described at the local scale by the relative movement of two neighboring cement particles [8]. When the critical strain (γ_c) is reached, the continuous percolation path is broken locally (change in the particle/particle contact), but this does not mean that the flow is initiated [15]. In fact, this critical strain of the order of 10^{-2} % is consistent with a change in the separation distance (h) as illustrated in Fig. 12-a (of the order of nm) [8]. However, the largest strain γ_0(peak in the shear stress-strain curve or transition strain in oscillatory measurement) describes large structural changes and reorganizations of cement particles in the shear plane corresponding to the initiation of flow. Thus, when the largest strain is reached, cement paste behaves like a liquid (steady state flow) and tend towards the dispersion state illustrated in Fig. 11-a. Thus, the largest strain involves a large change of the order of µm as illustrated in Fig. 12-b.

It thus appears that the macroscopic shear strain is closely related to the interparticle distance between cement particles which dictates the deformation capacity. This interparticle distance depends on several factors such as solid volume fraction and superplasticizer dosage, and conditions the magnitude of interparticle forces. However, when a percolation path is formed, the interparticle distance (h) depends only on the presence of superplasticizer [13,33].

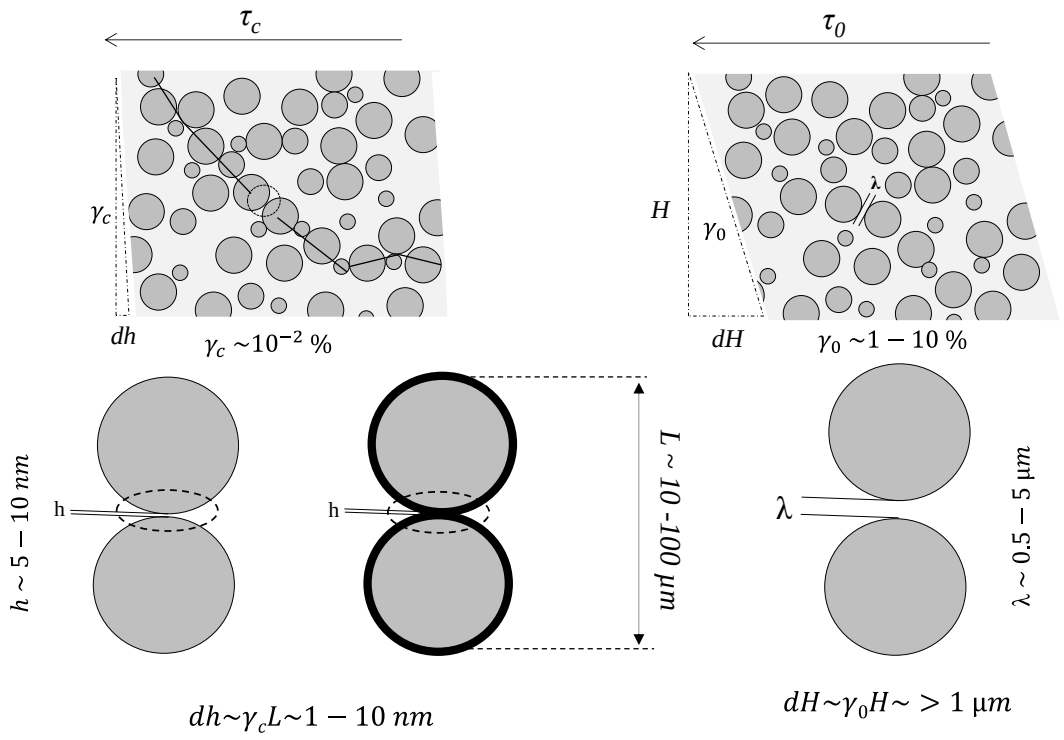


Fig. 12. Illustration of the formation of a percolation path and the shearing of a cement paste (in bold: early hydrates)

The critical strain γ_c is strongly affected by SP dosage. In fact, the electrosteric effect induced by the presence of superplasticizer leads to increase of separation distance (h) and thus to the decrease of the magnitude of attractive forces [13,33]. This could explain the increase of the deformation capacity of cement paste with superplasticizer, and thereby the variation of the critical strain. However, this critical strain is slightly affected by w/c ratio (in the usual concentration range). In fact, when flocculation occurs, the separation distance (h) depends very slightly on w/c ratio [33].

Furthermore, the largest strain (γ_0) associated with the flow onset seems to be more influenced by w/c ratio. It increases with decreasing w/c ratio [1] (Fig. 4). As reported by Guo et al. [34], the average spacing between cement particles increases with w/c ratio. The effect of w/c ratio on the largest strain (or transition strain) could be explained by the deformation capacity. In fact, increasing the solid volume fraction leads to an increase of the number of particles which may be approximately estimated as ϕd^{-3} (ϕ is the solid volume fraction and d is the mean diameter) [8].

This results in the decrease of the average spacing between particles [34] and the strain required to initiate the flow and to induce large structural changes is expected to increase.

4 Conclusions

Rheological characterizations using oscillatory method and yield stress measurements were performed to examine the deformation capacity of fresh cement pastes. The effect of w/c ratio and admixture on these viscoelastic properties can help to better understand the origins of the deformation capacity of fresh cement paste.

It was shown that water to cement ratio has no effect on the critical strain at the end of the LVED, but decreases the storage modulus. This reflects the decrease of the cement paste stiffness.

Furthermore, SP dosage was found to have a strong effect on the LVED. In fact, the increase of SP dosage leads to the increase of the critical strain and the decrease of the storage modulus reflecting an enhanced dispersion of cement particles.

The critical strain at the end of the LVED and the smallest strain in the shear stress-strain curve obtained by yield stress measurement could be associated with strong physical forces (colloidal forces enhanced by early hydrates formation), while the transition strain (G' = G") and the largest strain in yield stress measurement could be associated with large structural reorganizations leading to the flow onset.

Declarations

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