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Recent advances on yield stress and elasticity of fresh cement-based materials

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ABSTRACT

The interest in the elastic and yielding properties of fresh cement-based materials has recently grown due to the development of new processing techniques, which avoid the use of standard formworks. Without support, the material shaping relies only on the mechanical properties of the fresh material. Within this frame, the point of this paper is to gather the accepted knowledge along with the most recent advances on both yield stress and elasticity of fresh cement-based materials. In the first part, we will go through the physical and chemical origin of these macroscopic properties and their evolutions. In the second part, we will describe the way they can be measured while the third part will deal with the way they can be controlled and tuned. Finally, the most recent models for both properties prediction from mix design and processing modeling from rheological measurements will be described.

1. Introduction

The rheological behavior of fresh cement-based materials has been an important field of research for decades. It has, however, over the years primarily focused on the way fresh cement-based materials flow. As concrete, mortar or grouts processing mostly involves sub-processes such as mixing, pumping, spraying and pouring, non-Newtonian **fluids** mechanics was considered to be the sub-field of mechanical sciences that could improve our understanding of fresh cement-based materials processing.

The elasto-plastic behavior and the material ductility were therefore features that were considered to belong to the set of mechanical properties that only hardened concrete was concerned with and fresh cement-based materials were classified as non-Newtonian granular fluids.

It is interesting enough to note that beginning of setting was, within this frame, historically defined as the time required for the material to display an elastic modulus. It was however shown that fresh cement-based materials do display an elastic behavior for observation times as short as a few seconds after the end of mixing [1,2]. After such short time scales, the percolated network of interacting particles indeed display an elastic modulus of the order of several hundreds of Pa and a strength of the order of a few tens of Pa. 28 days and an extremely complex hydration reaction later, this strength has turned into several tens of MPa. As a force sensor able to measure a strength variation over 6 orders of magnitude does not exist, beginning of setting was therefore defined as the time required for the material to display an elastic modulus that was measurable using a standard concrete compression testing machine (i.e. unable to measure the low values of elastic modulus and strength typical of fresh materials). This contributed into strengthening the idea that fresh-cement based materials were pasty fluids with neglectable elasticity.

It has however to be acknowledged that, until recently, the knowledge of the elastic behavior of fresh cement-based materials was of little interest as they were supposed to flow from the mixer to the formwork, fill it properly under the sole effect of gravity and set. In order to ensure that the material properly fills the formwork along with the centimetric porosity between the reinforcing steel bars, high energy vibrating pokers (vibration amplitude of the order of a couple mms for frequencies of the order of couple hundreds Hz) were used to apply accelerations roughly ten times higher than the natural gravity acceleration to the fresh material. At such a level of stress, any interactions or elastic inter-particle network is destroyed and the material behaves indeed as a non-Newtonian liquid.

Only recently, with the increased industrial use of extremely fluid cement-based materials such as self-compacting or self-leveling mortars, concretes or floor screeds, elasticity and yield stress started to matter. Without vibration, the filling degree or the shape conformity was shown to depend on the competition between gravity and yield stress ([3]) whereas some features such as formwork pressure were

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related to the elasticity and structuration (i.e. the increase in elastic modulus or yield stress with resting time) of the fresh material [4], [108].

Even more recently, the development of 3D printing technologies for and by the concrete industry stressed the need for a better assessment and understanding of the elastic and yield properties of fresh cement-based materials. Most 3D printing applications and demonstrators are based on extrusion, where a cement-based material is extruded to form sequential layers via a digitally controlled nozzle mounted on a robot arm, gantry or crane. The processes are similar to conventional Additive Manufacturing processes except that the material and scale of manufacture generate unique challenges and questions: the formulation of mixes that are pumpable, yet stable in shape once placed without formwork; the production of reliable interlayer bonding; and how to control the geometry of printed parts within appropriate geometrical tolerances. All these questions relate to the yield stress and elasticity of fresh cement-based materials.

Within such a frame, the point of this paper is to gather the accepted knowledge along with the most recent advances on these features. In the first part, we will go through the physical and chemical origin of these macroscopic properties in the fresh state and their evolutions. In the second part, we will describe the way they can be measured while the third part will deal with the way they can be controlled and tuned. Finally, the most recent models for both properties prediction from mix design and process modeling from rheological measurements will be described.

2. Yield stress and elasticity in fresh cement-based materials: physical origin

2.1. Brownian motion, Van der Waals forces and buoyancy

It is now accepted that the dominant interactions in a fresh cement paste are the following: colloidal attractive forces, gravity forces and Brownian effects [5]. Hydrodynamic forces (including laminar viscous dissipation, particle kinetic energy and lubrication) only occur when the system is sheared and flows. Note that, once mixing is over and the interstitial fluid is forming a continuous phase, capillary forces in cement-based systems can be neglected.

The main competition in the system at rest involves therefore colloidal attractive forces, Brownian motion and gravity forces. This competition was reported to result in one of the following regimes [6]:

If **colloidal attractive forces dominate Brownian motion**, which is the case for most cementitious materials in industry, a percolated network of interacting particles appears within the suspension. It is able to withstand an external stress up to a critical value called yield stress. Because it originates from the attractive van der Waals forces [109], this yield stress scales with the inverse power two of the inter-particle separating distance and is therefore strongly dependent on the presence of adsorbed polymers at pseudo-contact points between particles (see Section 3). This percolated interaction network has a rigidity, which dictates in turn the material elasticity [1,2,7].

If **Brownian motion dominates colloidal attractive forces** (in the case of diluted systems or systems at high admixture concentration (see Section 3)), the suspension does not have any yield stress. The network of attractive colloidal interactions is instantaneously destroyed by Brownian agitation and is not able to withstand any external stress. In this particular case, Brownian motion could dominate gravity forces. The result would be a stable Newtonian viscous suspension. However, according to the order of magnitudes of the two phenomena, this cannot happen in the case of typical cementitious materials. Suspensions, in which Brownian motion dominates colloidal forces, shall therefore always be unstable and display high levels of sedimentation [5,8].

If **colloidal attractive forces dominate gravity forces**, particles are trapped in the colloidal interactions network and are therefore not able to rearrange their relative positions. The suspension is stable. There is neither bleeding nor sedimentation and the fresh paste stays homogeneous.

If **gravity forces dominate colloidal attractive forces**, particles may settle. This induces a relative displacement of the cement particles within the interstitial fluid or a relative displacement of the interstitial fluid between the cement particles. This phenomenon called “bleeding” in practice is time driven and is influenced by the viscosity of the interstitial fluid and the permeability of the porous medium formed by the interacting cement grains (which mainly depends on the solid volume fraction and on the average diameter of the grains [9]). It was shown recently that bleeding relates to the formation of preferred water extraction channels resulting from a local and partial rearrangement of the cement particles configuration [8]. As such, it is a heterogeneous process in contrast to the former approach in literature describing bleeding as a homogeneous consolidation phenomenon [10]. Within very specific conditions, bleeding may be adequately limited by the above mix design factors. It is in this regime only that fluid cement pastes allowing for the production of fluid concrete can be mix designed.

2.2. Hydrates nucleation, thixotropy and structuration

Casting of concrete occurs within the induction period, which is generally considered to be a period of little chemical activity. However, there are still the effects of cement hydration, where early hydrates form and subsequently impact the workability or rheology of the fresh suspension. This has been more precisely tied to C-S-H nucleation in both cement [7] and tricalcium silicate [1] systems, and more recently supported by Roussel et al. [2] through a description of structuration and thixotropy. In this latter study, the general behavior of fresh cement-based systems at rest was described, and it is again presented here in Fig. 1 through yield stress evolution and a microstructural view of cement interaction and C-S-H nucleation and growth. Immediately after mixing, the cement particles are in a dispersed state, where the degree of dispersion is dependent on mixing energy (Fig. 1a). Once at rest, the non-contact, colloidal interactions discussed in Section 2.1 lead to early (few *sec*) flocculation of the fresh suspension (Fig. 1b). From there, C-S-H nucleation occurs and forms bridges between cement particles/flocs (Fig. 1c), and gives rise to an increasingly interconnected, rigid structure through continued C-S-H nucleation and growth (Fig. 1d). This

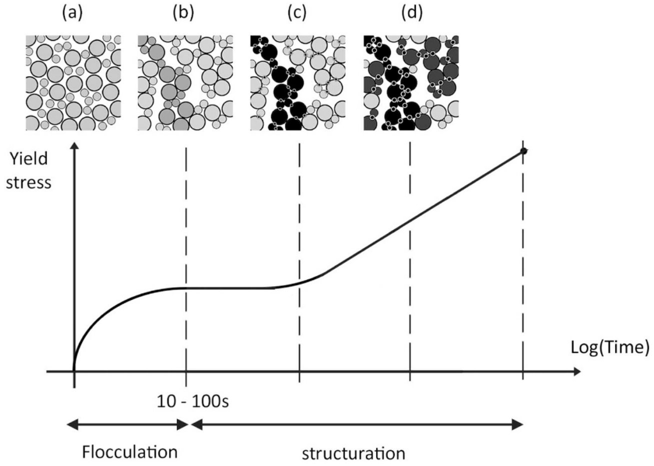

Fig. 1. General behavior of fresh cement-based systems at rest described through yield stress evolution and underlying cement particle interaction and C-S-H nucleation and growth. The freshly sheared suspension starts in a dispersed state (a), then exhibits initial flocculation due to non-contact interactions. C-S-H nucleation occurs, forms bridges between cement particles/flocs (c), and gives rise to an increasingly interconnected, rigid structure (d). Reproduced from [2].

structure underlies increase in yield stress (flow onset) and elasticity over time.

Thixotropy – structural breakdown and build-up – is theoretically a completely reversible phenomenon. However, this is not the case for cement-based materials due to the continuous progression of hydration. Cement thixotropy arises from a combination of general flocculation/deflocculation behavior, as well as formation/breakage of C-S-H bridges [2,11]. If there is sufficient shearing energy (i.e. mixing, pumping, casting), the aforementioned C-S-H bridges can be broken down and flow can be restored. At the same time, some C-S-H bridges will be irreversible under the given shearing conditions and a corresponding level of structure will remain. Over time, the presence of irreversible C-S-H bridges will increase (in size and frequency) [12,13], which gives rise to an increase in yield stress associated with flow onset.

Role of hydration on workability has been of practical significance for workability loss, where mixing/shearing can no longer restore flowability. And thixotropy has been of practical significance for select applications, e.g. SCC formwork pressure where it is now well accepted that structural build-up behavior of the fresh SCC has a direct effect on lateral pressure exerted on the formwork wall [108], [14,15]. More recently, the connection between structural build-up behavior and C-S-H nucleation has been shown [16–18]. The role of C-S-H nucleation on structural build-up kinetics (both flow onset and elasticity) becomes critically more important for AM, as recently summarized by Reiter et al. [19]. Short-term kinetics are important in controlling material shape stability immediately after deposition, while long-term kinetics (approaching setting) is important for determining building rate. It has been shown that yield stress evolution goes from linear to nonlinear over longer periods [20], which has more recently been tied to increase in solid volume fraction and decrease in packing fraction by C-S-H nucleation [16]. This linear to non-linear yield stress evolution has been incorporated into a theoretical framework to predict building rate for AM [20]. It can finally be noted that the behavior of the material becomes closer to the one of a brittle solid and further from the one of a plastic paste [21].

2.3. From cement paste to mortars and concretes

Adding particles such as sand and/or coarse aggregates to a cement paste to produce a mortar or a concrete can conceptually be considered as adding rigid inert non-Brownian non-colloidal particles into a yield stress fluid as long as the typical size of the constitutive elements of the paste (i.e. cement grains of average size of 10 μm) can be neglected in front of the typical size of the particles (i.e. sand or coarse aggregates of respective average size of 1 or 10 mm). In this specific case, the rheological properties of the suspension shall depend only on the rheological properties of the suspending fluid (as long as the presence of the particles do not affect it) and on the particle volume fraction, shape and size distribution. With the aim of providing such generic results, [22] have performed an experimental study on a broad range of materials (See Fig. 2). They have suspended beads of various sizes and made of various materials in very different pastes whose common point was to exhibit a yield stress. They showed that the dimensionless yield stress of such mono-disperse suspensions indeed relates to the particle volume fraction only. It should be noted that this should apply to any homogeneous and isotropic suspension of particles in a yield stress fluid as long as the particles have only mechanical interactions with the paste (i.e. when there are no specific physicochemical interactions between the particles, and between the particles and the paste). The same authors have moreover studied suspensions of coarse spherical particles in a cement paste and demonstrated that they behave exactly as any other suspension once all artifacts have been ruled out by adequate experimental protocols [23]. All the above studies emphasize the fundamental role played by the packing properties of the inclusions added to the cement paste [24].

From a thixotropy point of view, it was also shown that it is sufficient to know how the interstitial cement paste evolves in time to predict the mortar or concrete evolution (assuming there is no water absorption). As a consequence, if the mechanical impact of the non-colloidal particles is to increase the yield stress by a given factor, then their impact on the structuration rate of the paste is to increase by the same factor. It is thus sufficient to measure the cement paste yield stress evolution in time and to measure the increase of yield stress with volume fraction for a single resting time to infer the value of the structuration rate of the mortar or concrete at any time [23].

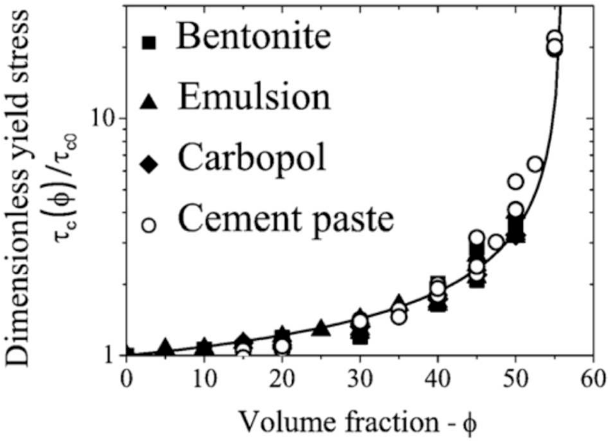

Fig. 2. Dimensionless yield stress (i.e. the ratio between the yield stress of the suspension for a given volume fraction of beads and the yield tress of the suspending fluid) as a function of beads volume fraction for various suspending yield stress fluids including cement pastes.
Reproduced from Mahaut et al. [23].

3. Yield stress and elasticity in fresh cement-based materials: measurements

3.1. Industrial test for yield stress measurements

Regardless of the exact standards or geometry of slump, slump flow, L-Box or J-ring tests, the following general procedure is common for these tests: a mold or reservoir of a given standard shape or volume is filled with the cementitious material to be tested. The material is poured, a mold is lifted or a gate is opened and flow occurs if the shear stress generated by gravity inside the sample is higher than the yield stress of the material. As the material is flowing, the thickness of the sample and, therefore, the stress generated by gravity decrease. If the stress in the tested sample becomes lower than the yield stress of the tested material, flow stops. The shape at stoppage is therefore directly linked to the yield stress of the tested material if inertia or surface tension effects can be neglected. Several correlations between the measured geometrical quantities such as slump flow and slump and yield stress can be found in literature [110,3,25–35].

3.2. Rheometry: flow onset and critical strain measurements

When the flow onset and critical strain of fresh cement-based materials are of interest, a typical measurement consists of using a rheometer and applying a constant low shear rate, starting from rest, and then observing the characteristic stress peak and critical strain associated with flow onset. However, as these materials are thixotropic, their rheological behavior depends on the flow history and their characterization requires a rigorous procedure to ensure reproducibility. Before starting the measurement, the suspension has to be pre-sheared to ensure that all tests start from the same destructed state [36]. Moreover, in order to study in detail the evolution of shear stress over a large range of strains, a compromise must be reached between the duration of the test and its accuracy.

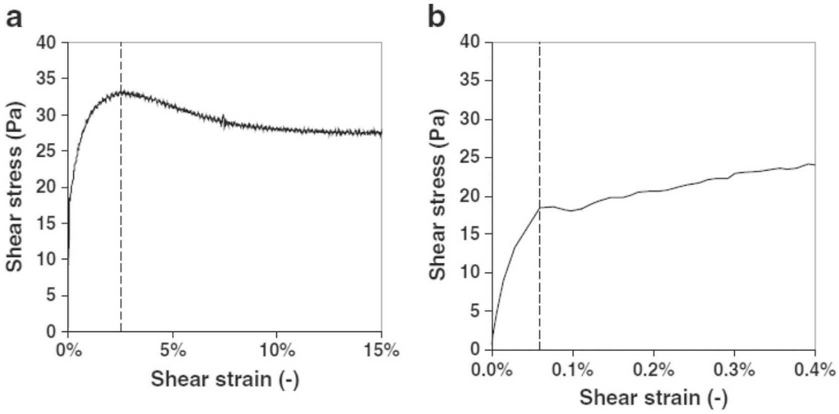

Fig. 3. Shear stress as a function of shear strain during a Vane test on a cement paste with a water to cement ratio of 0.4. (a) Linear shear strain scale from 0 to 15%; (b) Linear shear strain scale from 0 to 0.4%.
Extracted from Roussel et al. [2].

A specific measurement protocol has been developed by Roussel et al. [2] for cement suspensions. First, the sample is pre-sheared at 150 s^{-1} for 200 s. After 5 min of resting time, a constant shear rate of 0.005 s^{-1} is applied to the sample.

This protocol allows for the measurement of a linear increase of shear stress corresponding to the elastic behavior of the material in its solid regime. Above a critical strain around a few % and when shear stress reaches yield stress, the material starts to yield and flow (see Fig. 3a). This stress peak is associated to the breakage of the network of attractive colloidal interactions between cement particles. At a critical shear strain of the order of few hundredth of %, another peak can be identified and is associated to the breakage of the hydrates formed between flocculated cement grains (see Fig. 3b).

3.3. Rheometry: oscillations

Small amplitude oscillatory shear (SAOS) is a common way to probe the viscoelastic properties of soft materials, and it has been found to be suitable for fresh cement pastes to study hydration and stiffening behavior (or what we now term structuration) [37–40]. In SAOS, a small sinusoidal strain is applied to the material to obtain a stress response. The storage modulus (G') is the in-phase, elastic component of the response while the loss modulus (G") is the out-of-phase, viscous component. The complex modulus ($G^* = G' + G''i$) and phase lag provide further description of viscoelasticity. Through performing a strain sweep, i.e. progressively increasing amplitude, we can obtain a measure of critical strain, which marks the end of the linear viscoelastic regime (LVR) – theoretically the limit of the material's ability to respond elastically and keep its structure intact. Within the LVR, G' remains constant and independent of applied strain. If the critical strain is exceeded, there is a significant drop in G', indicating the structure has been irreversibly broken. A frequency of 1 Hz is commonly used for cement pastes and found to be within the LVR. And the critical strain is typically found to be in the order of 10^{-4}, which corresponds to the scale of C-S-H bridges that form between cement particles during the early stages of hydration [2]. Therefore, SAOS can be used as a tool to probe the rigid structure formed progressively through C-S-H nucleation and growth, discussed in Section 2.2.

By applying a sinusoidal strain within the LVR, we can obtain a continuous measure of structural build-up of a material at rest. For cement-based systems, it is well accepted that monitoring G' provides a measure of structure due to rigidification and, since the material is probed within the LVR, resultant elasticity. Further, G' is related to instantaneous (or apparent) shear modulus, which is the slope of the shear stress-strain curve obtained by applying a sufficiently low shear rate. Importantly, it should be noted that short-term (few *sec*) increase in G' is tied to colloidal interactions, while long-term linear increase in G' is due to C-S-H nucleation [2]. This has more recently been supported by Mostafa and Yahia, [41] in comparing G' and phase angle evolution between cement versus model calcium carbonate suspensions – in the latter there was a short-term increase in G' and decrease in phase lag due to percolation, and no long-term increase due to the absence of hydration and corresponding rigidification. A physico-chemical model has been proposed that can predict structural build-up due to colloidal interactions and chemical rigidification based on mix parameters [42].

It has been shown that increase in G' does not necessarily coincide with an increase in static yield stress due to differing mechanisms [17], i.e. G' arises from C-S-H bridges while yield stress arises from a combination of colloidal interactions and C-S-H bridges that remain unbroken at higher applied strains. However, since C-S-H nucleation is an overlapping mechanism, these parameters have also been found to be similar [43]. In evaluating structuration, it is therefore necessary to measure both yield stress (through flow onset) and elasticity (through oscillations). This becomes particularly important for AM, as we are interested in the contribution of both colloidal and hydration effects on the development of the undisturbed structure for controlling shape stability of the layer, building rate, and ultimately buckling stability of the layered structure. It should be noted that the potential of large amplitude oscillatory shear to characterize fresh cement pastes has recently been demonstrated [44]. Although it can be a powerful characterization tool for evaluating thixotropy, its suitability for cements and quantitative interpretation of data needs further exploration.

4. Yield stress in fresh cement-based materials: effects of admixtures

4.1. Repulsive inter-particle forces and decrease in yield stress

Several types of admixtures can decrease the strength of the flocculated network of cement particles in a paste by generating repulsive forces between particles and increasing therefore the average inter-particle distance (see Section 2.1) [45]. For instance, when adsorbed on cement surfaces, concrete dispersants can provide electrostatic and/or steric repulsion between particles. The most efficient and famous ones are the *comb*-shaped polycarboxylate ether (PCE) super-plasticizers that have a negatively charged backbone adsorbing on particles surface and non-adsorbing side chains inducing steric hindrance [45,46].

At equilibrium, adsorbed macromolecules have a preferred conformation of adsorption on the surface of cement particles [47,48]. As soon as two covered particles approach and the layers of polymer overlap, a repulsive steric force occurs between the particles. This comes from a change of adsorption conformation of the polymer, which results in a loss of entropy, together with a rise of osmotic pressure coming from an increase of the concentration of polymer between the two approaching particles, which prevents them from approaching further [49].

The coverage degree and the thickness of the layer of adsorbed dispersants are therefore of great importance as they dictate the minimum distance between two particles before repulsion and impose therefore the value of the attractive Van der Waals forces. This means that they rule the dispersion ability and therefore yield stress and elasticity. They also depend on the dosage of polymer and on the surface occupied by one molecule, which is itself dependent on the molecular structure of the polymer [47-49].

4.2. Attractive inter-particle forces and increase in yield stress

4.2.1. Bridging forces

Bridging forces arise when a polymer chain adsorbs simultaneously at the surface of two or more particles. For bridging to occur, the polymer chain must be long enough to reach the surface of at least two particles and must have an affinity with the surface particle. It was shown by Tadros [50] that an optimal bridging flocculation is attained at half particles surface coverage. At higher concentrations, an adsorbed polymer on one particle might not find an empty site on another particle. In cement based materials, most viscosity modifying admixtures (VMA) are able to bridge cement particles, which increases the macroscopic yield stress of the suspension to a certain extent [51,52] (see Fig. 4). Some VMAs also strongly modify the critical strain of cement paste. By comparing the flow onset of the reference cement paste and cement pastes containing polyacrylamide and cellulose ethers, we note that cellulose ether were found to allow for the mix design of softer systems (i.e. lower elastic modulus) in comparison with the reference cement paste and the cement containing polyacrylamide [51,52]. On the other hand, pastes containing polyacrylamide were found to exhibit a higher elastic modulus. Such organic admixtures are essential for promoting particle flocculation for shotcrete applications, mono-layer render mortar or tile adhesives [53] along with additive manufacturing of concrete [54].

4.2.2. Attractive depletion forces

Fig. 5 shows the evolution of a cement paste yield stress as a function of PCE dosage. In the first regime (i.e. low dosages), we note a decrease in yield stress as PCE dosage increases. However, above a critical concentration, the latter trend is inverted and an increase in PCE dosage leads to an increase in yield stress. For this PCE and in this dosage range, cement particle surfaces are fully covered by adsorbed PCE and any additional PCE remains in the suspending fluid. These results suggest that excess in super-plasticizer may be at the origin of attractive depletion forces, which causes a fluidity loss.

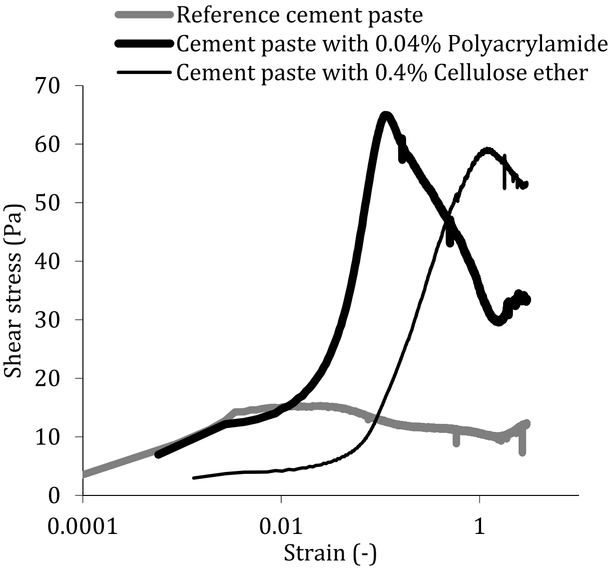

Fig. 4. Flow onset measurements for a reference cement paste and pastes containing Polyacrylamide and Cellulose ether (mass dosages).

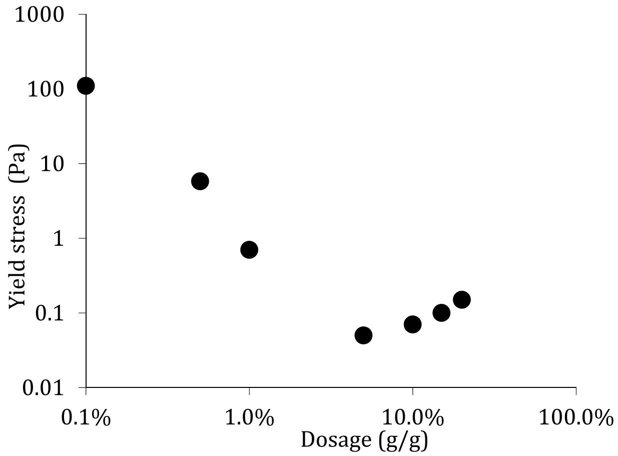

Fig. 5. Yield stress of cement paste as a function of PCE dosage (W/C = 0,3). Extracted from Bessaies-Bey et al. [55].

It is now accepted in the literature of colloidal particles that the addition of non-adsorbing polymer to a suspension can generate depletion attractive forces, which may cause particle flocculation [56,57]. When a polymer has no affinity with a surface it is excluded leading to a formation of a region of pure solvent. The differences in osmotic pressure between the polymer depleted (or pure solvent) region and the bulk polymer solution lead to an attraction between the particles. In cement based materials, Bessaies-bey et al. [55] showed recently that non-adsorbed polymers induce attractive depletion forces, which may lead to an increase in cement paste yield stress. These forces mainly depend on the polymer concentration rather than their molecular weight.

It should be kept in mind that, in the absence of super-plasticizers, Van der Waals attractive forces dominate depletion forces and the consequence of non-adsorbing polymers on yield stress is negligible. However, in the presence of super-plasticizers, the magnitude of the attractive van der Waals forces decreases (see Section 4.1) and attractive depletion forces induced by non-adsorbing polymers become important and greatly contribute to yield stress and elasticity.

4.2.3. Hydrophobic forces

Although surfactant molecules are mainly incorporated in cement based materials to stabilize aqueous foams, it was recently shown by Feneuil et al. [58] that these molecules can adsorb on the surface of cement particles and introduce attractive hydrophobic forces in the system.

When adsorbed at the surface of cement particles, surfactants can turn the surface hydrophobic. As hydrophobic surfaces tend to attract each other [59,60], the suspension flocculates and the yield stress increases. It should be kept in mind that, above a critical concentration of surfactant in solution, micelles may form and affect the mechanism of action of the surfactant.

4.3. Competitive adsorption between admixtures

Modern cement-based materials tend to include more than one type of admixture in order to achieve required rheological properties. However, the blending of these chemical admixtures has to be well controlled to limit incompatibilities and to achieve the intended effect. As shown in the above sections, the mechanism of action of most

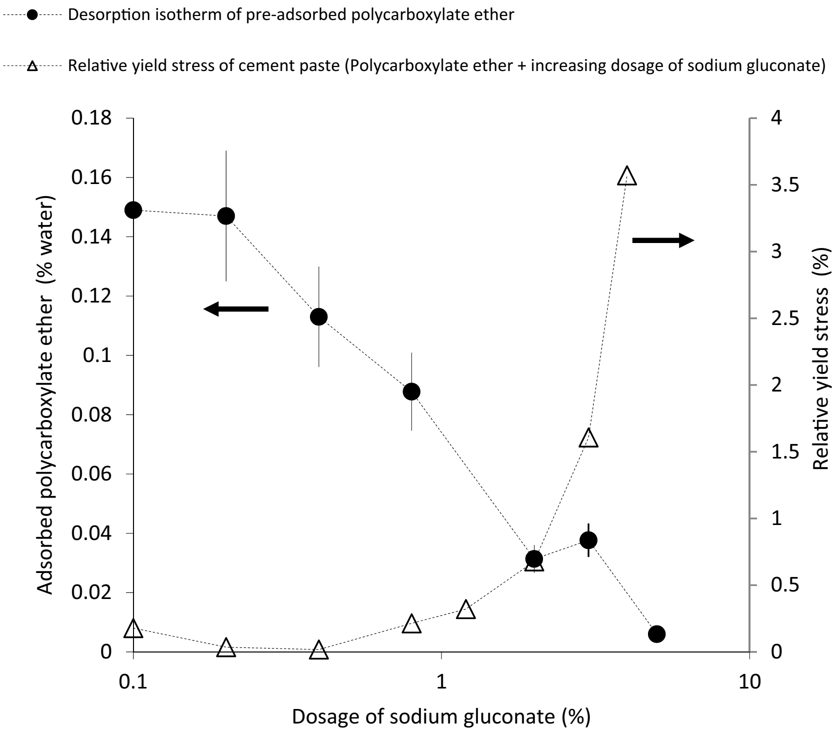

Fig. 6. Desorption of a superplasticizer (polycarboxylate ether) in the presence of a retarder (sodium gluconate) (left y axis) and consequences on the yield stress (right y axis). The relative yield stress is the ratio between the yield stress of the cement paste with admixtures and the yield stress of the reference cement paste.
Adapted from Bessaies-Bey et al. [66].

chemical admixtures is very sensitive to their adsorption on the surface of cement particles. The blending of these chemical admixtures can generate a competitive adsorption on particles surface, which will, in turn, influence their performances. Many examples of competitive adsorption between a superplasticizer and sulfate ions [47,48,61], hydroxides [62], citrates [63] and other organic admixtures [64–66] have been studied in literature. By occupying the adsorbing sites at the surface of cement particles, so-called “displacers” restrict the adsorption of super-plasticizer and considerably affect their dispersion efficiency as shown in Fig. 6 in presence of sodium gluconate. Depending on the industrial application, competitive adsorption can also be an advantage leading to synergetic effects between adsorbing species. Indeed, it was observed in [66] that a super-plasticizer can inhibit the adsorption of VMAs, which, in turn, enhances their stabilizing effects.

In addition, adsorption and desorption kinetics could be at the origin of the evolution of material rheological behavior over time. In some cases, the exchange could be rapid, as the desorption of a superplasticizer by sulfate [61] or sodium gluconate [66]. However, as the desorption of an already adsorbed macromolecule requires the simultaneous desorption of the anchor groups, the exchange could also be a very slow process in the order of hours, days or even years [67].

To control the outcome of competitive adsorption, several recent studies focused on the modification of the chemical structure and surface affinity of the organic admixtures [68–70]. Moreover, it should be kept in mind that competitive adsorption is only observed at high surface saturation (i.e. high surface coverage) where there are not enough sites for adsorbing species. The extent of this regime can therefore be controlled by tuning the polymer dosage, adsorbed conformation or adsorption energy.

4.4. Admixtures, hydration and structuration

Admixtures do not only modify the colloidal interactions at the origin of the yield stress and elasticity of the material. They may also affect the hydration reaction in the induction period and modify therefore the structuration at rest of the fresh suspension and the associated evolutions in yield stress and elastic modulus (see Section 2.2.). As for most of the admixtures that have the ability to adsorb on cement particles, PCEs, for example, affect hydration by delaying the setting and disturbing the chemical balance between the cement phases [71–74]. Among them, C_3S and C_3A are the most reactive and therefore the most relevant phases regarding the influence of their hydration on the evolution of the rheological properties. In the first minutes after contact with water, the principal hydration mechanisms are their dissolution and the nucleation and growth of their hydrates. C_3A reacts with calcium sulfate and water to form ettringite, and C_3S hydration produces portlandite and C-S-H, for which we have seen in Section 2.2. the major role in the structuration of cement-based materials at rest.

Several reasons were mentioned for the delay of hydration caused by PCEs: the complexation with Ca-ion, the perturbation of hydrates formation and the slowing down of C_3S dissolution [72]. Recent findings firstly highlight the blocking of active dissolution sites by adsorbed molecules as the most realistic explanation for the change of hydration kinetics that leads to a delay of cement setting [75]. Secondly, a direct quantified correlation was found between the retardation and the molecular structure and dosage of the PCEs (Fig. 7). This led for the first time to the possibility of mastering both rheological properties and side effects of using PCEs with respect to their molecular characteristics and therefore to an optimization of the molecular design [76] (See Fig. 8.).

Although the ions complexation and the inhibition or change of hydrates precipitation seem to have less impact on the decrease of reaction rate of cement, their influence on the location and the way hydrates develop is of great relevance regarding structuration build-up and microstructure development [77]. In C_3S pastes, nano-clusters composed of calcium and polymer complexes were observed in the pore solution [78]. This might be linked to the recent findings that PCEs stabilize globular precursors of purely synthesized C-S-H before they convert to the more commonly observed nano-foil like structure [79]. Nanoparticles composed of polymer and hydrate phases were also observed in pore solution of cement pastes [80]. The presence of such particles in the aqueous solution dispersed by the PCEs could most probably be at the origin of a transition from a heterogeneous to homogeneous nucleation [81], that would affect the bridging effect of C-S-H mentioned earlier as well as the final spatial distribution of the

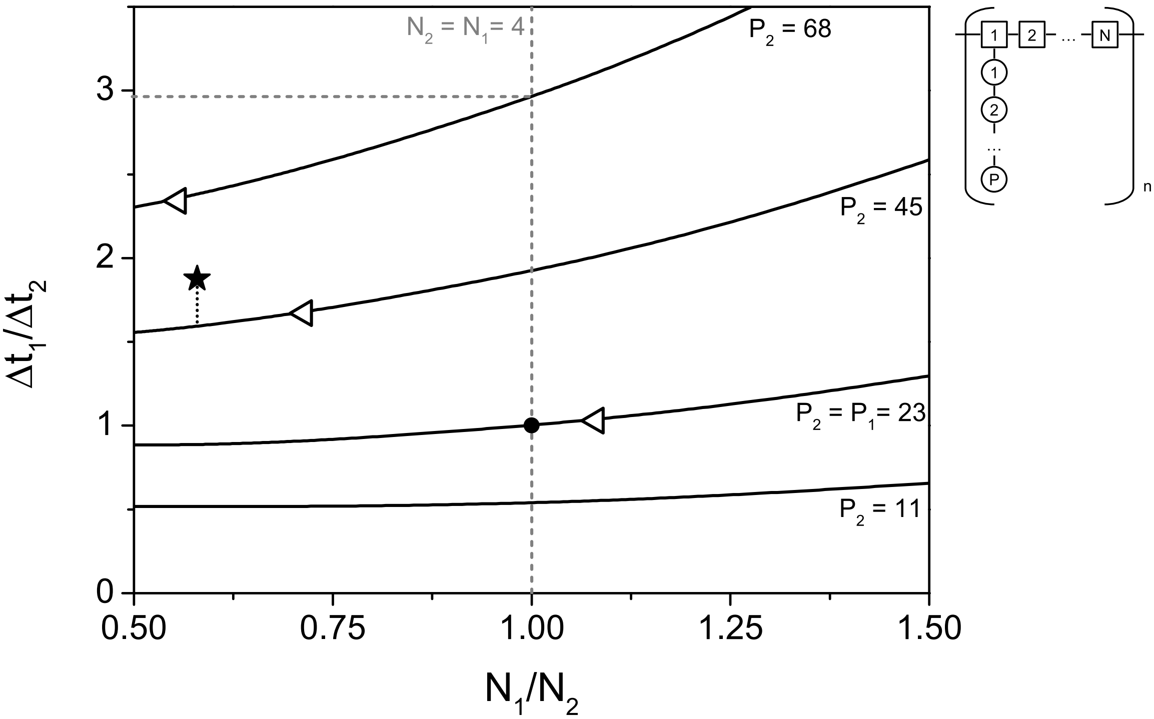

Fig. 7. Abacus of retardation showing the ratios $\Delta t_1/\Delta t_2$ function of N_1/N_2 Ratio. N is the number of monomers in the backbone for one side chain and P the number of monomer in one side chain. This plot shows the evolution of the retardation as a function of changes of structural parameters with respect to a reference polymer dosed to achieve the same dispersion ability. The reference is polymer 1 with $N_1 = 4$ and $P_1 = 23$. The black dot represents the case where polymer 2 has the same structural parameters as polymer 1. The curved lines determine the ratio of retardation $\Delta t_1/\Delta t_2$ for different side chain lengths. The vertical dashed line represents the case where $N_1 = = N_2$. The star represents a polymer that was used to experimentally prove that the prediction offered by this plot is realistic. In this case, for the same rheological properties, the abacus predicts that modifying polymer 1 to polymer 2 with $N_2 = 7$ and $P_2 = 45$ would reduce the retardation by a factor of 1.6. Experimentally, the retardation was reduced by a factor of 1.9.
Reproduced from Marchon et al. [76].

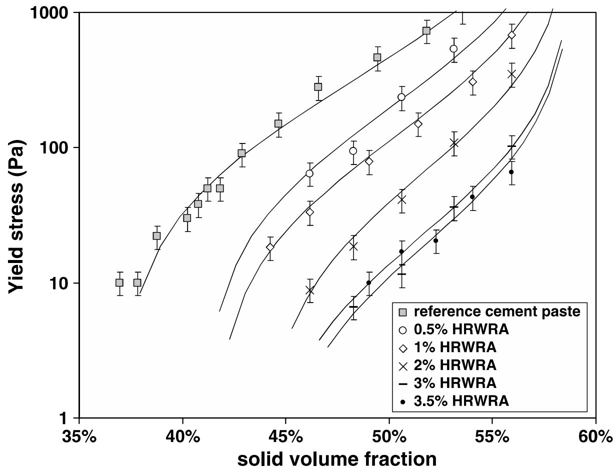

Fig. 8. Yield stress as a function of cement volume fraction for various dosages of High Range Water Reducing Admixtures (HRWRA). Experimental date points along with YODEL prediction (lines).
Reproduced from Perrot et al. [6].

phases in the microstructure [82].

Finally, a recent study focusing on the workability loss of cement pastes containing PCEs highlighted two very distinct and successive regimes [83]. The first one occurring along the induction period shows a linear evolution of the yield stress that is independent of hydration reactions, illustrating the thixotropic behavior of the system. After a so-called onset, the measured exponential increase in yield stress is directly proportional to the heat rate and to the specific surface area of the system. This correlation points out the dependency of rheological properties on the strong precipitation of hydrates in the acceleration period. With respect to PCEs influence, it was observed that this proportionality changes in presence of the polymer, due to the retardation effect, but does not seem to closely depend on the molecular structure of the PCEs.

More generally, admixtures are essential for applications such as concrete 3D printing, where a structural build-up is needed right after deposition of the concrete and followed by a fast stiffening to sustain subsequent layers [19]. Playing along with admixtures and targeting silicates along with aluminates seem to show great potential for printing concrete [54]. For example, this can be done by enhancing ettringite precipitation with shotcrete accelerators or blended cements with calcium aluminate cement for a fast surface development and rapid strength gain. However, the challenge is to choose the perfect mixture proportions between the different systems that are available to avoid an uncontrolled expansion or to not disturb the balance between the main phases of the system. Indeed, provoking ettringite nucleation or having a high aluminate content might strongly influence the sulfate consumption and silicate hydration [71,74]. In term of chemistry of hydration, the sulfate depletion is strongly accelerated and if it occurs before the strong precipitation of C-S-H, the presence of a very high content of aluminum in the pore solution inhibits the dissolution of the silicate phase and therefore delays the precipitation of C-S-H that is the source of the mechanical strength [84,85]. This has a detrimental impact on the early as well as on the late mechanical strength. In term of rheology, this causes a very rapid stiffening, called flash set, and subsequent loss of fluidity.

4.5. Nanoparticles and structuration

It was shown by Juilland et al. [86] that the mechanical action of mixing of cement paste results in the detachment of C-S-H from the surface of particles leading to the enhancement of the main heat peak of hydration. Recent work by Caruso et al. [80] highlighted the formation of nanoparticles in cement pore solution containing super-plasticizers. They asserted that these nano-size particles are either nano-C-S-H, nano-ettringite, nano-AFm, or intramolecular complexes of polymer and cations. More recently, Vandenberg et al. [87] showed that an appropriate combination of mixing energy and super-plasticizer dosage promotes the scratching of nanoparticles from the surface of cement particles and their stabilization in the suspending fluid and hence generates additional nucleation surfaces. These generated nanoparticles enhance the thixotropic behavior of cement-based materials and promote structuration.

In addition, it is possible to further tailor nucleation and structuration by introducing nanoparticles as additives. Highly purified attapulgite nanoclays have been demonstrated to be effective in enhancing thixotropy at relatively low additions (S. [88–90]. Their effect has been tied to the colloidal strain regime, which supports that the clays are enhancing electrostatic interactions between cement particles to enhance yield stress recovery immediately after shear [17]. Due to their high specific surface area, nanoparticles can introduce additional CSH nucleation sites to accelerate hydration, termed seeding effect [91], which can in turn enhance structuration in the fresh state. One challenge of incorporating any nanoparticle type in cement systems is dispersion, where dispersion degree will significantly impact the working mechanism. Therefore the seeding effect is sensitive to processing parameters, i.e. dispersion technique and mixing. This is the underlying reason why, in contrast to flow onset results where increase in yield stress is consistently observed, the effect of nanoclay on SAOS results is much more dependent on processing and pre-shear conditions [17,44,88].

5. Yield stress and elasticity in fresh cement-based materials: modeling

5.1. Yield stress modeling and YODEL

The YODEL is a first principle analysis of yield stress of colloidal particles suspension, which was shown to successfully predict the main parametric dependencies of cement suspensions yield stress [6,92–94]. This model writes:

$$\tau_P \cong m\frac{A_0 a^*}{d^2 H^2}\frac{{\varphi_c}^2(\varphi_c - \varphi_{perc})}{\varphi_{cm}(\varphi_{cm} - \varphi_c)} \tag{1}$$

where we have 5 material parameters: m is a pre-factor, which depends on the cement particle size distribution; It can be computed from a measurement of the particle size distribution. A_0 is the non-retarded Hamaker constant taken as 1.6×10^{-20} J; a* is typical size of the surface defects of cement grains and is of the order of several hundreds of nm [6]); d is the cement particle average diameter d_{50} and is of the order of 10 μm; φ_{cm} is the maximum packing fraction of cement grains. And 3 mixture variables: φ_c is the solid volume fraction of the cement particles in cement paste; φ_{perc} is the percolation volume fraction; It results from the competition between Brownian motion and colloidal attractive forces between cement particles, which, in turn, depend on the admixture dosage [6]. H is the average surface-to-surface separating distance between flocculated cement particles; It depends on the admixture dosage.

5.2. Flow and processing modeling

The previous sections have introduced the experiments allowing for the measurement of yield stress and the model allowing for the prediction of yield stress as a function of components properties and dosage. The present section refers to the mathematical models that link yield stress to the macroscopic flow behavior, by introducing its value into flow equations. As mentioned in the introduction, the common approach to model fresh cementitious materials is based on non-Newtonian fluid mechanics. Here, the macroscopic flow behavior is expressed by constitutive equations, which give relation between the shear stresses and velocity gradients [95]. The commonly accepted constitutive relations for fresh cement-based materials are Bingham and Herschel-Bulkley [96]. The Bingham model (Eq. (2)) captures a linear viscous behavior if the applied stress is higher than the yield value [97], while the Herschel-Bulkley approach [98] assumes that the material behaves non-linearly if the stresses are above yield stress value (Eq. (3)):

$$\tau = \tau_0 + \eta_{pl}\bullet\dot{\gamma} \tag{2}$$

$$\tau = \tau_0 + k\bullet\dot{\gamma}^n \tag{3}$$

where τ is shear stress, τ_0 is yield stress of the material, η_{pl} is plastic viscosity of the material, $\dot{\gamma}$ is the shear rate, k is consistency index and n is power law index. The constitutive relations are integrated into the conservation equations, which govern the fluid flow.

The abovementioned mathematical models found practical applications in numerical concrete flow simulations [99–101]. Due to the computational limits, a complete flow simulation that account for all concrete phases is still not possible; therefore, the above authors used different approximate models that aim to describe the macroscopic flow behavior (rather than its microstructure). Recently, in [102] the researchers studied numerically the effect of yield stress on the final shape in two concrete filling ability tests: slump and channel flow. They compared the numerical predictions of these benchmark flows obtained by several research teams, who used various numerical tools. The comparison demonstrated that, if segregation does not occur, the compared numerical simulations are able to accurately predict the benchmark flows, and concrete filling ability. The numerical results were in agreement with the analytical solutions proposed in [3,30,34], which claim that final shape and flow distance of a yield-stress material are determined by its density and the yield stress value, only.

The findings of this numerical benchmark study are of particular interest for the practical application of numerical simulations to predict industrial processes. The purpose of a numerical prediction is not to perfectly depict the process itself, but to predict its result (for instance, in case of concreting on site, one aims to predict if the formwork will be properly filled or not). Consequently, such a simulation focuses on the flow at stoppage, where the shear rates are rather low, and the contribution of the second part of the Eqs. (2) and (3) is negligible. It is therefore not crucial if the material behaves linearly or non-linearly at the higher shear rates – at the low shear rates at stoppage the yield stress is the dominating factor, that finally determines the flow length or the filling degree of a mold. This was recently demonstrated in [103], through large scale-laboratory castings and corresponding numerical simulations: for non-blocking cases, yield stress determines the final shape of the material and the proper filling of the form in practical applications.

5.3. Stability modeling of printed cement-based materials

The successful deposition of consecutive layers in a 3D printing process lead to an increment of gravity-induced stresses as an object is created. As the resistance of the printing material is initially low (i.e. in the order of the loads acting on the material) and no confining formwork is present, this increment in stress may lead to structural failure during the printing process, by either *elastic buckling* (illustrated in Fig. 9) or *plastic collapse.* In this phase, when the fresh concrete is generally at rest, the elastic-plastic behavior of the early age material,

Fig. 9. Elastic buckling during a 3D printing process.

and its structuration kinetics, are critical to control such failure [2,19,61].

In a recent paper, the rheological requirements to prevent both material yielding as well as self-buckling have been outlined [104]. It was shown that, for a typical wall of 2.5 m height, the gravity-induced stresses gradually increase with the rising height of the object, and reach a value of around 30 kPa in the critical bottom layer at the end of printing.

Consequently, in addition to an initial material yield stress required to control the layer shape immediately after extrusion (typically in the order of a couple tens to thousands of Pa), a structuration rate A_{thix} [33] is imposed to prevent plastic collapse when consecutive layers are placed. The minimum rate is dependent on the rising speed of the object, and may follow both a linear and non-linear trend [20,105]. Likewise, the initial elasticity and its evolution rate required to avoid elastic buckling, a common failure mode for the dominantly vertical slender shapes created by 3D printing, are imposed by the rising speed of the object, as well as its geometrical features. The rising speed, in turn, follows from the printing velocity, contour length, and layer dimensions. Thus, the rheological requirements of 3D printed concrete are fully process dependent.

The occurrence of failure by elastic buckling in a 3D concrete printing process was for the first time shown in a recent paper [56,106]. To assess the process dependent structural failure of an object during 3D printing, the authors proposed a numerical approach based on Finite Element Method (FEM) modeling. This approach includes the development of both the geometry and the material properties throughout a printing process, and thus, may predict if, and how, an object may collapse. The numerical simulations were validated by means of printing experiments. With a similar aim, a mechanistic model has recently been presented, to explore the influence of various process parameters on the mechanical performance of 3D printed wall structures [107].

The recent developments in the field of 3D concrete printing highlight the need to assess both yield stress and elasticity beyond the range commonly considered for fresh concrete. Whereas the rheological properties of concrete are often studied in the range of several Pa, they may reach the order of several tens to thousands of kPa in a 3D printing process. In this range, standard rheometers may not be adequate, which has led to the adoption of mechanical tests to characterize the early age properties. The results of such experiments additionally demonstrate a decrease of the critical strain with time at rest, which indicates a transition from plastic towards brittle failure as the material ages [21,56,106]. Consequently, where fresh concrete is often considered as a non-Newtonian fluid with a Von Mises yield criterion, at later ages, a solid mechanics approach based on a Mohr-Coulomb or Drucker-Prager criterion may be more suitable to assess plastic collapse in 3D printing processes.

6. Conclusion

This paper gathered the accepted knowledge along with the most recent advances on yield stress and elasticity of fresh cement-based materials. In the first part, the physical and chemical origins of these macroscopic properties and their evolutions were described. The second part of the paper focused on the way these properties can be measured while the third part dealt with the way they can be controlled and tuned. Finally, the most recent models for both properties prediction from mix design and processing modeling from rheological measurements were described.

The clear distinction in the research community between non-Newtonian fluid mechanics and fresh cement-based materials on one side and solid mechanics and hardened ones on the other side lasted for decades. However, it can be concluded from the above research trends that, nowadays, the boundary between these two fields is becoming narrow.

Because of the need to measure, understand and tune rheological properties of printable materials, the rheology and processing community is now exploring consistency and strength regimes that used to be considered as typical of a hardening material. In parallel, the hydration community keeps on improving its understanding of the setting process. Although being an extremely short phenomena relative to the life period of a concrete element, yield stress, elasticity, thixotropy, structuration and setting seem to be progressively described in literature as a continuous transition with the same physico-chemical origin.

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