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Rheological behavior of cement pastes under Large Amplitude Oscillatory Shear

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ABSTRACT

Cement pastes exhibit virtually all the rheological features of complex fluids. Thus, several rheological methods and setups have been used in the literature to characterize these materials. In the present investigation Large Amplitude Oscillatory Shear (LAOS) is for the first time exploited for cement pastes. LAOS can be used to characterize all the rheological properties within a single procedure. This technique is tested in the case of three different cement mixes: a Portland cement paste, nanoclay blended cement paste and a cement paste containing a hydrosoluble polymer. These mixes were selected in order to get rheological properties that are different both quantitatively and *qualitatively*. Indeed, addition of a low amount of nanoclay increased significantly the yield stress and the shear-thinning/thixotropic aspects of the cement paste, whereas addition of cellulose ether led to the decrease of yield stress and thixotropy. These non-linear rheological properties are discussed within the framework of LAOS.

1. Introduction

Fresh cement pastes, in particular those containing polymer admixtures, display almost all the properties that can be encountered in rheology: viscoelasticity, yielding, shear-thinning/shear-thickening, thixotropy/rheopexy, irreversible time evolution, etc. [1–4]. In addition, due to their multiphasic aspects, flow induced liquid-solid separation or segregation may take place under certain circumstances [5,6]. This complex rheological behavior may in particular explain the difficulty and even non-relevance of making comparison among the different results reported in the literature. Beyond the inconsistency of the reported measurements arising from the impact of the rheological setups and the data processing [7], the complexity of the rheological behavior itself, in particular yielding and thixotropy, may lead to non-comparable results [8,9]. Indeed several procedures, leading to different results, can be used to determine yield stress, thixotropy and aging [10,11]. For instance evolution at rest or aging (due to both hydration and thixotropic recovery) can be characterized using small amplitude oscillatory shear (SAOS) [1,11]. And different protocols can be used to characterize thixotropy: shear cycling, creep after shear [11,12], etc.

Although results for yield stress and flow curves for cement pastes have been reported in the literature, such properties cannot be defined rigorously in the case of evolving materials. Indeed these properties are dependent upon the duration of the measurement and the flow history. In addition steady state at a given stress/strain rate cannot be reached in the case of these materials. Therefore, from theoretical point of view, their flow curves cannot be determined. Properties infer from those curve are not intrinsic of material. Cement pastes are also highly sensitive to stress variations. Thus the oscillatory shear protocol for which one has smooth evolution of the stress is the most appropriate. To deal with the non-linear properties, as for example thixotropy or shear-thinning/thickening, the Large Amplitude Oscillatory Shear (LAOS) technique seems promising. Indeed, the evolution of the Pipkin diagram, which represents the evolution of non-linear viscoelastic properties at different frequencies and amplitudes [13–17], as a function of the paste age may turn out to be the most appropriate and complete rheological fingerprint of the material. Yet, the physical interpretation of LAOS data in the case of such complex materials is not expected to be straightforward.

In the present investigation the LAOS rheological procedure is tempted for the first in the case of cementitious materials. LAOS protocol has been developed and extensively used in the case of polymer solutions and melts [16]. It has then been applied to colloidal dispersions [18], and also in the case of industrial complex fluids such as food products [19], hair or skin gels [20], etc. Thixotropic fluids, for which even the theoretical aspects of LAOS are still under development [21], are much less considered in the framework of LAOS [15,17]. Application of LAOS to cementitious materials may appear then rather challenging since in addition to thixotropy, they exhibit irreversible time evolution due to hydration. The objective of the present exploratory study is to determine, even in a qualitative manner, which rheological features can be inferred from the LAOS procedure in the case of cement pastes. To illustrate this investigation three different mixes were considered at the

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same water/binder ratio: a pure cement paste, clay-blended cement paste and a polymer-blended cement paste.

2. Materials and methods

2.1. Materials

Portland cement type CEM1 52.5 was used in all the mixes. The nanoclay is a highly purified form of attapulgite (palygorskite). It is chemically exfoliated from bulk attapulgite to remove impurities such as smectite, bentonite and other swelling clays, making them effective rheology-modifiers for various materials, including cementitious materials. Palygorskite is a magnesium aluminum phyllosilicate type mineral. It consists of rod-like particles of an average length of L = 1.75 μm and average diameter of D = 30 nm. Due to their very high aspect ratio (r = L/D ~ 58), they can form a gel even at very low volume fraction provided they are dispersed into individual particles. Indeed, assuming an isotropic orientation distribution the critical volume fraction for which the close distance interactions (molecular origin such as van der Waals interactions) can estimated such that $nL^3 = O(1)$, where n is the number of particles per unit volume. The *crowding* volume fraction scales then as $O(1/r^2)$, which is vanishingly small. However, in practice the particles are more or less flocculated (stacked) depending upon the physicochemical properties of their surface and those of the solvent. Then the actual average aspect ratio should be much smaller. In any case, the fact that the clay particles are rod shaped is very favorable (compared for instance to plate-shaped clays as bentonite [12]) regarding their impact on the rheological properties (in particular the yield stress) when used as rheological modifiers in various materials.

Another type of rheological modifier was used, which is a cellulose ether (CE) based hydro-soluble polymer. It is a hydroxyethylmethylcellulose type. The CE is characterized in particular by its viscosity (40,000 cp), when dissolved in water at 2% by weight. The value of the viscosity gives an indication of the average molecular weight of the polymer. CE admixtures are generally comb-like polymers consisting of a hydrophilic backbone along which hydrophobic brushes are attached. In aqueous solutions the hydrophobic brushes associate to minimize contact with water making up then physical (reversible) crosslinks. Due in particular to these associative properties, CE based admixtures are characterized by a significant impact on the viscosity of the material [22], even when used in very low amount.

Three different formulations were considered in this study: a pure cement paste, a cement paste blended with 1% by weight of cement (bwoc) of nanoclay (NC) and a cement paste containing 0.1% bwoc CE. Tap water was used in all the mixes, and the water/powder ratio was fixed to 0.4.

The plain cement paste was mixed by hand during 2 min and then poured into the rheometer. Due to high tendency of NC particles to flocculate, in the case of the NC pastes, clay powder was first dispersed in water at 400 rpm during 5 min using a mechanical blender. Then the appropriate amount of cement powder was added to the clay dispersion, and the blended paste was mixed by hand for two more minutes. In the case of the CE-blended pastes, the cement powder was first dry mixed with the CE by hand for 1 min. Then, it was mixed (also by hand) with water for 2 min. Since CE is water soluble it was not necessary to use a mechanical blender as in the case of NC pastes.

2.2. Rheological measurements

2.2.1. Measurements

All the rheological measurements were performed with a controlled stress rheometer. In order to minimize wall slip, a cross-hatched plate-plate geometry was used. The plate was 40 mm diameter and serrations were distributed every millimeter. The gap was set at 1 mm for all the measurements. In order to start with the same flow history, a pre-shear was applied at a rate of 50 s^{-1} for 60 s followed by a period of rest for 60 s. The temperature was kept constant at 20 °C ± 0.1 °C using a Peltier system.

Since the materials considered are yield stress fluids it is more appropriate to perform the rheological measurements at controlled stresses. Our rheometer is actually a stress-controlled apparatus. In order to determine the transition from linear (SAOS) to non-linear (LAOS) regimes, an oscillatory stress sweep with an amplitude varying from 1 Pa to 100 Pa was performed. The time evolution of the pastes *at rest* (up to 30 min age) was considered through the evolution of the *linear* viscoelastic (SAOS) properties. Then, the evolution of the *non-linear* viscoelastic (LAOS) properties over the same period of time was determined by applying an oscillatory shear stress at different amplitudes, spanning the linear through the non-linear regimes. For more clarity protocol is described on Fig. 1. For each stress amplitude 3 different frequencies were considered (0.5 Hz, 0.75 Hz and 1 Hz). This relatively small frequency interval considered was dictated by the fact that: if the frequency is too low the evolution of the material during the LAOS measurement cannot be ignored, and if the frequency is too high instrument inertia may come into play. For each stress parameters (amplitude, frequency), 3 cycles of LAOS were performed each 3 min over the 30 min time interval. Similarly to the frequency, the stress amplitude was limited to 100% in order to avoid instrument inertia effects.

In the present investigation the evolution of the material during the 3 LAOS cycles is ignored. That is, transient effects are not taken into account to determine the LAOS parameters [17,23]. The transient effects in cement pastes include both rebuilding after shear (thixotropy) and change of microstructure due to hydration. These transient phenomena may take place at different time scales. Then, temporal evolution of the LAOS properties as it is considered here corresponds to those taking place at significantly larger time scales than the duration of the LAOS measurement.

Each test was performed three times to check for the repeatability of the measurements.

2.2.2. Data processing

In the present investigation a stress-controlled oscillatory shear protocol is considered. Contrary to the linear regime, for which there is no difference in viscoelastic properties between *stress* and *strain* controlled protocols, in the non-linear regime the two types of solicitations lead to different results [23].

In a LAOStress experiment a sinusoidal stress (τ) is applied at different amplitudes (τ_0)/frequencies (ω):

$$\tau(t) = \tau_0 \sin(\omega t) \quad (1)$$

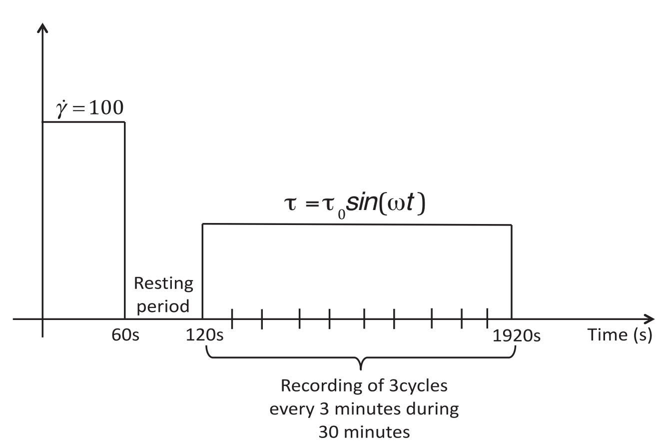

Fig. 1. Shear rheological protocol to measure evolution of LAOS behavior over time.