ADSORBING POLYMERS AND MACROSCOPIC VISCOSITY OF CONCENTRATED CEMENT PASTES

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ABSTRACT

Low water to cement ratio concretes are becoming more common in either the field of high strength concretes or low environmental impacts concretes. Although it is industrially feasible to reduce the yield stress of these materials in order to obtain some self-compacting properties by adding adequate amounts of super-plasticizers (SP) in the system, the viscosity of these concretes stays extremely high and may affect the casting processes. Recently, in industrial practice, some polymers were identified as having a viscosity reducing effect for a given slump flow value.

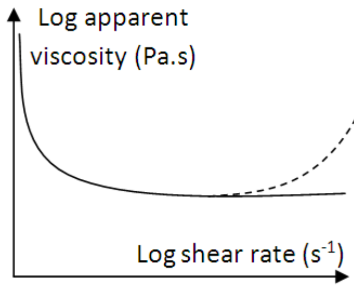
The work presented here aims at identifying some potential physical mechanisms at the origin of this decrease in viscosity. We focus here on the measurement of the part of viscosity that is not due to colloidal interactions. Our results show indeed that SP affect the residual viscosity, i.e. the apparent viscosity without yield stress contribution, of cement pastes.

Keywords: super-plasticizers; yield stress; viscosity; direct contacts

INTRODUCTION

When looking at the macroscopic rheological behaviour of cementitious materials, two parameters can be studied: the yield stress and the viscosity. The yield stress, easily measured thanks to industrial tests[1, 2, 3], is considered as the most relevant parameter to describe the workability and the ability of a material to reach a proper formwork filling[4]. However, for low water to cement ratio systems, the parameter viscosity, much more difficult to measure[5, 6], seems to be as well very important. In fact, the increase in solid volume fraction has dramatic consequences on the workability of the material and workers often complain about these "sticky" concretes that they are unable to vibrate and surface finish. Typical apparent viscosity measurements are shown in Fig. 1. It is now accepted that colloidal attractive interactions between cement grains are at the origin of the yield stress of the paste and that the competition between colloidal interactions and viscous dissipation is at the origin of the shear thinning behaviour at low shear rates[7]. Moreover, in the case of concentrated pastes, the competition between viscous dissipation and cement particles inertia may be at the origin of a shear thickening behaviour at high shear rates[7]. For intermediate shear rates, viscous dissipation may dominate all other phenomena in the paste. In this range, a Newtonian plateau can often be measured, on which macroscopic viscosity does not depend on shear rate. The presence of both yield stress and shear thickening makes therefore the measurement of what can be called viscous dissipation in such a system delicate. As yield stress plays a major role in the apparent viscosity at low to moderate shear rates for traditional pastes, the measured decrease in apparent viscosity could indeed only be the result of a decrease in colloidal interactions and macroscopic yield stress.

Figure 1. Typical apparent viscosity vs. shear rate for cement pastes: shear thinning followed by Newtonian plateau (solid line) and shear thickening (dashed line).



Before going into details, let us first recall here what we call viscous dissipation.

For non-Brownian, non-colloidal and diluted suspensions of spheres, there is the famous Einstein relation which holds in general for volume fractions lower than 5%:

$$\mu = \mu_0(1 + 2.5\phi) \quad (1)$$

with μ_0: Newtonian viscosity of the interstitial fluid and ϕ: solid volume fraction. For larger values of ϕ, experimental observations show that the apparent viscosity deviates significantly from the Einstein relation and eventually diverges when ϕ tends towards ϕ_{max}. Various empirical expressions have been proposed, the most famous one being the Krieger Dougherty equation[8]:

$$\mu = \mu_0 (1 - \frac{\phi}{\phi_{max}})^{-q} \quad (2)$$

with ϕ_{max}: maximum solid volume fraction and q=2.5ϕ_{max} for spheres. Recent studies suggest that q takes on the simple value of 2 for spheres[9]. For non-Brownian, non-colloidal and concentrated suspensions with direct contact between particles, a more complex relation describes the viscosity[10]. It takes into account the roughness k and the number of contacts in the particle network which participate to the overall dissipation and increase the macroscopic viscosity:

$$\mu = \mu_0 f\left(\frac{\phi}{\phi_{max}}\right) g(k, \frac{\phi}{\phi_{max}}) \quad (3)$$

For non-Brownian, colloidal and concentrated suspensions with direct contact between particles, there is another relation[7, 11]. It takes now into account the roughness, the number of contacts in the particles network and the flocculation state which depends on the magnitude of attractive colloidal inter-particle forces:

$$\mu = \mu_0 f\left(\frac{\phi}{\phi_{div}}\right) g(k, \frac{\phi}{\phi_{div}}) \quad (4)$$

with ϕ_{div}: solid volume fraction at which the viscosity diverges and $\phi_{div} < \phi_{max}$.

EXPERIMENTAL WORK

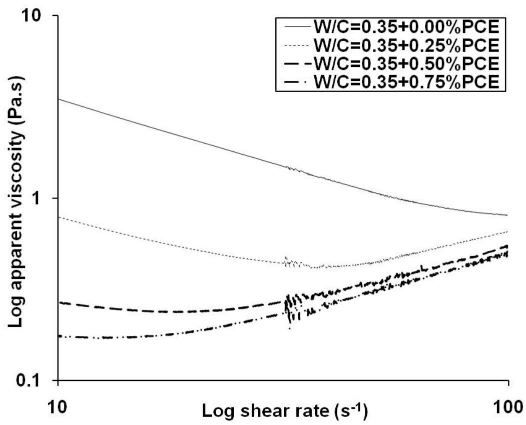
Materials and mixing protocol — A Portland cement ASTM Type I is used. All the cement pastes are prepared with W/C=0.35. The SP investigated here is a polycarboxylic ether (PCE). It is used in liquid form, and its dosage rate is expressed in percentage by mass of cement. For instantaneous addition, cement and 85% of the water with the polymer are first mixed together by hand and then mechanically mixed for 2 min. The cement paste is then left at rest for 20 min before the addition of the 15% remaining water. The paste is then mixed again for 2 min and finally left at rest for 10 min. For delayed addition, the polymer is diluted in the 15% remaining water.

Methods — For rheological measurements, a C-VOR Bohlin rheometer with a Vane geometry is used. The cup is filled with the cement paste and an increasing shear rate ramp is then applied followed by a decreasing shear rate ramp. Only the decreasing ramps are shown in the following. Moreover, cement pastes for which bleeding could be visually spotted are not considered in the analysis. For normal force measurements, the rheometer is equipped with parallel plates geometry. The procedure consists in measuring both normal and shear stresses while imposing a constant shear rate. Slippage can be neglected and a water trap is used to avoid water evaporation. As a pretreatment before XRD observations, the paste samples are freeze-dried after 30 min of hydration. The samples are then ground in a ring roll mill before being observed. For adsorption measurements, a Total Organic Carbon (TOC) analyser is used. After mixing, the paste is centrifuged for 10 min, and the supernatant is then extracted.

RESULTS AND DISCUSSION

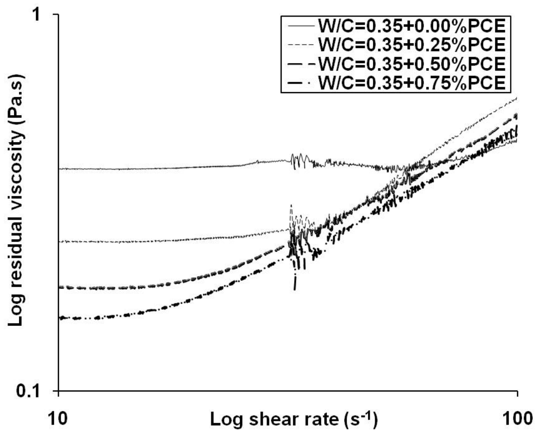
Apparent shear viscosity measurements — The apparent viscosity as a function of shear rate for various dosages of PCE is shown in Fig. 2. As expected, the reference paste is obviously a shear thinning fluid (*i.e.* apparent viscosity decreasing with shear rate). When polymer is added to the system, this shear thinning behaviour becomes less pronounced. This can be attributed to the deflocculating action of the polymer, which, through adsorption and steric/electrostatic repulsion, is able to decrease the magnitude of the attractive colloidal interactions[12, 13, 14]. The yield stress of the system decreases along with its contribution to apparent viscosity. A shear thickening behaviour is measured at high shear rates for the systems containing polymer. When polymer dosage increases, this shear thickening behaviour gets more pronounced.

Figure 2. Apparent viscosity vs. shear rate (delayed addition).



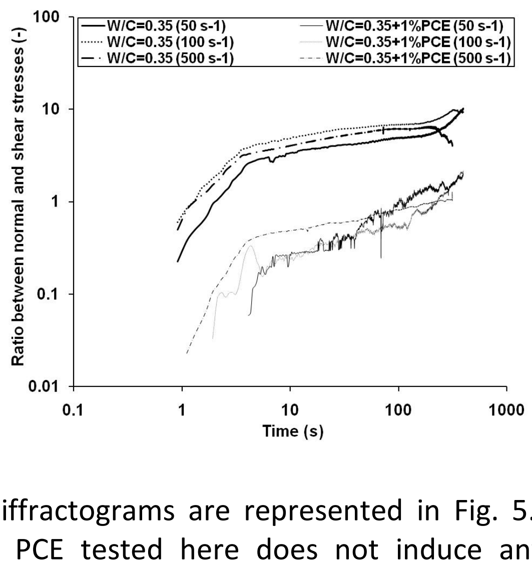
From the values of the apparent viscosity, we compute the values of the residual viscosity, *i.e.* the apparent viscosity without the yield stress contribution. This residual viscosity can be plotted as a function of shear rate and presents a plateau at intermediate shear rates, which is considered here as representative of the intensity of the viscous dissipation (Cf. Fig. 3). This viscous dissipation is affected by the presence of plasticizer and its dosage as the level of the plateau is decreasing when polymer dosage is increased. Finally, the shear thickening contribution to residual viscosity does not seem to depend on the plasticizer and its dosage. This suggests that shear thickening is not induced by the polymer itself but is always present in the system.

Figure 3. Residual viscosity $(\mu_{app} - \frac{\tau_0}{\dot{\gamma}})$ vs. shear rate.



Normal force measurements — The Fig. 4 shows the ratio between normal stress and shear stress as a function of time for three different shear rates for 0 and 1% of PCE. This ratio does not depend on shear rate in the range of shear rates studied and the most striking feature comes from the fact that, although the system volume fraction stays constant (W/C=0.35), the normal force drops drastically between the system containing polymer and the reference system. As the range of shear rates studied is high, the contribution of colloidal forces and therefore yield stress to this measurement shall stay low. As a consequence, this suggests that, when polymer is added, something changes in the system other than the value of yield stress.

Figure 4. Ratio between normal and shear stresses vs. time (instantaneous addition).



XRD analysis — Two diffractograms are represented in Fig. 5. They have the same aspect. Therefore, the PCE tested here does not induce any obvious changes in ettringite crystallization, and more generally, in the formation of hydration products.

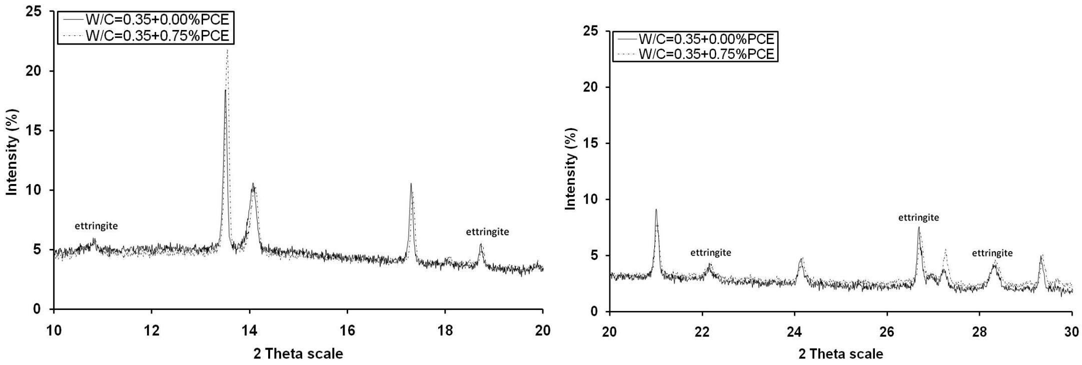
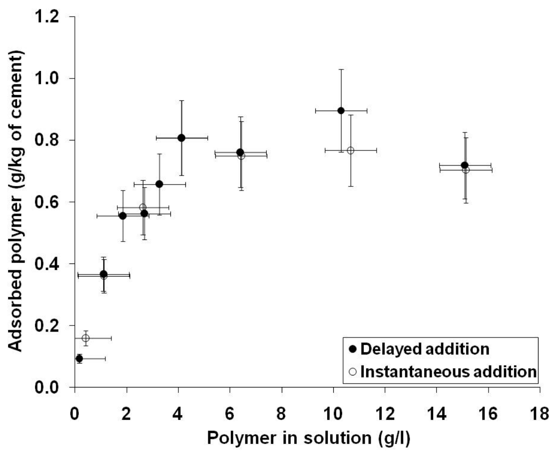


Figure 5. XRD analysis

Adsorption results — The adsorption isotherms for the PCE tested are shown in Fig. 6. There exists a saturation dosage for which the adsorption levels off and the amount of polymer staying in the interstitial fluid increases. Moreover, these results show that there is no adsorption difference between instantaneous and delayed additions.

Figure 6. Adsorption isotherms for the PCE tested.



ANALYSIS AND CONCLUSION

The rheological results suggest that there is a decrease in colloidal interactions intensity when adding PCE. However, there is also a decrease in viscous interactions intensity, as the residual viscosity decreases. Therefore, the decrease in the apparent viscosity cannot be attributed only to the decrease in the contribution of the yield stress to the macroscopic viscosity. Moreover, it is now accepted that, in a purely hydrodynamic system, normal stress difference is negative as flow is reversible and microstructure is isotropic. Normal forces are therefore associated to microstructure anisotropy, which strongly depends on the details of short-range interactions between particles such as direct frictional contacts[15, 16]. The measured constant ratio between normal and shear stresses is in agreement with the frictional origin of the normal forces[16]. This suggests that introduction of PCE leads to a decrease of the frictional contacts contribution. As the contact contribution and the yield stress are decreased, we expect the flocculation state of the system to decrease along with the ratio ϕ/ϕ_{div} . We can therefore list two potential mechanisms at the origin of the decrease in residual viscosity and in normal forces: either a decrease in flocculation through a decrease in the ratio ϕ/ϕ_{div} (*i.e.* a decrease in the total number of direct frictional contacts[16, 17]) or a change in contact contribution through a change in friction coefficient between flocs or grains (*i.e.* a change in the surface roughness). However, the second mechanism can be neglected for the following reasons. Firstly, as the thickness layer of the polymer (around a few nanometers) cannot compare with the typical roughness of cement grains (around a few hundred nanometers), the polymer itself cannot modify the physical roughness of the grain surface. Secondly, the XRD and adsorption results show that the nature of the minerals at the surface of the grains does not change much when polymer dosage increases. Finally, recent numerical simulations results in the field of dry granular media have shown that the decrease in friction coefficient needed to measure a consequence in terms of macroscopic behaviour of the mixture shall bring this friction coefficient from a value in the range of 0.6-0.7 for cement grains[18] down to a value in the range of 0.1-0.2, which is a very low value mostly associated to very smooth particles[10]. Therefore, keeping in mind the relation (4) and the first mechanism described above, these results suggest that polymer affects the total number of direct frictional contacts in the system, which means that ϕ/ϕ_{div} is modified. As the total solid volume fraction ϕ does not change, adsorbing polymers change the contribution of contacts to macroscopic viscosity by only changing the flocculation state of the suspension. By deflocculating the system, they change the way shear concentrates in the interstitial fluid between residual flocs and reduce the jamming of the system along with the overall contribution of frictional contacts between flocs[19].

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