



Adsorbing polymers and viscosity of cement pastes

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ABSTRACT

In this paper, we study the physical mechanisms at the origin of a decrease in viscosity of concentrated cement pastes containing adsorbing polymers. We suggest from our results, similar to other authors, that plasticizers are able to decrease viscous dissipation by modifying the flocculation state of the system, which, in turn, impacts the way shear localizes. Our experimental results suggest that shear concentrates in fluid layers, the thickness of which scales with the surface-to-surface separating distance between cement grains imposed by the adsorbed polymer conformation. These effects being identical for all polymers, we suggest that the residual difference between polymers in the final macroscopic viscosity comes from the more or less pronounced increase in the local viscosity of the interstitial fluid between neighboring particles. This increase could either be correlated to the concentration of non-adsorbed coils in the interstitial fluid or to the local concentration of adsorbed coil side chains.

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1. Introduction

Most academic researchers or practitioners quantify the consequences of a change in mix design on workability of fresh cementitious materials in terms of yield stress variations (*i.e.* in terms of variations in the critical value of the stress to be applied to initiate flow of the material). They sometimes do so without even knowing it by measuring, for instance, a change in slump or slump flow, this industrial test being, in most circumstances, directly correlated to yield stress [1–4]. Although cementitious materials are not only yield stress fluids (*i.e.* they are also thixotropic non-Newtonian viscous fluids [5,6]), this pragmatic approach is justified by the fact that yield stress is often the most relevant parameter to describe the ability of a material to fill, under its own weight (*i.e.* under the sole effect of gravity), a formwork or more generally a mold [7]. It is now accepted that this yield stress finds its origin in the colloidal interaction network between cement particles [8–11] more or less amplified by the presence of the rigid aggregates [12–15] and more or less modified by adsorbed polymers such as plasticizers [9].

Recent trends in mix design of cementitious products show however that water to cement mass ratio of modern cementitious materials is progressively decreasing [16]. This decrease in liquid content (or increase in solid volume fraction) leads to a decrease in the porosity of the hardened material and allows for increased mechanical performances or increased durability [17]. More specifically, within an environmental perspective, this decrease in porosity often allows for the substitution of pure Portland clinker by less efficient alternative binders

such as blended cements while maintaining the performances of the resulting hardened product [18]. This increase in solid volume fraction has however dramatic consequences on the workability of the material and workers at the building site often complain about these “sticky” concretes that they are unable to vibrate and surface finish. This “stickiness” and, more specifically, the additional stress needed to place the material have nothing to do with yield stress but seem to increase with the rate of shear applied to the material and therefore seem to relate to the energy dissipation occurring in the flowing concrete, which is at the origin of its viscosity.

From a practical point of view, this raises therefore the question of how to decrease this energy dissipation in the case of these “sticky” mixes with high solid volume fractions. A decrease in apparent viscosity (*i.e.* the ratio between shear stress and shear rate) when plasticizers are added to the paste is sometimes measured in literature [19–23]. It is moreover accepted, in the field of attractive suspensions [24], that particle flocculation, which finds its origin in the attractive colloidal interactions between particles, may have a very strong influence on viscosity by modifying the micro-structure of the flowing suspension and the way shear concentrates between flocs or particles. This is often described in the cement community as cement flocs releasing some water as de-flocculation occurs [25]. As a consequence, by changing the flocculation state of a cement paste, adsorbed polymers seem to be able to reduce both yield stress and viscosity. It could then be expected that, at a given water to cement ratio for a given cement, a given flocculation state would correspond to a given yield stress and a given viscosity no matter the polymer. However, during the recent Tenth International Conference of Super-plasticizers and Other Chemical Admixtures in Concrete held in Prague, Czech Republic, in October 2012, the existence of various super-plasticizer molecules allowing for various

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reductions in stickiness (*i.e.* reduction in apparent viscosity) at constant slump values (*i.e.* constant yield stress) was reported and discussed [26].

In this paper, we aim at improving, mostly from rheological measurements, the understanding of the physical mechanisms at the origin of the above effects. We suggest, from our results, similar to other authors, that, for a given mixing and polymer introduction protocol, plasticizers are able to decrease apparent viscosity by modifying the flocculation state of the system, which, in turn, impacts the way shear localizes and concentrates in fluid layers. Our measurements moreover suggest that the thickness of the fluid layers scales with the surface-to-surface separating distance imposed by the adsorbing polymers. These effects being identical for all polymers at a given flocculation state of the cement particles, we suggest that the residual difference between polymers on the final apparent viscosity of cementitious products comes from the more or less pronounced increase in the local viscosity of the interstitial fluid between neighboring cement particles.

2. Materials and experimental protocols

2.1. Cement

The cement used in this study is a Portland cement equivalent to ASTM Type I cement. Its chemical composition obtained through ICP-AES and ATD-ATG is given in Table 1. Its maximum packing fraction was estimated to be around 60% in [27] and its Blaine specific surface is $3650 \pm 100 \text{ cm}^2/\text{g}$. All cement pastes studied here are concentrated pastes and are prepared with a water to cement mass ratio (W/C) between 0.275 and 0.475. The total amount of water added to the system takes into account the water brought by the polymer added under liquid form.

2.2. Mixing protocols

It is now accepted that mixing and polymer introduction protocols have a very strong influence on the rheological behavior of the mixture. This effect may find its origins, of course, in the difference in shear history along with the thixotropic behavior of a cement paste but, more than anything, in a potential chemical interaction between the early hydrates and the adsorbing polymers [28–36].

We choose, in this work, to focus on the influence of plasticizers on the rheology of cement pastes. In order to isolate the rheo-physical effects, we decided to choose here some protocols, which seem to limit the consequences of any early chemical interactions such as intercalation or co-precipitation [30]. In order to reduce the potential consequences of these chemical processes, we first decided to use a mixing protocol, in which the polymer is added to the system 20 min after the first contact between the cement powder and water (*i.e.* we expect that most of the initial aluminates have already nucleated). The idea behind this choice is to create systems, in which a measured change in rheology is due to a change in direct or indirect interactions between mineral particles and not a change in the minerals themselves. Such a change could induce *e.g.* changes in colloidal properties or frictional interactions between grains, which could then prevent the independent measurement of the changes we are specifically interested in through this paper.

Therefore, a volume of around 400 mL of cement powder and 85% of the water is first mixed by hand and then mixed for 2 min using a Turbo test Rayneri VMI mixer at 840 rpm. The cement paste is then left at rest for 20 min before the addition of the polymer diluted in the 15%

remaining water. The paste is then mixed mechanically again for 2 min in the Turbo test Rayneri mixer. The cement paste is finally left at rest for 10 min before starting any measurements. This protocol is also used for the reference paste without polymer, which is therefore prepared in two phases like the other tested pastes.

It can finally be noted that all mixing and testing protocols were carried out at $20 \pm 1 \text{ }^\circ\text{C}$.

2.3. Polymers

We study here three polymers specifically produced for this study and purified from by-products.

The first one, polymer A, is a comb co-polymer in the flexible backbone worm regime defined in [37]. It is a poly-carboxylate with methacrylic acid backbone and polyethylene oxide (PEO) side chains prepared through an esterification process. We use here the following notation: this comb polymer contains n segments, each with one side chain. Each side chain contains P monomers. Each segment contains N backbone monomers. It can also be considered that the average grafting ratio is $1/(N - 1)$. Within this frame, $P = 23$, $N = 3$ and $n = 20$ for polymer A. Its molar mass, computed from its molecular structure, is approximately 25,000 g/mol.

The second one, polymer B, is also a comb co-polymer in the flexible backbone worm regime. It is also a poly-carboxylate with methacrylic acid backbone and polyethylene oxide (PEO) side chains prepared through an esterification process. The only difference comes from a lower grafting ratio as shown by the stretched molecular structures in Fig. 1. Its molecular parameters are $P = 23$, $N = 4$ and $n = 15$. Its molar mass, computed from its molecular structure, is approximately 20,000 g/mol.

The third polymer is a linear homo-polymer. It is a calcium naphthalene sulfonate. Its molar mass is 14,000 g/mol. We checked using XRD measurements on grinded cement paste samples frozen at $-195 \text{ }^\circ\text{C}$ by immersion in liquid nitrogen during 5 min after 30 min of hydration that, using our delayed addition protocol, the consequences of any interactions between aluminates and this polymer were negligible in our study. It can be noted that XRD measurements allowed us to detect such interactions in the case of instantaneous addition of polymer C even after such a short contact duration between cement and water. Our rheology and adsorption measurements moreover confirmed that a 20 min addition delay was sufficient to get some rheological parameters and adsorption isotherms that did not depend on the addition delay.

From literature [9], we can assume that the decrease in the magnitude of attractive forces between cement grains finds its origin mostly in steric repulsion in the case of polymers A and B whereas electrostatic repulsion plays a potential role in the case of polymer C.

2.4. Rheological measurements

2.4.1. Apparent shear viscosity measurements

The apparent shear viscosity measurements are carried out with a C-VOR Bohlin rheometer equipped with a Vane geometry. The Vane tool diameter is 25 mm and the outer cup has the following dimensions: 50 mm in diameter and 60 mm in depth. The cup of the rheometer is filled with the tested cement paste and the measurement sequence is started. The cement paste is first pre-sheared for 60 s to bring it to a reference structural state. An increasing shear rate ramp from 10 to 100 s^{-1} (with a logarithmic distribution of shear rates) is then applied for 200 s followed by a decreasing shear rate ramp for 200 s. Only the decreasing

Table 1
Chemical composition of the cement studied here.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Cl	CaO free	Ignition loss
21.04%	3.34%	4.14%	65.43%	0.83%	0.22%	0.35%	2.31%	0.02%	1.55%	1.53%

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