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Influence of organic admixtures on the rheological behaviour of cement pastes

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Abstract

The rheological properties of cementitious pastes used to proportion Self-Consolidating Concretes (SCC) have been examined, in particular, the influence of High range water reducing admixture (HRWRA) with that of Viscosity Modifying Admixtures (VMAs) have been compared. HRWRAs are known to have dispersing effects on the cement particles through steric and/or electrostatic repulsion, while the effects of VMAs are expected to stabilise the paste by increasing the viscosity of the aqueous solution. Both transient and steady state rheological behaviour of the cementitious pastes proportioned with different dosages of HWRA and VMA were considered. Experimental results show that the influence of VMAs on rheological properties is actually minor compared to that of HRWRAs. These results are discussed in the framework of rheology of concentrated suspensions.

Keywords: Cement paste; Rheology; High-Range Water Reducers; Viscosity Modifying Admixture

1. Introduction

Self-Compacting Concretes (SCCs) are characterized by their high fluidity so that they can be placed without vibration, easily fill small interstices of formwork and be pumped through long distances. On the other hand, the SCC cement paste has to be viscous enough to avoid gravitational or flow-induced segregation of larger aggregates. Since these two requirements are apparently contradictory, mix design of SCCs turns out to be critical, and it is not fully understood. The link between the flow (rheological) properties and the formulation is actually one of the key-issues for the design of SCCs.

In order to achieve the abovementioned SCC rheological properties, formulators combine use of High range water reducing admixtures (HRWRAs) with mineral and organic viscosity enhancing additives [1–4]. Mineral additives (fillers) include: fly ash, silica fume, limestone powder (used in the present study), etc. Mineral additives have the advantage of improving both the rheological (in fresh state) and the mechanical (in hardened state) properties of the concrete. Organic viscosity modifying admixtures (VMAs) are water-soluble such as cellulosic and polysaccharide-based (used in the present study) polymers.

The different additives, in particular HRWRAs and VMAs, improve the fresh properties of concretes primarily through their effects on the cement paste rheological behaviour. HRWRAs are known to achieve high fluidity of the paste through dispersion of flocculated cement particles [5–8]. This is a result of the adsorption of HRWRA chains on the cement particles' surface, which leads to steric and/or electrostatic repulsion between the haired grains [5]. VMAs improve the stability of the cement paste through mainly the increase of the viscosity of the aqueous solution [3,9].

A number of studies have been reported in the literature concerning the effect of the HRWRAs type and dosage on the rheological properties of the cementituous materials. Chandra and Björnström [10] compared the influence of lignosulfonic acid and melamine sulfonic acid based HRWRAs on the fluidity of mortars. The former was found to give more fluidity than the latter. In their study the fluidity was characterized using the spread of a cone, without detailed rheological study. Golaszewski and Szwabowski [11] considered similar but more general behaviour using a rotational rheometer.

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Since the primary action of HRWRAs concerns the cement particles and some types of fillers, there is a need to study in details the influence of HRWRAs on the rheological properties of cement pastes. At this scale, the cementitious material can be studied using conventional rheometers. Papo and Piani [12] considered the influence of various commercial HRWRAs on the rheological properties of cement pastes in both continuous and oscillatory shear flow. On the other hand the influence of VMAs on the rheological properties of cementitious pastes has been much less investigated [3]. Both HRWRAs and VMAs are then expected to influence significantly the rheological properties of cement pastes. In the present study we compare the influence of these two types of organic admixtures by considering both steady and transient rheological properties. Our results are interpreted in the framework of rheology of concentrated suspensions.

In previous studies concerning the steady state rheological behaviour of cement pastes various models have been proposed, including, Bingham, Herschel–Bukley, Casson, etc., and this is reviewed in Ref. [13]. Here, it is shown that the behaviour of the pastes depends upon the shear rate domain considered. Increasing the shear rate, the paste is first shear thinning then Newtonian and finally shear thickening.

As has been pointed out recently by for instance Roussel [14], cement pastes present significant transient effects, related to their thixotropic properties [15–18]. It is then important to determine the actual steady state properties by considering the transient behaviour of the measured stresses.

2. Experimental

2.1. Materials and formulation procedure

2.1.1. Cement

The cement used here is Portland CEM I 52,5 PM ES CP2 from Teil in France. Its physical properties and chemical composition are reported in Table 1.

2.1.2. Fines

The fines are ground limestone (PEKETTY A), with specific gravity of 2.7 and Blaine fineness of 2900±650 (cm^2/g). The granular size distribution of the fines, as determined by laser granulometry, is similar to that of the cement (see Fig. 1).

2.1.3. Superplasticizer

The superplasticizer used here was polycarboxylic ether type (Glenium 27). The origin of its dispersing effects is both electrostatic and steric (it comprises long lateral chains) repulsions. It is usually used as a High range water reducing admixture to proportion high performance concretes.

Table 1
Chemical composition and physical properties of the cement

Chemical composition (%)		Physical properties	
C_3S	69	Specific gravity	3.15
C_3A	<5		
C_4AF	5.8	Specific surface (Blaine) (cm^2/g)	3400 (cm^2/g)
CaO/SiO$_2$	2.88		
MgO	0.78	Mean particle size	18.5 (μm)
Al$_2$O$_3$	2.99		
Gypse	2.7		

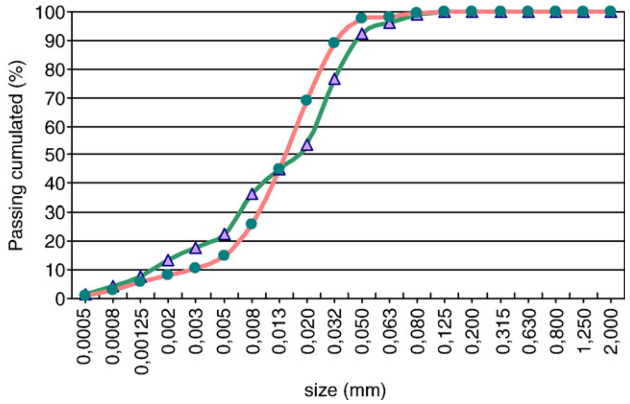

Fig. 1. Granular size distribution of solid particles: cement (●); fines (▲).

2.1.4. Viscosity modifying agent

The VMA was polysaccharide type (Foxcrete) (kindly supplied by J. Amboise and J. Amboise from INSA-Lyon, France). It was provided as a suspension in an aqueous solution with a concentration of 20% by weight.

2.1.5. Mixing procedure

The mixing procedure consisted of the same set of steps for the pastes considered (Table 2). We used a laboratory paddle-pan mixer.

2.1.6. Mix design

The formulation of the reference paste is reported in Table 3; it is used in practise to proportion SCCs. Different pastes have been prepared by varying either HRWRA or VMA dosage.

By changing HRWRA and VMA content of the reference paste, 6 other pastes were prepared: P-40PS (12 g HRWRA/1000 g cement), P-20SP (16 g HRWRA/1000 g cement), P+20SP (24 g HRWRA/1000 g cement), P+40SP (28 g HRWRA/1000 g cement), P-40VMA (6 g VMA/1000 g cement), P+40VMA (14 g VMA/1000 g cement).

2.2. Rheological measurements

2.2.1. Apparatus

The transient and steady state behaviours of the pastes were characterized using a stress-controlled shear rheometer (Strestech® from Rheologica). In order to minimize sedimentation effects on rheological measurements, a co-axial cylinders geometry was chosen. In such a geometry, the tested material is subjected to

Table 2
Mix procedure

Step	Cement +fines	Water+HRWRA +VMA addition	Mixing at low speed (95 RPM)	Mixing at high speed (165 RPM)
Duration of mixing (min)	5	0.5	4	2

Table 3
Composition of the reference paste

Cement (G)	Filler (G)	Water (G)	HRWRA (G)	VMA (G)
1000	330	300	20	10

an approximately uniform shear rate provided that the gap between the cylinders is sufficiently small compared to the diameter of the inner cylinder. On the other hand the gap has to be much greater than the larger heterogeneity length scale in the material in order to provide average measurements. In our case, the inner (mobile) cylinder was 25 mm diameter and outer (fixed) cylinder 29 mm. The gap was thus 2 mm, which satisfies the above-mentioned conditions in the case of the pastes considered here.

The temperature was fixed at 20 °C (to within 0.1 °C) thanks to a circulating liquid system. In order to prevent evaporation of the paste's water the measurement system was sealed.

2.2.2. Measurement procedure

The influence of shear rate and time of shearing on the rheological behaviour of the pastes were considered. The paste was introduced into the measurement system at an age of 15 min during which it was held at rest. The rheological measurements were started after a period of rest of 2 min in the measurement system. All the rheological measurements were undertaken during the induction period during which the hydration rate is very low. In the present study we deliberately avoid discussing the potential influence of hydration on the rheological behaviour in detail [19]. However, it is known that at small shear rates, rheological measurements are affected by hydration.

Measurements using two different gaps (2 mm and 1 mm) indicated that wall-slip was not significant for the shear rates considered here.

3. Results and discussion

3.1. Transient behaviour

Fig. 2 shows the transient behaviour of the effective viscosity (stress divided by shear rate) as a function of time for different shear rates. Only results for the reference paste are shown here, but the results for the other tested pastes are similar. The dependence of the stress upon time of shearing is, as expected, related to the thixotropic character of the paste [14]. If we assume that the paste is actually thixotropic, the effect of shear rate on the transient behaviour can be explained as follows [20,21]. At the beginning of shearing, all the pastes have approximately the same history from the mechanical point of view: shearing at different rates and different periods during mix design and introduction into the measurement cell. These mechanical actions along with the period of rest before shearing would lead to a certain paste microstructure determined by a given initial distribution of floc sizes. This initial microstructure corresponds to a certain effective (or apparent) viscosity. During rheological measurements, at any time there is a competition between microstructure rebuilding, due to colloidal interactions activated by the Brownian motion, and shear-induced breakdown of flocs whose size is greater than a certain value depending upon shear rate. Actually, the behaviour of our material does not exactly follow this scenario. At small shear rates (0.5 s^{-1} in Fig. 2) the viscosity starts to decrease and then increases without reaching steady state even during the maximum time interval considered here (up to 2 h). This behaviour has already been reported in the literature and is attributed to hydration phenomena [16].

In order to check whether the increase of the viscosity is actually due to hydration, we performed a transient experiment in the case of paste in which the cement has been replaced by the fines. It is to be noticed that the fines have approximately the same granular size distribution than the cement (see Fig. 1). The evolution of the viscosity for different shear rates for this inert paste is shown in Fig. 3. The viscosity is higher than cementitious pastes because the HRWRA has probably no contribution to the dispersion of filler aggregates. It can also be seen that even at low shear rates steady state can be reached in this case. This demonstrates that the long time increase of the viscosity in the case of the cementitious pastes is related to hydration process.

At small shear rates (0.5 s^{-1} in Fig. 3) the viscosity increases before reaching steady state. This can be explained as follows: at low shear rates the flocs which can be broken down are greater than those making up to the initial granular structure of the paste. The equilibrium between rebuilding and breakdown, which would

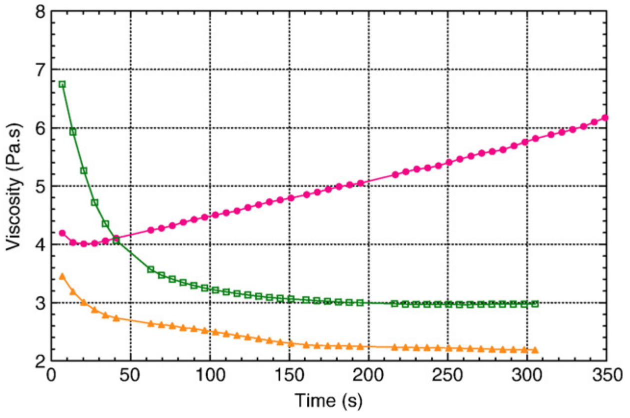

Fig. 2. Transient rheological behaviour of the reference paste for different shear rates: (●) 0.5 s^{-1}; (□) 5 s^{-1}; (▲) 30 s^{-1}.

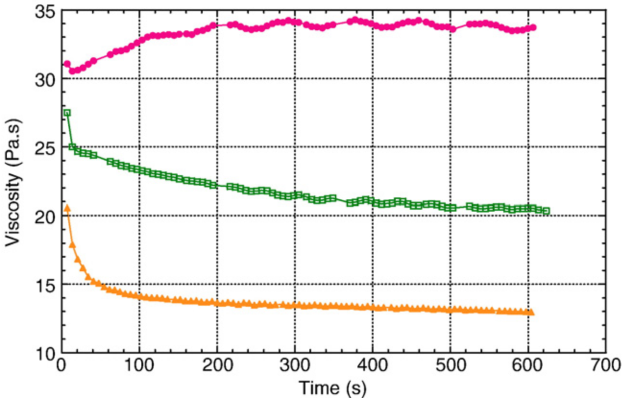

Fig. 3. Transient rheological behaviour of a paste in which the cement is replaced by the filler. (●) 0.5 s^{-1}; (□) 1 s^{-1}; (▲) 2 s^{-1}.

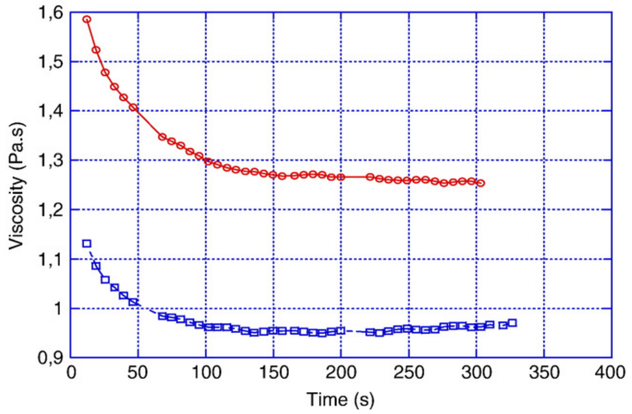

Fig. 4. Influence of the initial state on the transient rheological behaviour at $70\ \mathrm{s}^{-1}$: (○) without pre shearing; (□) pre shearing at $50\ \mathrm{s}^{-1}$ for 1 min.

lead to a steady state of stress, would correspond to the formation of a more flocculated paste. This may explain the increase of the stress (or viscosity) against time. In the present study we deliberately restrict ourselves to short time behaviour of the viscosity in order to avoid hydration effects.

With increasing shear rate, smaller and smaller aggregates can be broken down. Indeed, the higher the shear rate, the smaller are the flocs that can be broken down by the viscous forces, and the viscosity then decreases. At relatively high shear rates, equilibrium can be reached after a certain characteristic time which decreases with increasing shear rate. In this case the hydrates formed following the hydration process can probably be broken down by the shear stress, which would lead to steady state.

The experimental results reported in Fig. 4 show that the steady state viscosity depends upon the shear history of the paste. There is a significant difference between the steady state values obtained without and with pre shearing (here at $50\ \mathrm{s}^{-1}$ for 1 min). These results indicate that the pastes are only partially thixotropic. This is expected since the main driving force of floc rebuilding is Brownian motion. Most of the grains making up the paste are much larger than 1 m (see Fig. 1) and therefore are not subject to Brownian motion.

3.2. Steady state behaviour

For each shear rate, the paste is sheared until steady state is reached. The behaviour of the steady state rheological behaviour is considered for the different pastes studied here. Only shear rates for which steady state can be obtained are considered.

3.2.1. Typical rheogram of the paste

Fig. 5 represents the behaviour of the steady state effective viscosity as a function of shear rate in the case of the reference paste. In contrast with what has been reported in the literature [13], the rheological behaviour of the paste throughout the whole shear rate interval investigated cannot be described by a single rheological model. Below a certain shear rate value (approximately $70\ \mathrm{s}^{-1}$ in the case of the reference paste, see Fig. 5), the paste behaves as a power–law shear thinning fluid. The paste possesses also a yield stress. This is discussed in more details further on (see Section 3.2.4). The power–law rheological behaviour is followed by a Newtonian plateau, where the viscosity is roughly independent of shear rate. At high shear rates (above $120\ \mathrm{s}^{-1}$ in Fig. 5), the paste becomes slightly shear thickening. The position and extension of shear rate interval corresponding to each region of the rheogram depends upon HRWRA dosage as can be seen in Fig. 6.

The shear thinning part of the rheogram can be attributed to shear-induced dispersion of cement aggregates. The higher the shear rate, the finer are the aggregates at equilibrium between shear breakdown and Brownian activated rebuilding (along with hydration). For a given solid volume fraction, the viscosity will decrease when the aggregate size decreases. This is discussed in more details in Section 3.2.2. Above a certain shear rate, there is no significant further breakdown of flocs, which leads to the Newtonian plateau. The shear thickening part of the rheogram is

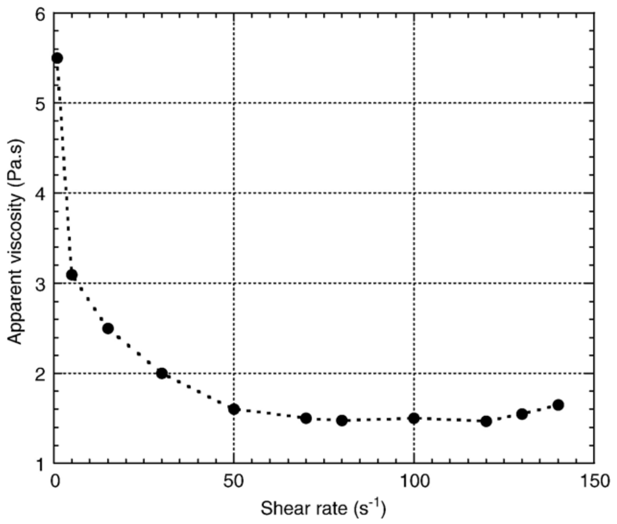

Fig. 5. Steady state rheological behaviour of the reference paste.

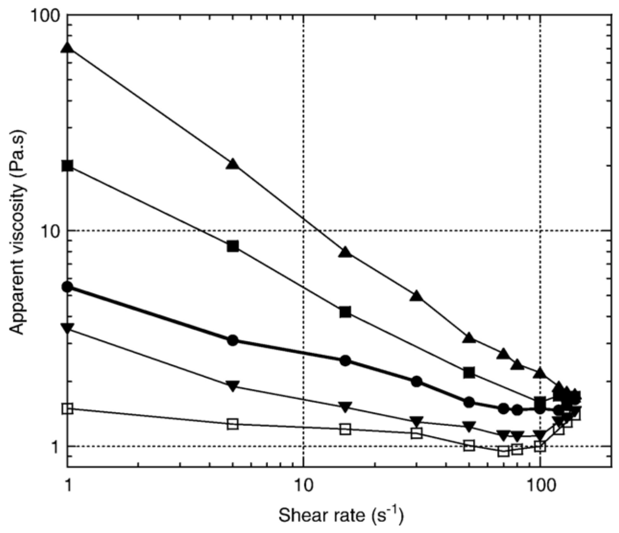

Fig. 6. Influence of the SP dosage on the paste's rheogram. (●) Reference paste; (▼) P+20SP; (□) P+40SP; (■) P-20SP; (▲) P-40SP.

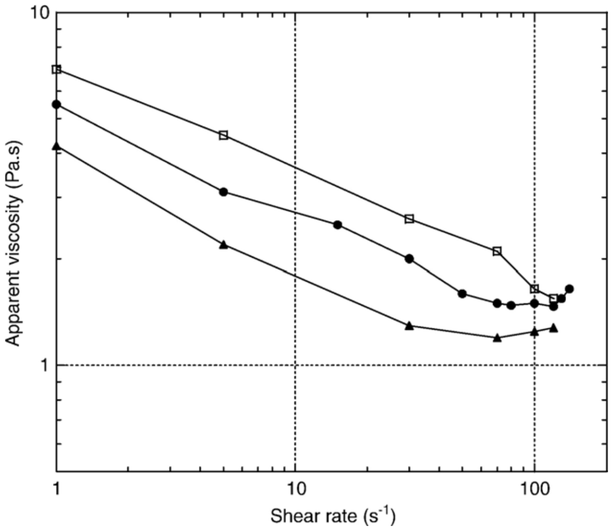

Fig. 7. Influence of the VMA dosage on the paste's rheogram: (●) reference paste; (▲) P-40 VMA; (□) P+40 VMA.

akin to a characteristic behaviour of granular concentrated suspensions, and generally attributed to dilatancy effects [22].

3.2.2. Influence of HRWRA content

Fig. 6 represents the evolution of the paste rheogram for different HRWRA dosages. It can be noted that the reference admixture does not have the lowest viscosity as one would expect for a SCC paste. This can be understood if we consider that we have to avoid solid contacts among larger scale aggregates in the corresponding concrete in order to avoid loss of workability and blockage. The paste has then to be viscous enough to play its role of lubricant.

As expected the viscosity of the paste is highly sensitive to HRWRA content. For any given shear rate the viscosity decreases with increasing HRWRA addition. For the lowest value of HRWRA content considered in the present study, the paste is shear thinning throughout the whole shear rate interval investigated. One has to probably use higher shear rates to get the Newtonian plateau and further the shear thickening part of the rheogram. Addition of more HRWRA helps dispersion of aggregates and lowers the shear rate value for appearance of the Newtonian plateau. For the highest dosage of HRWRA considered here, the shear thinning part of the rheogram almost disappears. In this case, the paste is highly dispersed due the HRWRA action. There are almost no more flocs to breakdown with shear.

3.2.3. Influence of VMA content

Fig. 7 represents the evolution of the paste rheogram for three different concentrations of VMA. It can be seen that the effect of the VMA on the pastes rheogram is less significant than the effect of HRWRA. One can question to what extend the viscosity at the aqueous solution is increased by adding VMA. To this end, we considered the rheological behaviour of aqueous solutions of VMA at different concentrations. Fig. 8 represents the rheograms of these VMA solutions. The polymers' solutions are power–law highly shear thinning fluids.

The initial concentration of the VMA solution in the reference paste is ~ 3.3%; the viscosity of the aqueous solution would then increase by more than 2 orders of magnitudes at small shear rates (see Fig. 8). This may explain the stabilising effect of the VMA. Fig. 8 shows that between 0.1% and 10% the viscosity varies only by a factor 4. This can then explain the small influence of the VMA dosage on the rheogram of the pastes (see Fig. 7) where the concentration only varies between 2% and 5%.

3.2.4. Influence of the polymer admixtures on the rheological properties

The rheograms reported above show that at sufficiently low shear rates, the pastes behave as power–law fluids. Fig. 9 represents the evolution of the stress as a function of shear rate in the shear thinning part of the rheogram, for different dosages of HRWRA. These results indicate that the rheological behaviour of

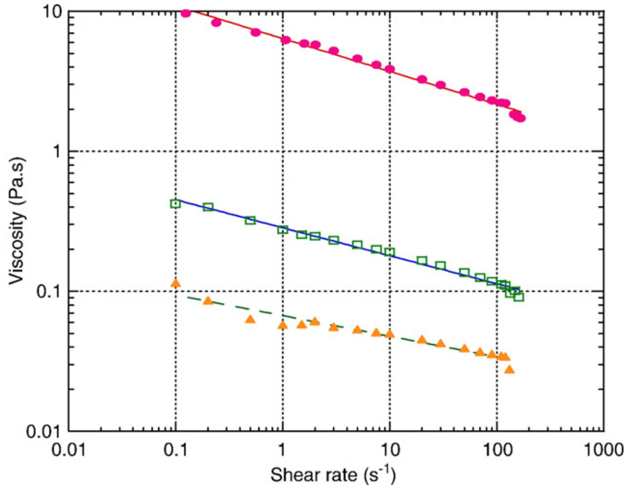

Fig. 8. Rheological behaviour of the VMA for different concentrations by weight in water: (●) 20%; (□) 10%; (▲) 0.1%.

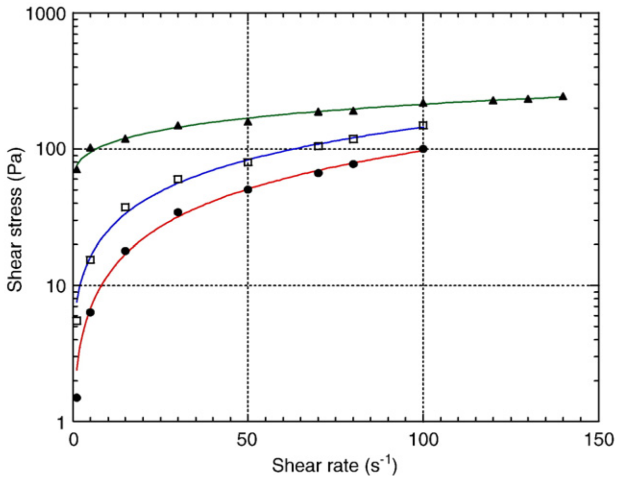

Fig. 9. Shear stress against shear rate in the shear thinning part of the rheograms. The continuous lines represent the best fit with the Herschel–Bulkley model. (□) Reference paste; (●) P+40SP; (▲) P-40SP.

the pastes can be modelled fairly well using a Herschel–Bulkley (HB) model:

$$\sigma = \sigma_y + k\gamma^n \tag{1}$$

Where:

σ_y	the yield stress,
k	the paste's consistency
n	the shear thinning index.

The Herschel–Bulkley model has often been used to describe the rheological behaviour of cementitious pastes and concretes. However it is generally assumed that this model is valid throughout the whole shear rate interval investigated. It is possible to do the same thing here, however the fit would be inaccurate leading to an underestimation of the yield stress and the consistency, and an overestimation of the shear thinning index.

The best fit of the HB model with our experimental measurements in shear thinning part of the rheograms leads to the rheological parameters of the pastes, including the yield stress, the consistency and the shear thinning index. These parameters are reported in Table 4 for the different HRWRA contents considered.

3.2.5. Comparison between the influence of HRWRA and VMA on the rheological behaviour

From the experimental results reported above it can be concluded that the effect of HRWRA on the rheological properties of cementitious pastes is much more significant than that of the VMA. This can be qualitatively understood using a typical model developed for highly concentrated granular suspensions. For instance, using the Krieger–Dougherty [23] model the effective viscosity of the paste can be written as:

$$\mu = \mu_0\left[1-\frac{\varphi}{\varphi_M}\right]^{-[\eta]\varphi_M} \tag{2}$$

where:

μ_0	the viscosity of the interstitial fluid,
φ	the volume fraction of the cement and filler aggregates,
φ_M	the volume fraction corresponding to maximum packing,
$[\eta]$	is the intrinsic viscosity (viscosity at infinite dilution) defined by: $[\eta] = \lim\limits_{\varphi\to 0}\frac{\eta-\eta_f}{\eta_f\varphi}$

The intrinsic viscosity represents individual contribution of the particles to the viscosity, and depends upon their geometry. For non-Brownian spherical hard particles, the intrinsic viscosity is equal to 2.5, and Eq. (2) reduces into the Einstein's expression for dilute suspensions of spheres [24].

Table 4
Influence of the HRWRA dosage on the paste rheological parameters including, the shear thinning index, consistency and yield stress

	P-40SP	P-20SP	Reference	P+20SP	P+40SP
Yield stress (Pa)	1.18	3.12	4.51	17.43	60.9
Consistency (Pa s^n)	1.2	2.45	3.05	6.23	15.21
Shear thinning index	0.95	0.86	0.83	0.75	0.5

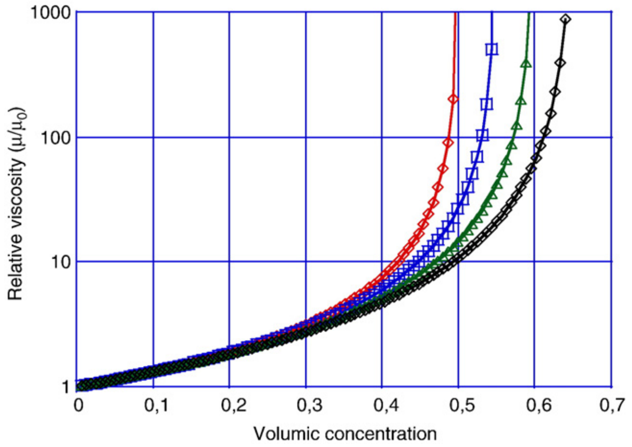

Fig. 10. Viscosity as a function of concentration for different φ_M (volume fraction corresponding to maximum packing) according to the Krieger–Dougherty model: (◇) φ_M=0.5; (□) 0.55; (△) 0.6; (◇) 0.65.

It is worth noting that the Krieger–Dougherty model has been developed for suspensions in a Newtonian fluid. In our case, the liquid phase is a shear thinning polymer solution, and the apparent viscosity is a function of shear rate, which is not taken account in Eq. (2). To our knowledge there is no equivalent Krieger–Dougherty model for suspensions in shear thinning fluids. Our discussion here is only qualitative, so we assume that this model is valid for any given shear rate. μ_0 may be a function of a local shear rate that is greater that the applied one.

The maximum packing concentration φ_M depends upon the geometry of the particles and their polydispersity; for high aspect ratio particles φ_M may be close to 1. φ_M can also be quite large for a certain particle size distribution. If we assume that the aggregates making up our pastes are approximately spherical (actually they have irregular and fractal form), by varying the dosage of HRWRA and VMA the only parameters affected in Eq. (2) are μ_0 and φ_M.

Fig. 10 represents the evolution of the viscosity versus volume fraction for different volume fractions of maximum packing as predicted by Eq. (2). It can be seen that at high concentrations the viscosity is highly sensitive to φ_M. For instance, for a given concentration close to 0.5 the viscosity can be divided by two orders of magnitudes if φ_M is increased close to 0.65. The dispersion of the flocs by the HRWRA may lead to such an increase of φ_M, and consequently a large decrease of the viscosity. On the other hand the VMA is expected to change only the viscosity of the interstitial fluid μ_0, which may not have such a significant effect on the paste's viscosity compared to φ_M as it can be readily seen from Eq. (2).

4. Conclusion

An experimental investigation into the influence of organic additives on the rheological properties of cement pastes was presented. Both transient and steady state rheological properties were considered and it was found that the steady state rheological parameters were dependent upon the initial conditions. The pastes are then only partially thixotropic. The pastes rheograms were found to be more complex than reported by previous studies. They were split into three parts: for relatively low shear rates the pastes behaved as a power–law shear thinning fluid, this is followed by a Newtonian plateau and at high shear rates the paste showed a shear-thickening behaviour.

The influence of HRWRAs dosage on the rheological properties was compared to that of VMAs. It was found that the rheological properties of the pastes are much more sensitive to HRWRAs than VMAs. This has been interpreted using the Krieger–Dougherty model for concentrated granular suspensions. In fact, this model indicates that the rheological properties of the pastes would mainly depend upon the configuration of the granular skeleton and less on the fluid phase. The above result can then be understood since VMAs mainly affect the aqueous solution (by increasing it viscosity) while HRWRAs can drastically change the granular phase configuration (dispersion of the flocs).

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