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Effect of various superplasticizers on the rheological properties of Portland cement pastes

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Abstract

In the present work, the influence of the addition of some superplasticizers employed for maximising the solid loading of Portland cement pastes has been investigated. Cement pastes were prepared from deionized water and a commercial manufactured ordinary Portland cement 32.5 R (produced by Buzzi Unicem). Cement and water were mixed with a vane stirrer according to ASTM Standard C305. The water/cement ratio was kept fixed at 0.32. Three commercial superplasticizing agents produced by Ruredil were used: they are based on a melamine resin (Fluiment 33 M), on a modified lignosulphonate (Concretan 200 L), and on a modified polyacrylate (Ergomix 1000). Rheological tests were carried out at 25 °C by using the rate controlled coaxial cylinder viscometer Rotovisko–Haake 20, system M5-Osc., measuring device MV2P with serrated surfaces. The tests were performed under both continuous and oscillatory flow conditions. Ergomix 1000 presents a different behaviour as that of the other two superplasticizers studied, because it shows a marked shear-thickening behaviour above a critical deflocculant concentration and slight elastic effects particularly at high dosages as well.

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Keywords: Rheology; Portland cement; Cement paste; Admixture; Superplasticizers

1. Introduction

The study of cement paste rheology is needed to supply a useful tool for controlling cement production, for achieving further information on the chemistry of cement, as well as for special applications, such as injections of cement suspensions in loose soils. Moreover, a knowledge of the rheology of fresh cement pastes may contribute to a better understanding of the flow behaviour of mortars and concrete.

Fresh cement pastes are highly concentrated suspensions; their rheological behaviour is generally very complex, it being dependent of several factors of different nature, such as:

- physical factors (the water/cement ratio, the cement grain shape and size, etc.)
- chemical and mineralogical factors (the cement composition and its structural modifications due to hydration processes, etc.)
- mixing conditions (stirrer's type and rate, the stirring time, etc.)
- measurement conditions (the measuring instruments, the experimental procedures, etc.)
- presence of additives.

In the present work, the influence of the addition of some superplasticizers on the rheological properties of fresh cement pastes was studied. Superplasticizers are nowadays widely employed in cement technology, since they improve workability at a given water/cement ratio, or, on the other hand, they permit the same workability to be obtained as that of plain cement paste with a great reduction in water content, as well as final products with higher mechanical strengths to be manufactured.

The increase in cement paste fluidity by the addition of a water reducer is connected with the dispersing action exerted by the adsorption of admixture molecules on the solid surface, which modifies the zeta potential of particles or favours their dispersion on account of a phenomenon of steric impediment.

The present paper has been undertaken in order to evaluate by means of rheological techniques of both rotational and oscillatory type the effectiveness of three commercially available superplasticizers.

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A lot of experimental work concerning cement pastes rheology is available in the literature [1–10].

2. Experimental part

2.1. Materials

Cement pastes were prepared from deionized water and a commercially manufactured ordinary Portland cement 32.5 R (produced by Buzzi Unicem). Cement pastes were prepared with a vane stirrer (Ultra-Turrax T50, Janke & Kunkel, IKA-Labortechnik) according to ASTM Standard C305. The water/cement ratio (W/C) was kept fixed at 0.32. Three commercial superplasticizing agents produced by Ruredil were used. They are based: (1) on a melamine resin (Fluiment 33 M; dosage recommended by the producer: 1–5 ml/100 g of cement); (2) on a modified lignosulphonate (Concretan 200 L; recommended dosage: 0.7–1.5 ml/100 g of cement); (3) on a modified polyacrylic resin (Ergomix 1000; recommended dosage: 0.5–1.5 ml/100 g of cement). The superplasticizers were employed within a concentration range including the dosage recommended by the producer.

2.2. Apparatus and procedures

Rheological measurements were carried out using the rate-controlled coaxial cylinder viscometer Rotovisko–Haake 20, system M5-Osc., measuring device MV2P with serrated surfaces (R_i = 18.4 mm ; R_o = 21 mm; h = 60 mm). The temperature was kept strictly constant at 25 ± 0.1 °C. The tests were accomplished under both continuous and oscillatory flow conditions. The following rheological procedures were applied:

a) *Continuous flow conditions*: Tests under variable shear rate (hysteresis cycles): a first hysteresis cycle was drawn 1 min after mixing; changes in shear rate were made at the constant shear acceleration of 7.31 s^{-2}; the maximum shear rate reached was 439 s^{-1}. The same sample was subjected to a second hysteresis cycle 1 min after the previous one. The down curves of the second hysteresis loop have been utilized as flow curves for the cement pastes examined.

b) *Oscillatory flow conditions*: A 0.1 to 1 Hz frequency sweep with 0.2 rad of constant strain was applied, after determining the limits of linear viscoelastic region by means of strain sweep experiments from 0.1 to 1.5 rad of strain at a 0.1 Hz constant frequency. Fig. 1 illustrates an example of strain sweep to which pastes were subjected. All the oscillatory experiments started 1 min after sample preparation.

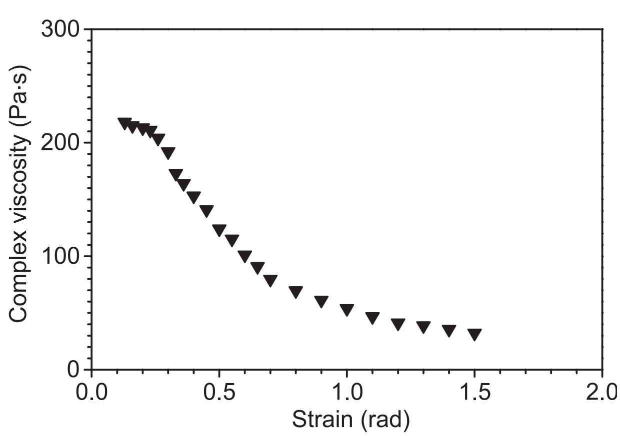

Fig. 1. Complex viscosity versus strain for the 0.32 W/C cement paste (frequency = 0.1 Hz).

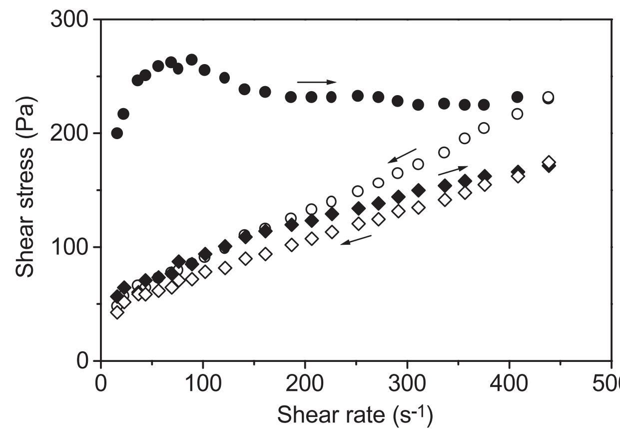

Fig. 2. Shear stress versus shear rate hysteresis cycle for the 0.32 W/C cement paste.

3. Results and discussion

3.1. Continuous flow tests

According to procedure (a), two hysteresis cycles were drawn after sample preparation. In the case of the cement

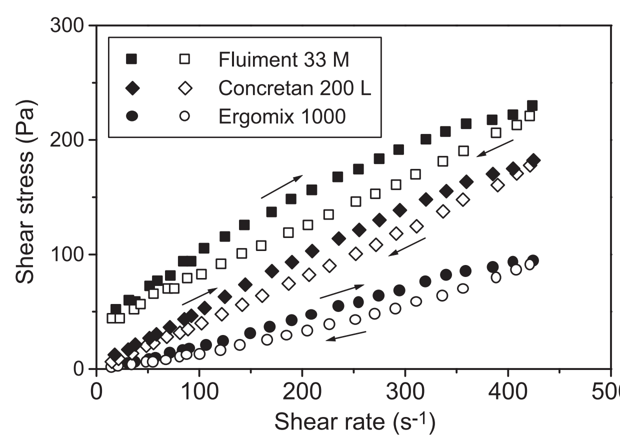

Fig. 3. Second hysteresis cycle obtained for some cement pastes (Fluiment 33 M: 0.5 ml/100 g of cement; Concretan 200 L: 1 ml/100 g of cement; Ergomix 1000: 1 ml/100 g of cement).

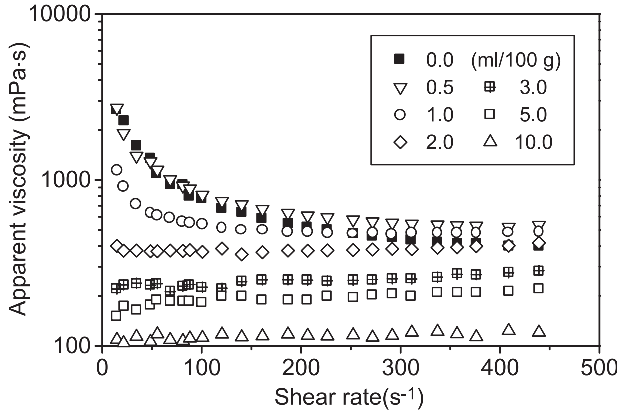

Fig. 4. Apparent viscosity versus shear rate flow curves for the 0.32 W/C cement pastes investigated at various Fluiment 33 M concentrations.

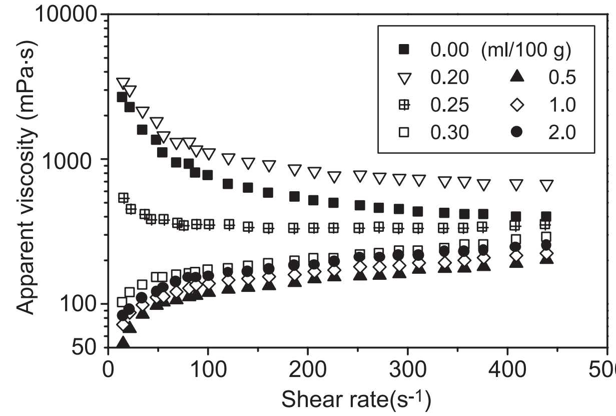

Fig. 6. Apparent viscosity versus shear rate flow curves for the 0.32 W/C cement pastes investigated at various Ergomix 1000 concentrations.

paste prepared without additive, the first cycle shows a shape similar to that already described in previous papers [8,10]: the down curve lies on the lower shear stress side than the upper one, i.e. structure breaks down during the test; the second hysteresis loop presents both up and down curves of shear-thinning type and the rheological behaviour is strictly thixotropic (see Fig. 2). The addition of superplasticizer breaks about some modification in the pattern of second hysteresis cycle, in that the down curve lies on the lower shear stress side than the upper one for each superplasticizer and for each additive concentration, thus indicating that structure breaks down; nevertheless, the down curve may be of newtonian, shear-thinning or shear-thickening type, it being dependent of the nature of additive (see Fig. 3).

Figs. 4–6 report the apparent viscosity versus shear rate flow curves derived from the down curve of the second hysteresis loop and obtained for the cement pastes investigated in the present work: the flow curves are strongly dependent on both nature and amount of deflocculant. It can be observed that all the suspensions prepared with Fluiment 33 M and Concretan 200 L present an initial shear-thinning behaviour till a limit deflocculant concentration above which a newtonian behaviour is evident (see Figs. 4 and 5).

On the other hand, the addition of Ergomix 1000 brings about, after an initial shear-thinning behaviour, a marked shear-thickening behaviour above a critical deflocculant concentration of about 0.25 ml/100 g, as can be clearly seen in Fig. 6. The shear-thickening behaviour could be explained in terms of polyacrylate chain interactions, i.e. nonadsorbed segments of polyacrylate molecules extending towards the water solution interact with each other. A similar rheological behaviour has been found for polyacrylate in Ref. [11].

By an examination of Fig. 7, the results indicate that, whereas in the case of Fluiment 33 M and Concretan 200 L apparent viscosity, except at very low dosages, always decreases with superplasticizer concentration (hence no optimum dosage can be determined), Ergomix 1000 apparent viscosity—dispersant concentration (c_d) plot presents a minimum in correspondence to $c_d = 0.5$ ml/100 g (the optimum dosage).

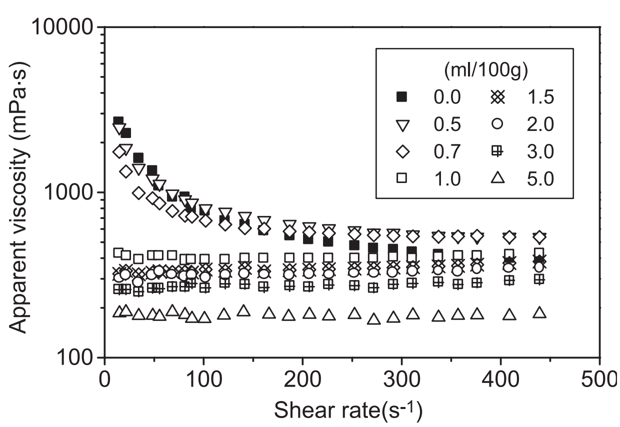

Fig. 5. Apparent viscosity versus shear rate flow curves for the 0.32 W/C cement pastes investigated at various Concretan 200 L concentrations.

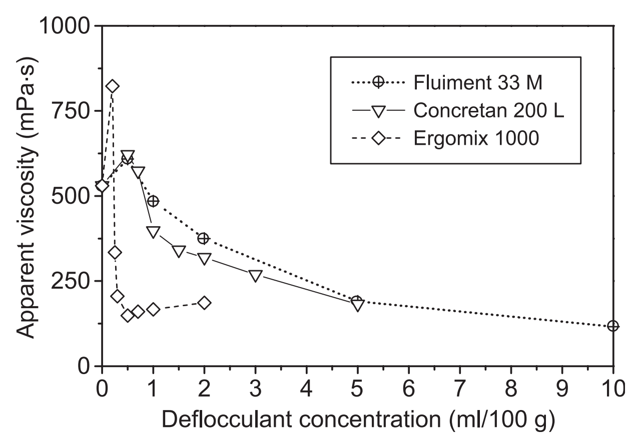

Fig. 7. Apparent viscosity versus deflocculant concentration as function of the dispersant nature (shear rate = 200 s^{-1}).

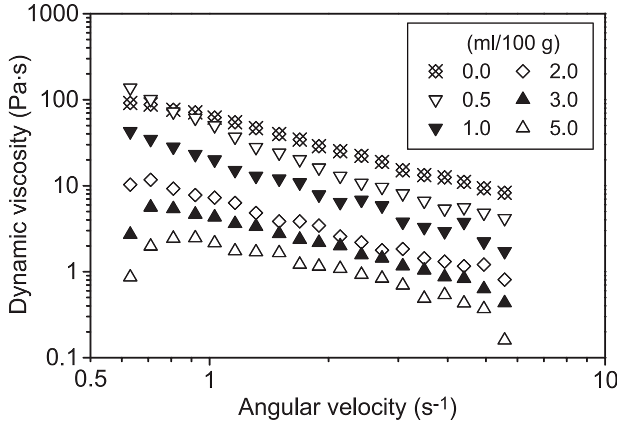

Fig. 8. Dynamic viscosity versus angular velocity for the 0.32 W/C cement paste + Fluiment 33 M (0.2 rad of constant strain).

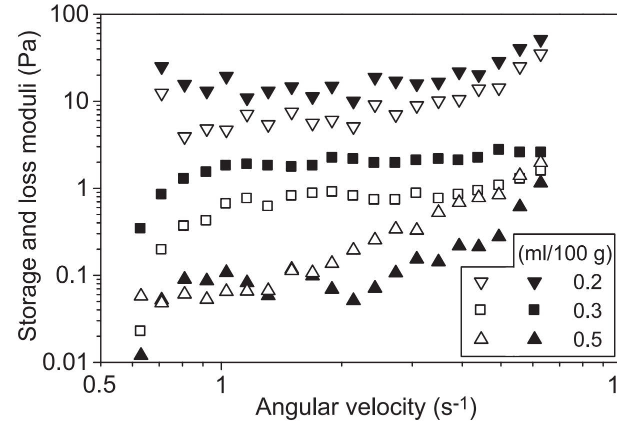

Fig. 10. Mechanical spectra: storage modulus (open symbols) and loss modulus (solid symbols)—angular velocity (frequency) for the 0.32 W/C cement paste + Ergomix 1000 (0.2 rad constant strain).

3.2. Oscillatory flow tests

Oscillatory flow tests were accomplished in order to evaluate more accurately the efficiency of the dispersing agents employed. As far as the dynamic viscosity variation with angular velocity (frequency) is concerned, a monotonic decrease of dynamic viscosity has been detected (see Fig. 8).

By examining the mechanical spectra, i.e. the plots of storage (elastic) modulus G' and loss (viscous) modulus G'' versus angular velocity (here illustrated in Figs. 9 and 10), the results indicate that Fluiment 33 M and Concretan 200 L present a similar behaviour (see Fig. 9): G'' is always higher than G', that is there is a predominance of viscous behaviour for each superplasticizing concentration as well as no sol-like to gel-like transition is evident; in addition, both G' and G'' values are nearly independent of angular velocity at low superplastizing concentrations, whereas at very high dosages an increase of both G' and G'' up to a nearly constant value is noticed with increasing frequency. On the contrary, in the case of Ergomix 1000 addition (see Figs. 10 and 11), the elastic modulus becomes higher than the loss one for concentrations above the optimum dosage and for high frequencies. The highest elasticity caused by Ergomix 1000 can be associated to a resulting much more developed agglomeration caused by polyacrylate chains. This mechanism is fully compatible with that previously suggested for explaining shear-thickening behaviour brought about by Ergomix 1000.

4. Conclusions

Among the three superplasticizing agents investigated in the present work, that based on a modified polyacrylic resin (Ergomix 1000) behaves as the most effective one to be used in the Portland cement pastes here employed, in that it promotes the lowest viscosity values within the dispersant concentration tested. In addition, the rheological results indicate that Ergomix 1000 has an optimum dosage which is in perfect agreement with that suggested by the

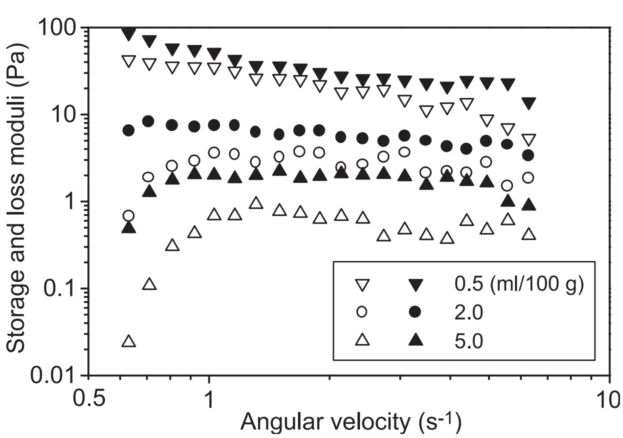

Fig. 9. Mechanical spectra: storage modulus (open symbols) and loss modulus (solid symbols)—angular velocity (frequency) for the 0.32 W/C cement paste + Fluiment 33 M (0.2 rad constant strain).

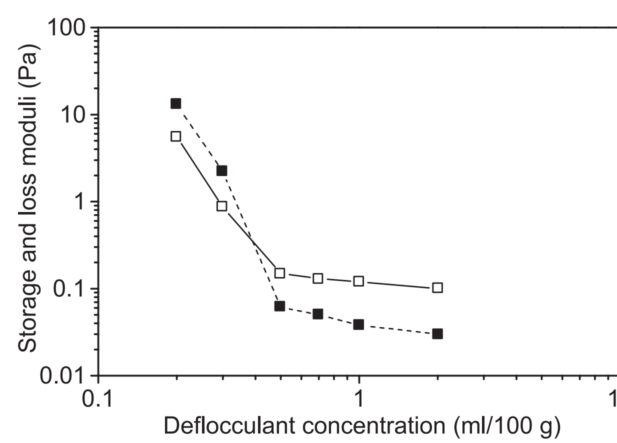

Fig. 11. Storage modulus (open symbols) and loss modulus (solid symbols) versus deflocculant concentration for the 0.32 W/C cement paste + Ergomix 1000 (angular velocity = 2 s^{-1}).

producer. Moreover, Ergomix 1000 presents a different rheological behaviour as that of the other two superplasticizers studied, since it shows marked shear-thickening properties above a critical deflocculant concentration as well as slight elastic effects. The shear-thickening behaviour can be explained by the presence of linear polyacrylate chains, which at high deflocculant concentrations causes disperse phase aggregation instead of particles repulsion. The highest elasticity caused by Ergomix 1000 can also be associated to a resulting much more developed agglomeration caused by polyacrylate chains. This mechanism is fully compatible with that previously suggested for explaining the shear-thickening behaviour of the polyacrylate.

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