



Comparative study of the yield stress determination of cement pastes by different methods

Mokrane Bala · Rachid Zentar · Pascal Boustingorry

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Abstract Different methods have been proposed in the literature to determine the yield stress of cement grouts. These methods may present wide differences especially for thixotropic materials such as cement pastes. In this paper, different mixtures of water–cement–superplasticizer were studied for various w/c ratios and superplasticizer dosages. From shear tests of the mixtures in a rheometer, yield stress was determined in different ways: by identification on the experimental flow curve or by modelling flow curve through different rheological models. The conventional rheological models as Bingham model and Herschel–Bulkley model are not in agreement in the majority of the cases studied especially at low shear rates where thixotropy can be observed. In order to enhance the modelling in this area and allows to accurately determine the yield stress, we compared the results obtained through the conventional rheological models to that obtained by a thixotropy model. From the obtained results, it turns out that the latter allows to better predict the behaviour of thixotropic cement grouts and their yield stress.

Keywords Rheology · Cement pastes · Yield stress · Viscosity · Thixotropy

1 Introduction

The prediction of the rheological behaviour of concretes is at the centre of current concerns of the concrete industry for different reasons. The shortage of good quality standard materials combined with variable properties of available materials imposes to improve existing models to take into account these variations at the design stage of concrete. The main reasons for improving the predictive models are, of course, saving time and cost at the design stage. Moreover, in the framework of sustainable development, these improvements could allow to optimize with almost no additional cost the performances of designed concrete.

Several rheological studies of concrete have shown that the concrete behaviour at the short time could be assimilated to yield stress fluid [1, 2]. The yield stress of a cementitious material indicates the critical stress value at which the material will start or stop flowing, which is an important property when placing the material [3]. The yield stress of concrete is impacted not only by the granular skeleton (packing density, grain shape, particles size distribution...) but also by the quality of the cement paste that fills the voids between the grains [4–6].

M. Bala (✉) · R. Zentar
LGCgE-GCE, Institut Mines Telecom Lille-Douai, 764 bd
Lahure, BP 10838, 59508 Douai, France
e-mail: mokrane.bala@imt-lille-douai.fr

P. Boustingorry
CHRYSO France, 7 Rue de l'Europe,
45300 Sermaises du Loiret, France

From physical point view, the yield stress is a manifestation either of particles interactions (Van der Waals attraction forces) between colloidal grains of sizes close to one micrometre or of solid friction between grains [7–9]. This property is evolving over time according to the physicochemical changes due to the phenomena of hydration (setting phase) of cement. Several methods exist for determining the yield stress of cement pastes [3, 10–12]. We can distinguish those based on the experimental interpretation of the flow curves and those based on modelling the experimental curves by using a rheological model.

In the first family of methods, specific test procedure, using increasing shear rates and/or shear stress experiments, could be undertaken [13–15]. For tests with controlled shear stress (increasing shear stress), the yield stress could be identified as the stress which corresponds to the initiation of shearing in the cement paste [13]. In routine tests with standard material, this procedure is generally difficult to achieve [12]. An alternative approach for the determination of the yield stress is through the use of dynamic oscillatory measurements, in which the material is subject to a sinusoidal strain and the resulting stress is measured as a function of time and frequency [16]. Equivalent method by using a controlled shear rate could allow the identification of the yield stress by determining the intercept (from experimental data) on the axis of shear stress [10, 11, 17]. This later is defined hence as the yield stress [17]. In the same family of methods, using decreasing shear rate and/or shear stress, the yield stress could be identified when a sudden instability is recorded on the flow curve [11]. This instability could be materialised in the case of controlled shear stress as a sudden decrease of the shear rate with the decrease in the shear stress, or in the case of controlled shear rate test as an increase of the shear stress with the decrease of shear rate. This phenomenon is generally explained as the possible competition between the build-up of the structure of cement paste in opposition to the destroying effects induced by the shearing [10, 11].

In the second family of methods, generally, a rheological model integrating the yield stress is identified by minimising the difference between the model prediction and the experimental data [11, 12]. In this order, several rheological models are proposed in the literature. These models in addition to the number of parameters are different by the type of phenomenon able to model and the extent of the

validity of these models with the level and the range of shear rates.

Vance et al. [11] have shown that the range of the shear rate influences the response of cement pastes by a linear or nonlinear law as well as the corresponding yield stress. They found that for a shear rate values between 5 and 100 s^{-1} , the flow curve is linear and the Bingham model (Eq. 1) shows a good correlation with the experiments. The parameters of Bingham model indicate the colloidal forces and the viscous dissipation [18, 19].

For a shear rate range between 0.1 and 100 s^{-1} , the flow curve is nonlinear and a shear stress plateau is expected at low shear rates (in a logarithmic scale presentation). This is in line with the work published by Banfill [17], Schwartzentruber et al. [13] and Vance et al. [11]. Vance et al. find that Bingham model is not satisfactory and that Herschel–Bulkley model (Eq. 2) can better represent the nonlinearity of the flow curve. The authors have explained the shear stress plateau by the degree of the build-up of the material that resists to the flow. The Herschel–Bulkley model, in the conditions cited above, gives a good correlation with the experience [13, 14]. Moreover, it allows to predict the shear-thickening or the shear-thinning behaviour of cement pastes [11]. The yield stress, in this case, corresponds to the asymptote of the flow curve [11]. For concentrated fluids (low w/c ratio), the modified Bingham model (Eq. 3) can be used to show the degree of shear-thickening behaviour in high shear rates and the shear stress plateau in low shear rates [20].

The rheological models cited above make it possible to describe the behaviour of fluids in the steady-state, which is not always the case for cement pastes. According to Roussel et al. [21], the flow of cement pastes at low shear rates is strongly influenced by the phenomenon of thixotropy. This latter is the property of decreasing viscosity under a constant shear stress or shear rate in time and returning the initial state gradually (build-up) when the shear stress or shear rate effect is removed [22]. The thixotropy can be evaluated by different ways [23]. Roussel et al. [24, 25] have proposed a thixotropy model which makes it possible to represent the flow curves by taking into account the degree of the build-up of the material through a dimensionless coefficient denoted λ . At a zero shear rate, it is assumed that the build-up level increases at a constant rate [24]. The build-up



parameter is, therefore, time-dependent. It competing with the degree of breakdown of the material which depends on the imposed shear rate. In the case of shear-thickening behaviour, the hydrodynamic dissipation is taken into account in the model [26].

At last, the thixotropy model of Roussel et al. is expressed in terms of apparent viscosity (Eq. 4) or in terms of shear stress (Eq. 5). Equations 4 and 5 describe the rheological behaviour of the cement pastes and can be used to model the experimental flow curves [26]. Therefore, the calculation of the yield stress by the thixotropy model of Roussel et al. [24] seems interesting and makes it possible to reproduce the real conditions of a shear test of cement pastes.

$$\text{Bingham model: } \tau = \tau_0 + \mu_{pl} \cdot \dot{\gamma} \quad (1)$$

$$\text{Herschel–Bulkley model: } \tau = \tau_0 + K \cdot \dot{\gamma}^{n_e} \quad (2)$$

$$\text{Modified Bingham model :} \quad (3)$$

$$\tau = \tau_0 + \mu_{pl} \cdot \dot{\gamma} + C \cdot \dot{\gamma}^2$$

$$\text{Thixotropy model of Roussel et al. :} \quad (4)$$

$$\eta = \eta_\infty (1 + (\alpha\theta\dot{\gamma})^{-n}) + \beta\dot{\gamma}$$

$$\tau = \eta\dot{\gamma} = \eta_\infty (\dot{\gamma} + (\alpha\theta)^{-n} \cdot \dot{\gamma}^{1-n}) + \beta\dot{\gamma}^2 \quad (5)$$

In these equations, “ τ ” is the shear stress (in Pa), “ τ_0 ” is the yield stress (in Pa), “ μ_{pl} ” is the plastic viscosity (in Pa s), “ $\dot{\gamma}$ ” is the shear rate (in s^{-1}), “ K ” is the consistency index (in Pa s), “ n_e ” (dimensionless coefficient) is the flow index (the fluid is shear-thickening if $n_e > 1$ and shear-thinning if $n_e < 1$), “ C ” is a constant which represents the intensity of shear-thickening (in Pa s^2), “ η_∞ ” is the value of the viscosity on the Newtonian plateau at high shear rates (in Pa s), “ α ” is the degree of breakdown of the material, “ θ ” is a time constant for the structure build-up rate, “ n ” is a dimensionless coefficient which represents the degree of dependence of the viscosity on the build-up parameter “ λ ” and “ β ” is the hydrodynamic dissipation coefficient.

In this paper, comparisons between measured and calculated yield stresses throughout modelling the flow curves using different rheological models is undertaken. These comparisons are made on cement pastes with different characteristics. The main objective of the present study is to assess the ability of discussed models to predict the yield stress and to explain the physical phenomenon observed during the

experiments. It is to note that this study is developed in the framework of more general project aiming to predict the rheological behaviour of concrete knowing few rheological characteristics of the cement paste and the packing density of the granular skeleton.

2 Materials and methods

In this research work, Portland cement type CEM I 52.5 R [27] from LafargeHolcim Saint-Pierre-La-Cour is used. The particle size distribution of the cement was measured using laser diffraction particle sizing analyzer of type Beckman Coulter LS 13,320 and its absolute density was determined by a helium pycnometer of type Micromeritics Accupyc 1330. In order to investigate a wide range of yield stress, in addition to the study of cement pastes with different ratios of water to cement, the effect of the addition of superplasticizer on the yield stress is also discussed. The superplasticizer is of type CHRYSO[®] Fluid Optima 206 conforming to EN 934-2 norm [28]. It is a new-generation of polycarboxylate superplasticizer which contains 20.3% of dry extract of polymers incorporated preferably in mixing water.

Before proceeding to the rheological measurements on cement pastes, the saturation dosage of the cement by the superplasticizer must be determined. This dosage is defined by the amount of superplasticizer beyond which the cement grains no longer adsorb polymers or the adsorption stabilizes [29]. In order to determine the superplasticizer saturation dosage, the AFREM method is used [30]. The test consists of measuring the flow time of 500 mL of cement grouts (cement–water–superplasticizer mix) through a Marsh cone with an orifice diameter of 8 mm. The measurements are represented by a curve giving the flow time of the Cement–Superplasticizer (C–SP) system as a function of the superplasticizer dosage (fixed water/cement ratio). The curve obtained gives the critical dosage corresponding to the saturation point (the minimum of the curve). When the superplasticizer is added beyond the saturation point, the fluidity of the C–SP system is no longer improved. It only increases the risks of sedimentation and delay setting time of the cement due to the superplasticizer overdose. Finally, we note that the flow time measurements are realized after 5 min from the cement–water–superplasticizer contact.



Table 1 Experimental program and materials dosage

Cement dosage			Superplasticizer dosage		Water dosage (w/c ratio)		
In (g)	Absolute density in (g/cm ³)	In (cm ³)	% in dry extract	% in diluted state	0.4	0.5	0.6
150	3.17	47.3	0.00	0.00	Mix 1	Mix 5	Mix 9
			0.12	0.60	Mix 2	Mix 6	Mix 10
			0.24	1.20	Mix 3	Mix 7	Mix 11
			0.37	1.80	Mix 4	Mix 8	Mix 12

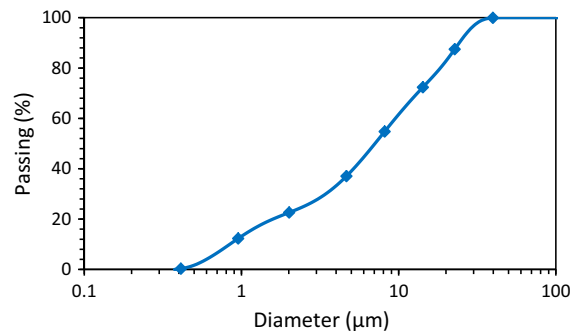
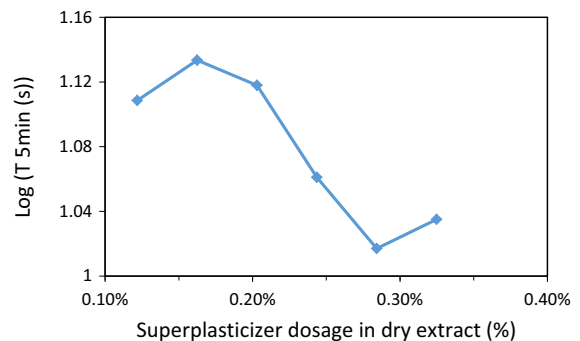
For the measurement of the rheological characteristics of the different cement pastes, ANTON PAAR MCR102 rheometer is used. The adjustments made before starting the tests are the temperature of the test (20 °C) and the adjustment of the inertia system. During this study, the coaxial cylinder geometry, with a fixed gap between the shearing surfaces of 1 mm is used. Before the rheological measurements, the cement pastes are mixed in a double rotation mixer during 4 min.

The procedure of rheological measurements starts 5 min after the beginning of mixing with a pre-shearing at 100 s⁻¹ during 60 s to eliminate any influence of the sample build-up history. Then, the shear rate applied varies from 100 to 0.01 s⁻¹ following a descending ramp in logarithmic scale (4 measurements are taken each decade). The shear stress measurements are realized until steady state has been achieved (defined by two consecutive apparent viscosity measurements within 5% of each other). The test duration is generally between 5 and 10 min. The choice of a wide shear rate range makes it possible to test mixtures with high or low yield stress. Three different measurements were made for each mixture.

In the experimental program the water to cement ratio in mass (w/c) varies from 0.4 to 0.6 (by 0.1 increments) and the superplasticizer dosage varies from 0 to 0.36% (dry extract) with an increment of 0.12%. In Table 1, the experimental program is summarised. It is composed of 12 mixtures different by the w/c ratio and/or the amount of superplasticizer.

3 Results and discussions

The particle size distribution of the cement used in this study is shown in Fig. 1. On this curve, we note that the maximum diameter of the cement grains is 50 microns. This result is conform to several studies

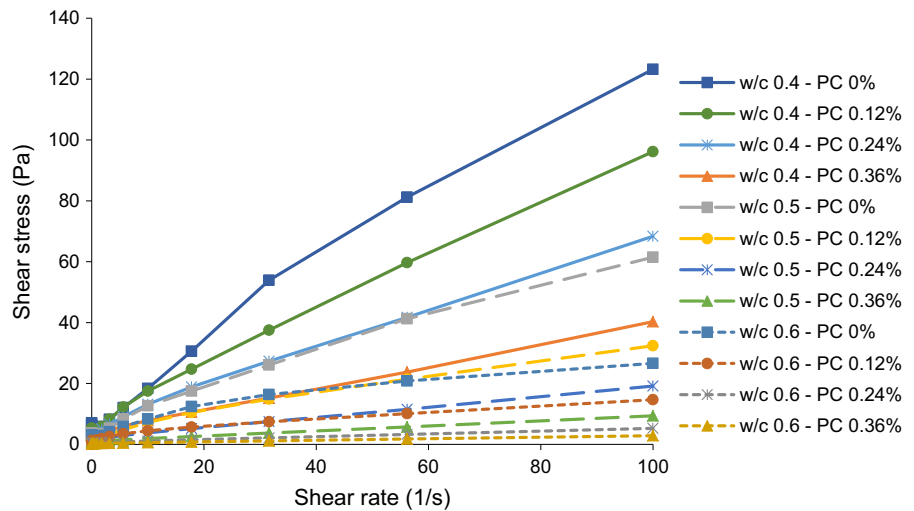
**Fig. 1** Particle size distribution of CEM I 52.5 R**Fig. 2** Saturation dosage of the superplasticizer

undertaken on this type of cement [31]. For the coaxial cylinder geometry used in the rheometric study, the gap is 1 mm which respects the condition that the gap is greater than 10 times the maximum diameter of tested materials in the rheometer [17].

The saturation curve of the superplasticizer according to the AFREM method is presented in Fig. 2. The flow time after 5 min of the cement–water–superplasticizer contact is plotted versus the dry extract of the polymers (superplasticizer). The flow time axis is presented in logarithm scale to allow a better view of the curve. Figure 2 shows that the flow time of the cement grout through Marsh cone decreases when the



Fig. 3 Shear stress curves of mixtures (w/c ratio varies from 0.4 to 0.6 by 0.1 increment and superplasticizer dosage from 0 to 0.36% by 0.12% increment)



superplasticizer dosage increases. The flow time then increases by exceeding a dosage of 0.28%. This indicates that the superplasticizer improves the fluidity of the cement grout until it reaches the saturation dosage of 0.28% in dry extract of the superplasticizer (1.4% in the diluted state). By exceeding this dosage, the apparent viscosity of the cement grouts can reach very low values that cause the sedimentation of the cement grains at the Marsh cone orifice and increase the flow time. These results allow to justify the three different superplasticizer dosages used in the present study (0.12%, 0.24% and 0.36%). The first dosage corresponds to a state where the cement is under-saturated, the second dosage is about to ensure the saturation of the cement and the third dosage corresponds to the over saturated state of cement.

In terms of flow curve, following the protocol described above, in Fig. 3 the results for the 12 tests undertaken are represented.

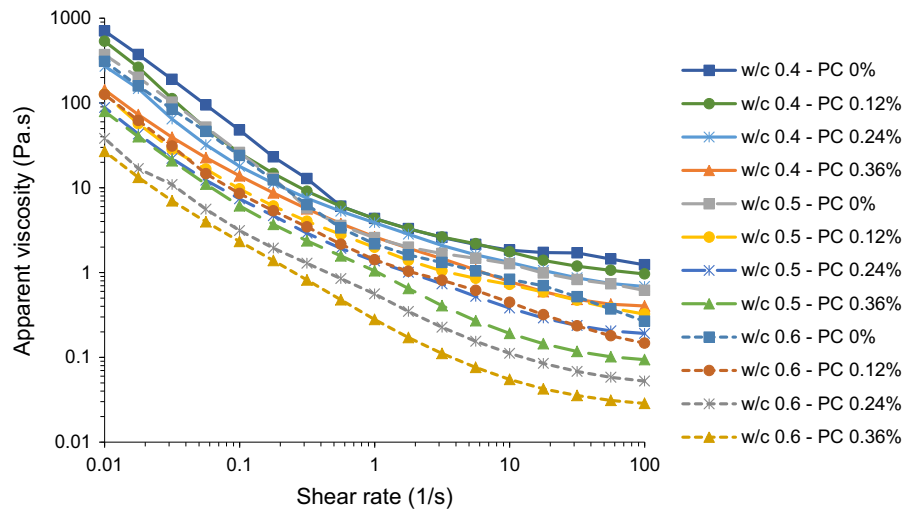
From Fig. 3 we can see that for a given shear rate, the shear stress decreases significantly by increasing the w/c ratio. For a shear rate of 100 s^{-1} , the shear stress decreases from about 123 Pa for cement paste with w/c equal to 0.4 to almost 27 Pa for w/c equal to 0.6. The addition of the superplasticizer Polycarboxylate (PC) in the cement paste decreases also the shear stress and allows to reach the same shear stresses with lower w/c ratio (w/c = 0.4 with 0.24% of PC and w/c = 0.5 without PC for example). However, the efficiency of the superplasticizer seems to be optimum with the dosage equal to the saturation dosage as defined in Fig. 2. For cement pastes with

superplasticizer dosage over the saturation amount, no significant effect is noticed on the evolution of the flow curves.

In terms of apparent viscosity, the calculated results from Fig. 3 are shown in Fig. 4. As expected, accordingly to the test protocol undertaken, the apparent viscosity increases with the decrease of the shear rate. This tendency is verified for all the different tests. The apparent viscosity calculated is also affected by the w/c ratio and the superplasticizer dosage. An increase of w/c ratio induces a decrease in the apparent viscosity. In the same way, an increase of the superplasticizer dosage induce a decrease of the apparent viscosity. However, as for the flow curves of Fig. 3, the effect of the superplasticizer on the apparent viscosity seems to be limited when the dosage exceeds the saturation dosage. These results are mainly due to the decrease in solid volume concentration or the decrease of the viscous dissipation following the modification of the flocculation state of the cement grains by the addition of the superplasticizer [6, 32]. However, the amount of adsorbed polymers may influence the efficiency of the superplasticizer [32], which explains that the decrease in apparent viscosity is much greater for a w/c ratio of 0.6 (as shown in Fig. 4).

In Fig. 5, the shear stress is plotted versus the apparent viscosity in log–log scale for different w/c ratios and superplasticizer dosages. From this figure, it can be seen that both the shear stress and apparent viscosity decrease when w/c ratio and/or superplasticizer dosage increase. It is confirmed also that the

Fig. 4 Apparent viscosity curves in log–log scale of the different mixtures (w/c ratio varies from 0.4 to 0.6 by 0.1 increment and superplasticizer dosage from 0 to 0.36% by 0.12% increment)



efficiency of the superplasticizer is more significant when w/c ratio is high. Otherwise, the apparent viscosity decreases at high shear stresses indicating a shear-thinning behavior [20] and increases significantly at low shear stresses indicating flow instability.

In order to evaluate the yield stress from the different flow curves measured, as discussed above different methods of determination are used.

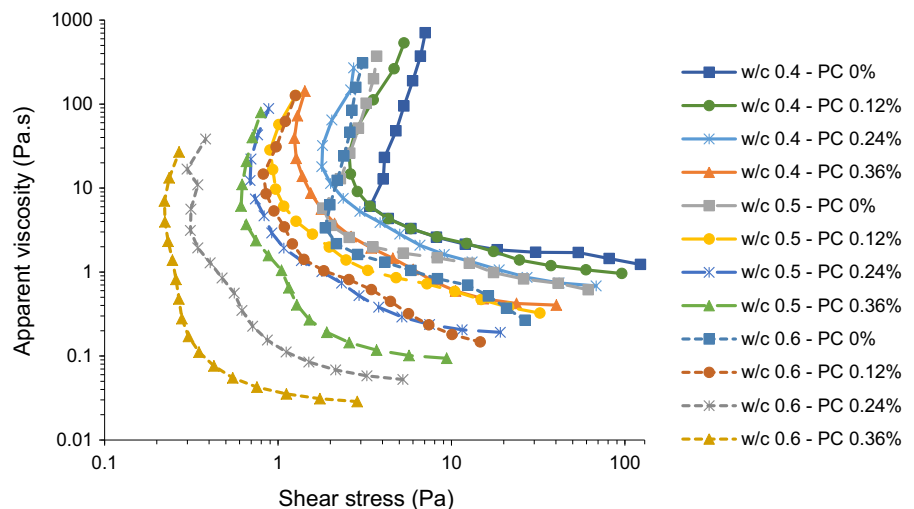
In the first family of methods, the flow curve in the semi-logarithmic scale (as shown in Fig. 6) is used.

The yield stress is defined as the minimum value reached by the shear stress on the pseudo plateau observed for low shear rates. This value corresponds to the critical stress that allows the fluid to remain in a stable flow [10, 11] and known as the “dynamic yield

stress” [16, 33]. At very low shear rates (less than 0.03 s^{-1}), shear stress tends to increase indicating flow instability (thixotropic behavior). In this zone, the build-up (aggregation) speed of the cement grains is greater than the speed of breakdown by the shear gradient (a state of competition is starting between build-up and breakdown forces). This instability of flow can be identified by the formation of shear bands [9, 10, 24, 25, 34, 35]. The phenomenon of sedimentation of grains or agglomerates of cement grains can amplify the shear stress in this zone.

The yield stresses defined by the minimum value reached by the shear stress on the pseudo plateau are reported in Fig. 7 as a function of the superplasticizer dosage and the w/c ratio (Fig. 7a) or the solid fraction

Fig. 5 Shear stress versus apparent viscosity in log–log scale of the different mixtures (w/c ratio varies from 0.4 to 0.6 by 0.1 increment and superplasticizer dosage from 0 to 0.36% by 0.12% increment)



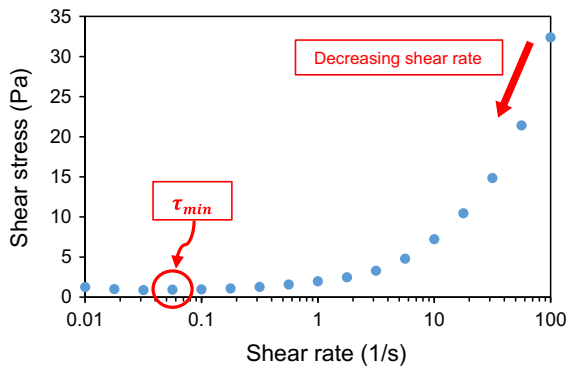


Fig. 6 Shape of experimental flow curves on semi-log scale and identification of the yield stress (for $w/c = 0.5$ and $PC = 0.12\%$)

of cement grains (Fig. 7b). From Fig. 7a, we can address the same conclusions on the effects of the w/c ratio and the impact of the superplasticizer dosage on the yield stress (Fig. 7a) as on the shear stress (Fig. 3) of cement pastes. However, to highlight the efficiency of the superplasticizer to reduce the yield stress in comparison to the increase of w/c ratio, in Fig. 7b, the yield stress is plotted versus the solid fraction for the different dosage of the superplasticizer. From these curves we can observe a substantial reduction in the yield stress (comparison between the curve with 0% superplasticizer and the curve for 1.2% superplasticizer), due to the addition of the superplasticizer in comparison to the effect of the solid fraction (expressed by the slope of the curve in Fig. 7b).

In the second family of methods investigated in this paper to identify the yield stress, models predictions of four rheological models are compared. For each rheological model (Bingham, modified Bingham, Herschel–Bulkley and Roussel et al. model), a specific identification strategy is applied. This allows a more reliable comparisons between the predictions of the different methods.

As the models performances are different and in order to define the ability of a given model to predict the observed behavior, the experimental data of the different tests were plotted in different scales: a linear scale, semi-logarithmic scale and bi-logarithmic scale. Figure 8 shows an example of those representations for $w/c = 0.5$ pastes. From the obtained results, different observations could be made:

- In the linear scale (Fig. 8a), the flow curves are linear in the range of high shear rates ($10\text{--}100\text{ s}^{-1}$).

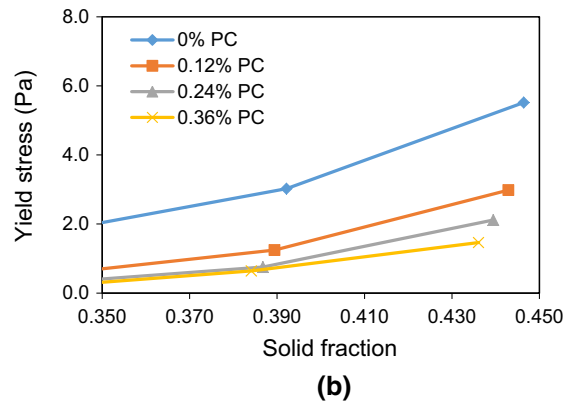
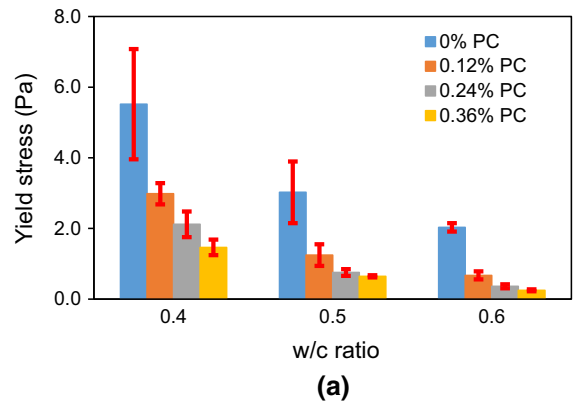


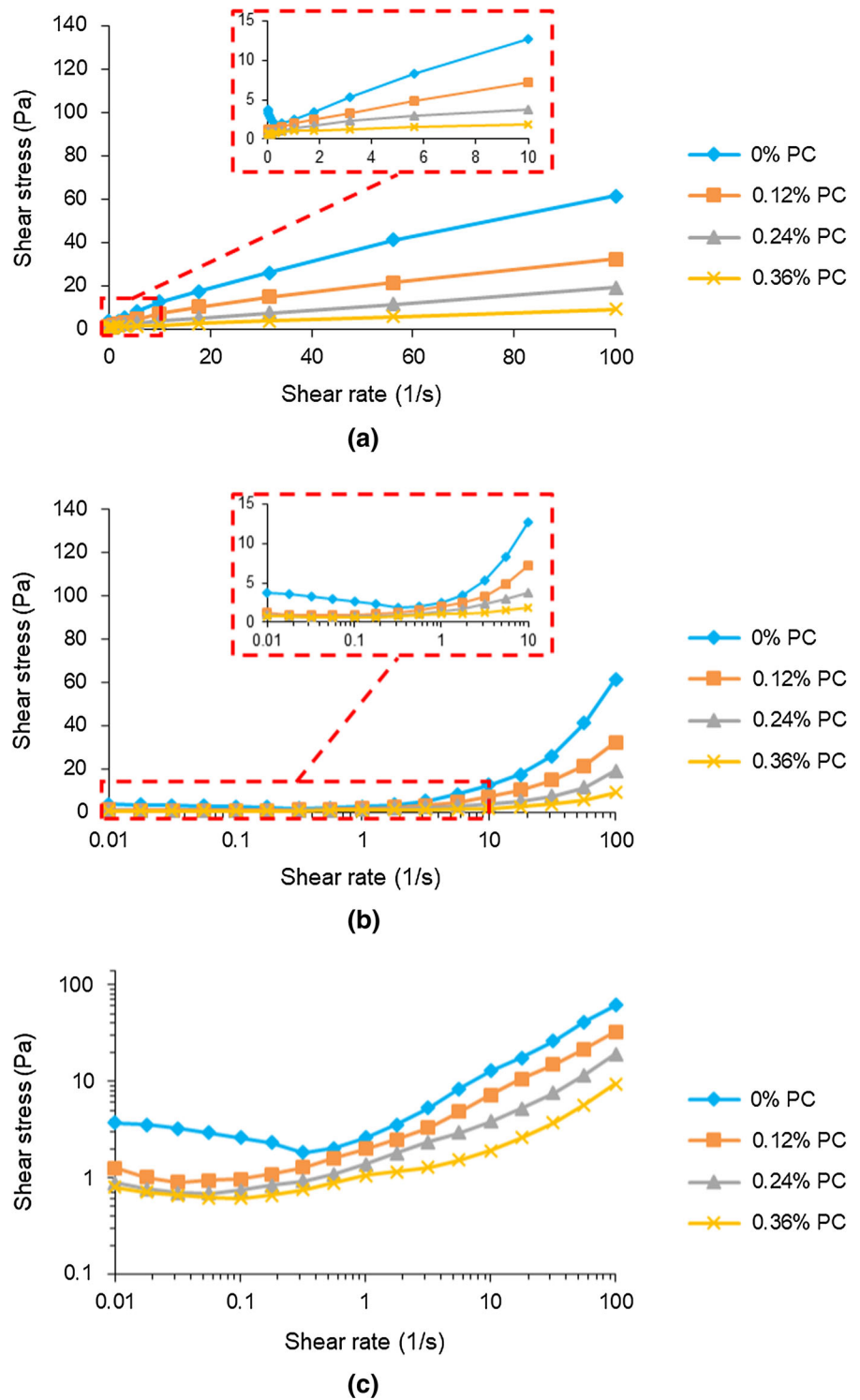
Fig. 7 Evolution of the yield stress determined from the experimental flow curves as a function of the superplasticizer dosage and: **a** w/c ratio and **b** solid fraction

Then, a curvature is observed between 10 and 1 s^{-1} . Then, the curves are again linear in the range of low shear rates. Finally, at very low shear rates the shear stresses increase.

- In the semi-logarithmic scale (Fig. 8b), a pseudo plateau of shear stresses is noted and an increase of shear stress is observed at very low shear rates (less than 0.3 s^{-1}) indicating a thixotropic behavior.
- In the log–log scale (Fig. 8c), the flow curves seem to be linear between 100 and 0.5 s^{-1} . The curvature observed on the linear scale has been linearized on log–log presentation (before that the shear stresses increase). This indicates that a power law is the most suitable for reproducing the experimental flow curve in this range.

The objective of the present work is to improve the determination of the yield stresses of cement pastes. In this context, the observations from Fig. 8 allow to deduce that for more accurate determination of the

Fig. 8 Shear stress curves for $w/c = 0.5$ in different scales: **a** linear, **b** semi-log and **c** log–log scale



yield stress, Bingham model (linear) and Roussel et al. model can be applied. Bingham model represent plastic fluids and exhibit a linear shear-stress shear-

rate behavior at low shear rates. In this case, the yield stress corresponds to the shear stress at zero shear rate. Hence to determine the yield stress accurately by the



Table 2 Calculated parameters of different rheological models

Mixtures	Bingham model		Herschel Bulkley model			Modified Bingham model			Roussel et al. model			
	τ_0	μ_{pl}	τ_0	K	n_e	τ_0	μ_{pl}	C	τ_0	η_∞	$\alpha * \theta$	n
Mix 1	2.65	1.58	2.04	2.27	0.88	2.61	1.71	- 0.005	4.03	1.25	0.49	1.20
Mix 2	2.43	1.55	2.14	2.23	0.81	3.67	1.16	- 0.002	2.33	1.72	1.28	1.32
Mix 3	2.13	2.31	1.31	2.42	0.70	3.19	0.82	- 0.002	1.84	1.70	1.45	1.20
Mix 4	1.60	0.84	1.08	1.51	0.68	2.15	0.44	- 0.001	1.28	1.47	1.36	1.04
Mix 5	1.37	1.23	1.00	1.75	0.78	2.43	0.85	- 0.003	2.25	0.75	0.52	1.19
Mix 6	1.10	0.68	0.80	1.08	0.74	1.47	0.47	- 0.002	0.91	1.25	1.96	1.13
Mix 7	0.86	0.40	0.58	0.76	0.66	1.16	0.21	0.000	0.69	0.78	1.54	1.11
Mix 8	0.74	0.16	0.50	0.46	0.58	0.85	0.09	0.000	0.60	0.45	1.07	1.13
Mix 9	1.45	0.80	1.09	1.18	0.79	2.52	0.51	- 0.003	2.18	0.78	0.51	1.13
Mix 10	0.92	0.47	0.66	0.85	0.61	1.36	0.22	- 0.001	0.79	0.96	2.00	1.24
Mix 11	0.39	0.09	0.24	0.28	0.57	0.46	0.06	0.000	0.27	0.49	2.90	1.22
Mix 12	0.24	0.03	0.25	0.08	0.94	0.25	0.03	0.000	0.22	0.10	0.56	1.06

Bingham model, it must be applied only in the linear part of the flow curves at low shear rates. Otherwise, Roussel et al. model describes the thixotropic behavior of fluids at very low shear rates such as the cement pastes studied in this work. The yield stress is considered in this case as the minimum shear stress that allows the fluid to remain in stable flow.

Otherwise, Herschel–Bulkley model (power law) and modified Bingham model (polynomial function) describe pseudo-plastic fluids. It seems that these models are able to predict the yield stress at low shear rates and to determine the shear-thickening or the shear-thinning behavior of the cement pastes at high shear rates.

Hence the strategy of parameter identification is as follow:

- For Bingham model (Eq. 1), two linear parts of the flow curve are identified. The fitting is undertaken on the linear part of the flow curve observed at low shear rates between 5 and 0.1 s⁻¹.
- The identification of the parameters of Herschel–Bulkley model (Eq. 2) is undertaken on all the experimental points which are in the stable flow zone (steady state). However to avoid some variabilities in the identification problem, the power relation (Eq. 2) is transformed to a linear relation (Eq. 6) through a logarithm function. The Herschel–Bulkley parameters (τ_0 , K and n_e) are

determined then by a linear regression law in a logarithmic scale.

$$\text{Log}(\tau - \tau_0) = \text{Log}(K) + n_e \times \text{Log}(\dot{\gamma}) \quad (6)$$

- For modified Bingham model (Eq. 3), the parameters are determined by a non-linear regression law following least squares data fitting method. The modelling is realized on all the experimental points which are in the stable flow zone (situated beyond the critical stress).
- Finally, Roussel et al. model is used to describe the thixotropic behavior of cement pastes. The determination of the model parameters (Eq. 4) is undertaken by a non-linear regression law following least squares data fitting method. The model is applied on all the experimental points (even those located in the flow instability zone).

The obtained results in terms of models parameters identification are summarized in Table 2 and the modelled flow curves are showed in Fig. 9 (for w/c = 0.5 and PC = 0.12%). From these results, the effects of the w/c ratio as the superplasticizer dosage on the yield stress identified from all the models are confirmed. However the comparisons of the absolute values show a very high discrepancies. Herschel–Bulkley model predicts the lowest values in term of yield stresses whereas modified Bingham model shows the highest values. Bingham and Roussel et al. models predict the best value in comparison to the

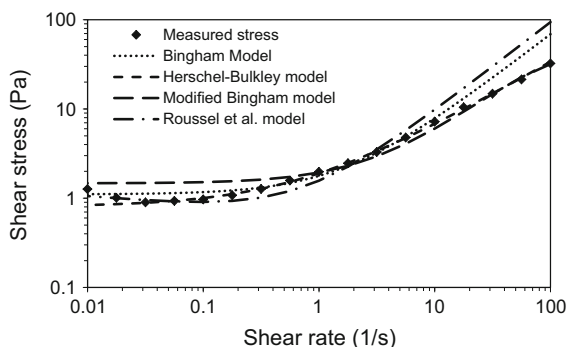


Fig. 9 Modelled flow curves expressed in shear stresses for $w/c = 0.5$ and $PC = 0.12\%$

measured values as shown in Fig. 10. Otherwise, the values of the flow index ($n_e < 1$) of Herschel–Bulkley model shows that the behavior of all the mixtures is shear-thinning. Moreover, the values of the shear-thinning intensity coefficient “ c ” and the hydrodynamic dissipation term “ β ” of modified Bingham model and Roussel et al. model respectively are close to zero indicating a shear-thinning behavior. Several studies have confirmed that cement pastes usually exhibit a shear-thinning behavior [13, 20, 36, 37].

To highlight the ability of the different models to reproduce the experimental flow curves, on Fig. 9, comparisons between the experimental curves with the prediction of the different models (where the parameters are identified according to the procedure explained above) are shown for $w/c = 0.5$ and $PC = 0.12\%$. From these results we can note that the Bingham model and Roussel et al. model present the

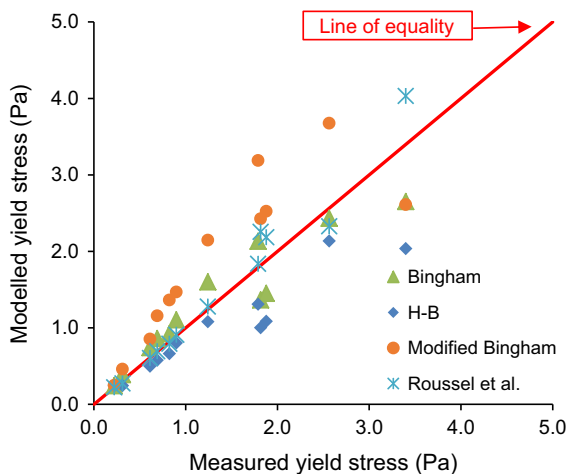


Fig. 10 Comparison of measured and modelled yield stress



best prediction of experimental data at low shear rates. For high shear rates ($5\text{--}100\text{ s}^{-1}$), these models give larger errors. The coefficient of determination R^2 varies from 0.90 to 0.99. This result is expected for Bingham model because of the fitting was realized on the linear part of the flow curve located in the range of low shear rates. Roussel et al. model overestimates the shear stresses at high shear stresses. However, it can predict the thixotropy phenomena of cement pastes (increase shear stress beyond a critical shear rate) and allows to better predict the shear stresses in the range of low shear rates. The increase of shear stresses is observed when the thixotropy occurs.

Herschel–Bulkley model gives the better correlation with the experiment data (R^2 between 0.97 and 0.99). Vance et al. [11] confirms that Herschel–Bulkley model gives a good correlation with the experience in wide range of shear rates variation. The last model tested is modified Bingham model. This latter makes it possible to represent accurately the nonlinear flow curves and gives a good correlation with the experiments (R^2 between 0.98 and 0.99).

In Fig. 10, the yield stresses obtained by the different rheological models as described above and those determined experimentally by identification of the minimum of stresses (critical stress) are compared. The obtained results show that thixotropy model of Roussel et al. allows to predict almost the same values as the experimental yield stresses. For this model, the average difference in absolute value don’t exceed 7%. The Bingham model shows moderate differences with experience, the average absolute difference reaches 19%. However, the non-linear models of Herschel–Bulkley and modified Bingham show larger difference with the experiments (34% and 32% respectively). The values of modelled yield stresses confirm that Herschel–Bulkley model predicts smaller values (as found by Vance et al. [11]) and modified Bingham model superior values.

The results showed in Figs. 9 and 10 confirm the efficiency of Roussel et al. model to describe the behaviour of cement pastes in the range of low shear rates. The yield stresses values measured through the rheometric protocol was confirmed by Roussel et al. model. Furthermore, this latter has the advantage of prediction of the critical shear rate and shear stress below which no steady-state may be achieved (predict the thixotropic behaviour of cement pastes).

4 Conclusion and perspectives

This paper presents the rheological study of cement pastes over a wide range of w/c ratios and superplasticizer dosages. The experimental shear rate/shear stress curves and the corresponding yield stresses were compared to the modelled curves using conventional rheological models and a thixotropy model. The results obtained allow to address the following conclusions:

- The saturation dosage of the cement in superplasticizer determined by the method of AFREM is confirmed by the rheometric analysis. A significant decrease in the yield stress is observed until the saturation dosage is reached. Above this dosage, the effects seem moderate. Moreover, the effect of the superplasticizer seems more effective when the w/c ratio is high.
- Three different zones are observed from the experimental flow curves: pseudo-plastic zone (non-linear part) at high shear rates, a plastic zone (linear part) at low shear rates and instability flow zone at very low shear rates (shear stress plateau and increased shear stress indicating a thixotropic behaviour).
- Four rheological models was applied for modelling the flow curves and determining the yield stresses: a thixotropy model of Roussel et al. and three “conventional” models: Bingham, modified Bingham and Herschel–Bulkley. It appears that each model has a better representation of one zone of the flow curves. Roussel et al. model can be applied at very low shear rates to represent the thixotropic behaviour of cement pastes and Bingham model can be applied at low shear rates in the plastic zone (linear part). On the other hand, modified Bingham model and Herschel–Bulkley model can be applied at high shear rates to represent the pseudo-plastic fluids.
- For determination of yield stress, two types of methods were used: the method by identification of the instability flow point (critical stress) from experimental data and the method by modelling the flow curves following different rheological models. From the results obtained, it appears that the thixotropy model of Roussel et al. allows better prediction of the yield stress in comparison to the experimental method since this model present a

better prediction of experimental shear stresses at low shear rates where the yield stress is obtained. This is valid for a wide range of yield stresses. For the three other classical models tested, it is found that Bingham model gives medium difference unlike Herschel–Bulkley model and modified Bingham model that present a larger differences in estimating the measured yield stress. Herschel–Bulkley model and modified Bingham model underestimates and overestimates respectively the yield stresses.

The experimental program and the modelizations realized allow not only to describe the rheological behaviour of the cement pastes at low and high shear rates but also to improve the precision in the determination of the yield stress with the thixotropy model of Roussel et al. in comparison with conventional rheological models. In the perspective of this study, the determined yield stress of cement pastes will be exploited to go back to the yield stress of the concrete following the approach of Mahaut et al. [38] by combining the results of this study with the study of the properties of the granular mixture.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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