Extended rheological characterization of cement pastes: squeeze flow plus rotational rheometry

R.G. Pileggi[2], A.M. Betioli[1], F.A. Cardoso[2], V.M.John[2]
[1]*Federal University of Santa Catarina, Florianópolis, Brazil*
[2]*University of São Paulo, São Paulo, Brazil*

ABSTRACT

The adaptability to different materials classes (concretes, mortars, fiber-cement, etc.) and applications methods (injection, pumping, spraying, casting, extrusion, etc.) is an essential feature of cement pastes. As a rule, each material/application system demands a set of characteristics of the fluid pastes. For that reason, the rheological characterization methods applied in cement pastes should identify all the requested properties. The main problem associated to this approach is the lack of a single technique able to perform such complete characterization. As an alternative, extending the rheological characterization of cement pastes by associating complementary techniques overcomes the lack of information of single test procedures. Hence, in the present work, cement pastes prepared with distinct cellulose - based polymer additions (HEMC - hydroxyethylmethyl cellulose) were evaluated by associating the traditional rotational rheometry to the less explored squeeze flow testing method.

1 Introduction

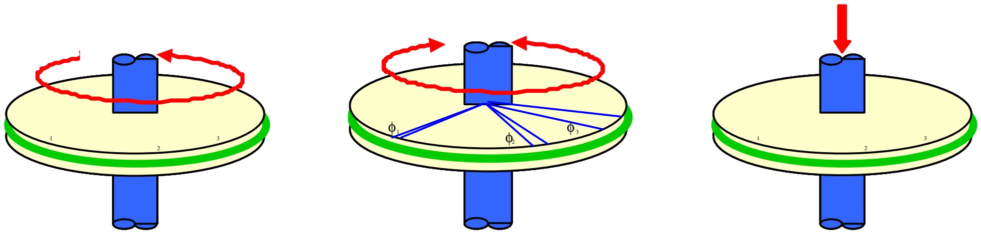
Cement pastes are widely used in different materials (concrete, mortars, fiber-cement, etc.), which can be processed by various methods. This variety of material/application systems requires different rheological characteristics of the fresh cement.

The flow behavior of cement pastes is traditionally measured by rotational strain rate sweep tests, which aims to simulate, in a certain way, flow-related processes as mixing and transport. In addition, the rheological changes associated to the cement setting, which affects the viscoelastic nature of fluids under stationary conditions, are evaluated by dynamic oscillatory shear tests. Both cited methods are rotational and maintain the geometry constant during the tests.

Conversely, many processing methods such as extrusion, compression forming and application of mortars submit the material to shear and elongation. In these processes, geometric restrictions cause different characteristics to become more important during flow, like friction, especially for highly concentrated suspensions. Therefore, in order to simulate these conditions the squeeze flow technique is indicated.

For building materials, a pioneer study was conducted by Min *et. al* [1] with cement pastes, but the method has been widely used to determine the flow properties of highly viscous pastes (food, cosmetics, polymers, composites and ceramic pastes) [2-6], as it overcomes some of the common problems of conventional rheometry such as slip, disruption of plastic materials and the difficulty to load very thick fluids and fiber-containing materials.

Despite having the same plate-plate geometry, schematic illustrated in Fig. 1, each method provides distinct rheological solicitations, since the magnitude of the applied strain (high for the strain rate sweep and low for the oscillatory), the type of movement (rotational or vertical) and the geometric restrictions are different in each case.



(a) Strain rate sweep (b) Oscillatory shear (c) Squeeze flow

Fig. 1 Schematic illustration of the rheological methods setup: (a) strain rate sweep, (b) oscillatory shear and (c) squeeze flow. The same plate-plate geometry provides different shear solicitations.

Thus, the main goal of this paper is to evaluate the rheological behavior of cement pastes with and without cellulose-based (HEMC) polymer additions by different test methods: rotational strain rate sweeps, oscillatory shear and squeeze flow.

2 Materials and methods

The Portland cement used for this study was a CPIIF32 with up to 5% of limestone filler, designation according to the Brazilian standard (Tab. 1). Commercial cellulose (hydroxyethylmethyl cellulose - HEMC) (Tab. 2) was added in 0.25 % by weight of cement. Two pastes (0% and 0.25% of HEMC) were prepared with a water/cement ratio by weight equal to 0.38. The powder materials and deionized water were mixed in a laboratory rotational mixer for 4 minutes in 300 rpm. Despite the evaluation method used, the first rheological measurements in the pastes were conducted 15 minutes after the beginning of the mixing procedure.

Cellulose ethers are commonly used as water-retaining agent and as viscosity modifiers for self-compacting mortars and concretes, but the retarding effect on the cement hydration is a secondary and uncontrolled effect [7].

Tab. 1 Characteristics of Portland cement.

Physical	Blaine surface area (NBR/NM 76/98)		330m^2/kg
	Initial and final setting time (h:min) (NBR/NM 65/03)		3:05 – 4:45
	Compressive strength (MPa) (NBR 7215/96)	3 days	25.8
		7 days	31.9
		28 days	40.0
Chemical	Loss on ignition (%)		5.10
	Insoluble residue (%)		0.76

Tab. 2 Physical characteristics of HEMC polymer.

Protective colloid (a)	Glioxal*
Substitution degree (a)	1.40-1.70
Molecular mass (a)	300.000 a 400.000 (g/mol)
Particle size (a)	0.25mm
Apparent density of the powder (b)	1.28g/cm^3
Viscosity (c)	40.000 mPa.s

*Aldehyde's family, acid character, hygroscopic and soluble in water.
(a) characteristics determined by the polymer producer.
(b) determined by helium picnometry (Quantachrome - MVP-5DC).
(c) solution at 2%, at 20ºC with constant shear strain 2.55s^{-1}.

The rheological methods used the different cement pastes were: strain rate sweep, oscillatory shear and squeeze-flow, described as follows:

- Strain rate sweeps

The rotational test consists of ramping from low to high shear strain rate while measuring the resulting shear stress. The measurements were conducted in a rotational rheometer (AR 2000, TA Instruments). The setup used was sandpaper-covered parallel plates with 40 mm in diameter and gap of 1 mm. A hysteresis-cycle, in which the strain rate was firstly ramped from 0 to 100s^{-1} in 2 minutes and immediately decelerated back to 0s^{-1}, over additional 2 minutes, was carried out on the samples 15 and 60 minutes after mixing.

- Oscillatory shear

Differently from strain rate sweep, this method can determine the viscoelastic characteristics of the material [8-10]. As the fluid is submitted to very small strains (within the linear viscoelastic range – LVR), which does not perturb the structure being formed during hydration, both the elastic (storage modulus - G') and the viscous (viscous modulus - G'') components of the material can be pointed out [11]. The consolidation of the suspension can be evaluated through the change in G' values with time.

The oscillatory tests were performed in the same equipment used for the strain rate sweeps (AR 2000, TA Instruments). The critical deformation was determined by a strain sweep test, increasing the strain from 10^{-5} up to 10^{-1}. In time sweep tests, the samples were submitted to a strain of 10^{-4} with constant frequency (1Hz) for 60 minutes.

- Squeeze-flow

The squeeze flow technique is based on the compression of a cylindrical specimen between two parallel plates by controlled force or displacement rate. Both elongational and shear strains are generally occur in most tests and, depending on the material/plate boundary conditions and on the geometric setup, one or the other type of solicitation can be predominant [2,3].

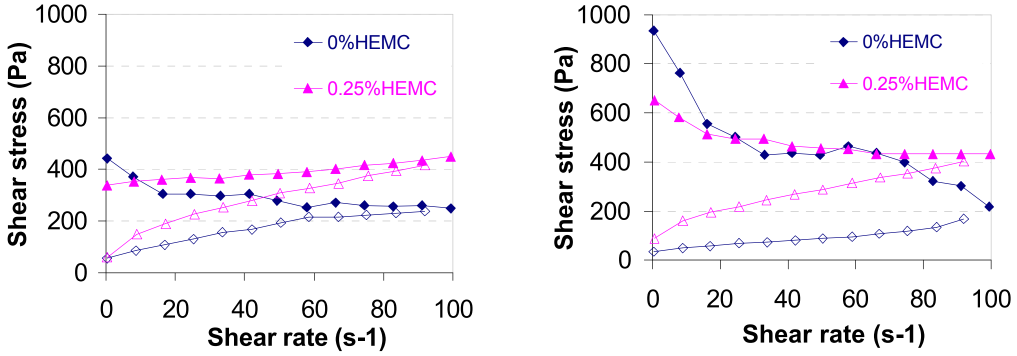
As fresh cement pastes generally do not present sufficient yield stress to maintain a desired shape, the squeezing tests were performed with the material in a container, as conducted by Min *et al*. [1]. These authors determined that using a diameter ratio ($D_{container} / D_{top\ plate}$) higher than 1.7 the repulsive force caused by the container walls during squeezing can be neglected. Therefore, in the present investigation, cylindrical samples of 76.2 mm in diameter and 10 mm in height (with a polymeric molding ring as the container) were squeezed by a top plate of 25.4 mm in diameter ($D_{container} / D_{top\ plate}=3$). Both bottom and top plates were polished stainless steel tools. The tests were conducted in a universal testing machine INSTRON (model 5569) using 10 and 1000 N load cells. A 3.5 mm - displacement with a constant downward velocity of 0.1 mm/s was imposed on the specimens and the resulting squeezing force was measured.

3 Results and discussion

- Strain rate sweeps

The shear stress-shear rate and the calculated apparent viscosity results for the cement pastes at 15 and 60 minutes are respectively shown in Fig. 2 and Fig. 3. All suspensions exhibited some degree of shear thinning, as the apparent viscosity calculated by shear stress / shear rate ratio decreased with the increase of the shear rate.

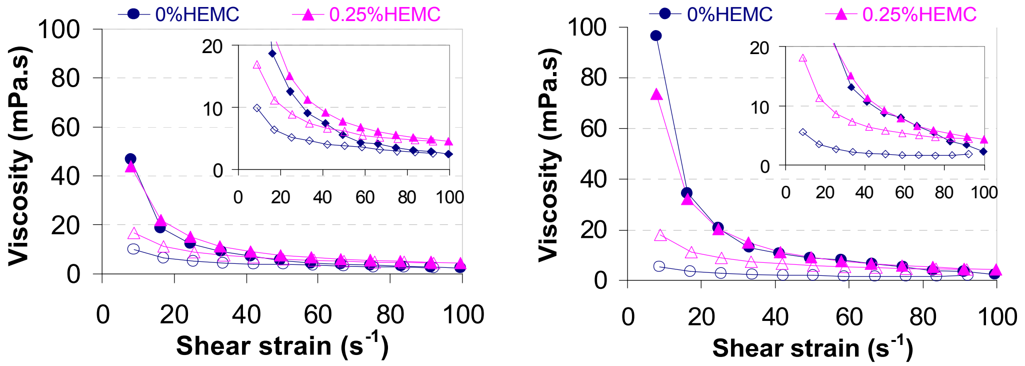
The rheological shear stress profile of the pure cement points its flocculated nature up. Increasing the shear rate breaks down the three dimensional network of particles formed in water [9,10,12], probably resulting in the reduction of the moving units dimensions, so that the shear stresses at high shear rates are smaller than in the lower ones. After 60 minutes, the same behavior was observed with higher stress values though, indicating the presence of stronger agglomerates as a result of the hydration process.



(a) 15 minutes

(b) 60 minutes

Fig. 2 Shear stress versus shear rate hysteresis cycles for cement pastes with 0% and 0.25% of HEMC at. Full symbols: increasing shear rate. Hollow symbols: decreasing shear rate.



(a) 15 minutes

(b) 60 minutes

Fig. 3 Apparent viscosity results of cement pastes with 0% and 0.25% of HEMC tested 15 (a) and 60 (b) minutes after mixing. Full symbols: increasing shear strain. Hollow symbols: decreasing shear strain. Viscosity range of 0-20 mPa.s is magnified. Viscosity values at very low shear rates are not shown.

Cellulose polymer (HMEC) addition changed the rheological behavior at 15 minutes of hydration to a Bingham fluid with superior shear stress and viscosity at high shear rates. At 60 minutes, a stronger agglomerated structure was observed, which may be attributed to a stiffer polymer gel, thus increasing the shear stresses [13].

After the structure breakage, the shear stresses during the decreasing-rate ramp were lower for the pure cement paste when compared to the 0.25% HEMC paste. This trend is associated to the greater polymer network rebuilding velocity in comparison to the cement. Moreover, the polymer reduced the hysteresis area of the sample tested at 60 minutes, indicating that a small content of cellulose polymer decreases the instability degree of cement pastes [13,14].

The polymer contribution to the cement stabilization was further confirmed by the reduction in the yield stresses (Tab. 3), given that this parameter is generally associated to the particles agglomeration state [9].

Tab. 3 Yield stress values determined by various rheological methods. Strain rate sweep ($\tau_{0\ \mathrm{SRS}}$) - estimated by the extrapolation of the stress - shear rate curve to zero shear rate. Oscillatory ($\tau_{0\ \mathrm{Oscillatory}}$) - determined by the critical strain multiplied by the storage modulus. Squeeze flow ($\sigma_{0\ \mathrm{Squeeze}}$) – transition point from elastic to plastic behavior.

HMEC	$t_{0\ \mathrm{SRS}}$ (Pa)		$t_{0\ \mathrm{Oscillatory}}$ (Pa)	$s_{0\ \mathrm{Squeeze}}$ (Pa)	
(%)	15 min	60 min	15 min	15 min	60 min
0	440	930	43	100	500
0.25	340	650	11	-	-

The results clearly differentiated the rheological behavior of the cement suspensions with and without the cellulose polymer addition under flow conditions. However, the intense shear verified during the tests promoted the rupture of the cement hydrates that were being formed during the test time. Therefore, strain rate sweep tests are not suitable to evaluate the setting characteristics of cement pastes, which can be identified through dynamic oscillatory shear tests.

- Oscillatory shear

According to the strain sweep tests, the cement suspensions without and with polymer addition exhibited narrow linear viscoelastic region (LVR) with small similar critical deformations, 3.7 and 3.3 x 10^{-4}. Such small values, which agree with literature [8,10], usually point up to flocculated suspensions. In this case, the particles are held together by short-range surface forces, thus forming continuous networks that do not withstand large deformation without breaking [10]. The tested polymer content was not enough to increase the cement deformation capacity.

The viscoelastic behavior of the tested systems was determined trough time sweep tests performed using a strain (10^{-4}) smaller than the critical deformation, in order to avoid the rupture of the material’s structure. Figure 4 exhibits the storage (G’) and the viscous modulus (G”) evolution of both tested systems with time. A solid-like behavior was predominant in the tested suspensions, given that G’ was higher than G”. Moreover, the G’ increase was more pronounced than G”.

These results confirmed the intense consolidation promoted by the electrostatic and van der Waals attractive forces [15], which increase with the raise of the ionic strength as cement dissolution [16] and formation of hydrated products [17] proceed.

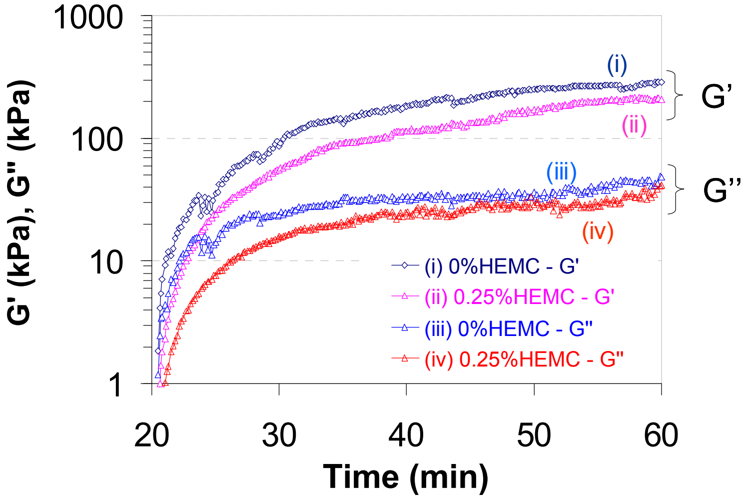


Fig. 4 Storage (G') and viscous (G") modulus as a function of hydration time for plain cement pastes and modified with 0.25% wt of HEMC.

The small polymer content added to the cement reduced both G' and G" values. This behavior may be explained by the retarding effect of this polymer on the hydration of cement and by the dispersion stabilization effect associated to molecules of this kind, that introduced steric repulsive barriers against the particles attractive forces, thus retarding the flocculation [14].

This stabilization mechanism was further confirmed by calculating the yield stress in oscillatory tests, estimated by multiplying the critical strain value and the storage modulus at this strain, $\tau_{0osc} = G' \times \gamma_{crit}$ (Eq. 1) [18]. The addition of HEMC polymer caused a 75%-drop on the yield stress as exhibited in Tab. 3. The smaller oscillatory yield stress values attest the less intensive shear conditions of this method.

The association between strain rate sweep and oscillatory shear tests improved the comprehension about the cellulose polymer influence on the rheological behavior of cement suspensions. In fact, the flow and the consolidation behavior were truly analyzed. However, both testing methods do not comprise the compressive geometrical changes that cement pastes may be subjected when squeezed between coarse aggregates and during different processes. For that reason, both suspensions were also evaluated by squeeze-flow, a conventional method for the rheological characterization of food and composites [2,5], but seldom used to investigate cementitious materials.

- Squeeze-flow

Min et al [1] previously determined that the typical load vs. displacement profile of cement pastes squeezed between parallel plates under constant velocity shows three main stages. The first region, in small strains, is characterized by a linear elastic behavior, while the second stage relates to plastic deformation or viscous flow where the material can deform considerably with low increase in the applied force [1,6]. In region III, the force required to squeeze the material increases substantially, known as the strain hardening stage. The extension of strain in which second and third stages occur depends on some features of the system such as interparticle distance and friction.

The squeeze flow results for the cement pastes tested 15 and 60 minutes after mixing are shown in Fig. 5. For the plain cement paste tested after 15 minutes the load increased almost linearly up to 1.5mm of displacement, when it started to show a strain-hardening character as the force required to squeeze the material increased more intensely and the final load registered was 2.2N. After 60 minutes the strain-hardening became more evident with an exponential increase starting at smaller displacement (0.75mm) than for the 15-minute sample. The loads were shifted higher and the squeezing force at 3.5mm was 21.2N, an increase of almost 10 fold due to consolidation effects. These pure cement samples did not exhibit a considerable plastic or viscous flow (second stage), where the increasing rate of the load is low.

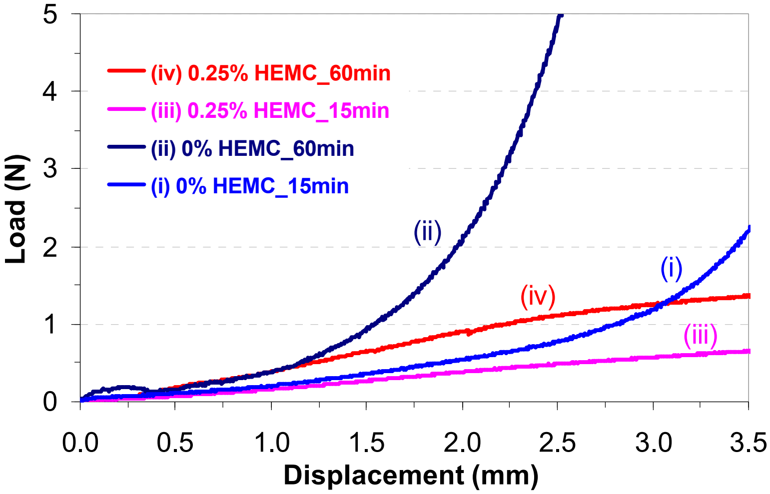


Fig. 5 Load - displacement results for the cement pastes with 0% and 0.25% HEMC squeezed 15 and 60 minutes after mixing.

On the other hand, the HEMC polymer-containing samples presented a remarkable plastic deformation stage. The load curves of the 15-minute samples for the two compositions were similar up to 1.5mm of displacement, but for higher displacements the HEMC sample did not display a strain-hardening behavior, as the load curve continue to increase slightly. A similar trend is observed for the samples tested after 60 minutes. The use of the polymer not only changed the load – displacement profile, but also decreased the final squeezing forces. At 15 minutes the load at 3.5mm of displacement was reduced 70% from 2.2N (pure cement paste) to 0.65N (HEMC sample), while after 60 minutes the load dropped from 21.2N to 1.4N (94% of reduction).

During the squeeze flow tests, as the gap was reduced the confinement of the particles in the vertical direction decreased their separation distance, therefore, frictional forces became more intense. The high lubricant ability of the HEMC polymer decreased significantly the friction between particles, and, as a water-retaining agent, the polymer also promoted an increase in the water viscosity [13], enhancing the lubrication capacity of the fluid in which the particles were immersed. Consequently, the polymer effect on the rheological behavior of the cement pastes was more intense for large displacements, where friction is the main resistance against the flow of the system. The HEMC polymer also retards the hydration kinetics of the cement, thus the expressive reduction of 94% in the final squeezing load for the HEMC samples after 60 minutes is caused both by lubricant and retarding effects.

The squeeze flow results analyzed in terms of load and displacement are sufficient to evaluate the behavior of different materials. Nevertheless, the technique allows the determination of rheological parameters such as elongational viscosity (Fig. 6) and yield stress (Fig. 7).

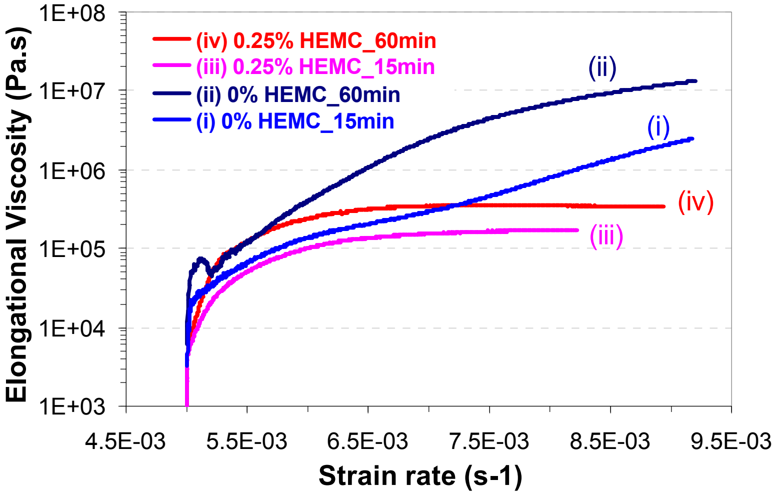


Fig. 6 Plots of the elongational viscosity vs. elongational strain rate of the polymer-free and 0.25% HEMC compositions tested 15 and 60 minutes after mixing.

For the squeeze flow experiments the biaxial extensional or elongational viscosity $\left(\eta_B\right)$ was calculated dividing the stress $\left(\sigma_B\right)$ by the extensional strain rate $(\dot{\varepsilon}_B)$, (Eq. 2): $\eta_B = \sigma_B/\dot{\varepsilon}_B = 2L\left[h_0 - (vt)/v\pi R^2\right]$, where: L is the load, h_0 is the initial sample height, v is the squeezing velocity, t is the time elapsed after the beginning of the test and R is the radius of the upper plate [2].

As can be seen in Fig. 6, the viscosity values increased considerably for the pure cement paste, whereas for the paste with 0.25% HEMC the viscosity reached a plateau. Final viscosity values dropped more than one order of magnitude due to HEMC addition. As the tests were performed with constant displacement rate, the variation in the elongational strain rate was caused by the reduction of the height of the samples. Due to this geometry change, a new solicitation is always being developed within the material, since the 3D particle and fluid distributions must constantly change to promote the flow of the whole material. This particular difference provides to the method the capacity to identity the influence of friction-related features on the rheological behavior of concentrated suspensions.

For the determination of the yield stress, first the load – displacement data was transformed into stress – displacement curves (dividing the load by top plate area) and, then, the initial part of these plots were magnified in order to allow the determination of the transition from the initial elastic stage to the viscous or plastic deformation one [19]. The exact point of the curve where the transition from stage I to stage II occurs would be ideally the yield stress of the material. Therefore, the procedure proposed to estimate the yield stress is based on the intersection of linear extrapolations of stages I and II, as illustrated in Fig. 7 for the pure cement paste tested after 15 minutes.

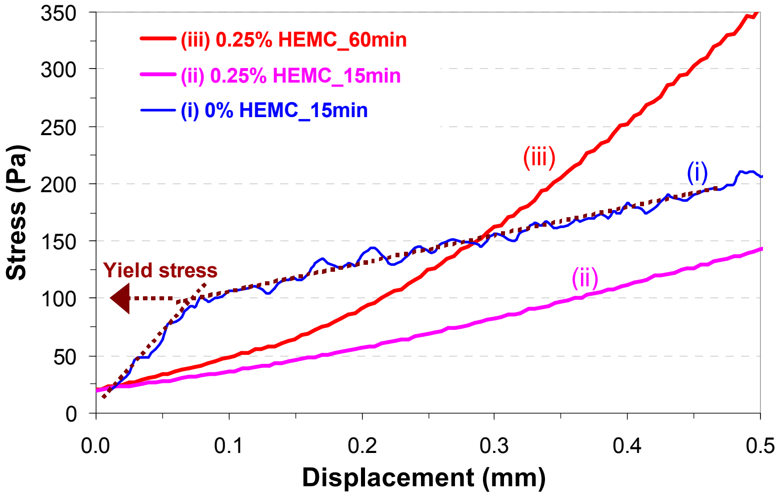


Fig. 7 Plot of the initial region of the stress vs. displacement curves of the polymer-free and 0.25% HEMC compositions. Geometrical procedure proposed to determine the yield stress of the material.

The plain cement paste presented a yield stress of 100 and 500 Pa, 15 and 60 minutes after mixing (plot not shown), respectively. As expected the consolidation of the paste increased the yield stress of the paste. For the composition with 0.25% of HEMC an interesting result was found. These samples did not display a transition from a linear elastic behavior to a plastic or viscous one even after 60 minutes, as observed on Fig. 7.

Despite the fact that no yield stress could be determined for the HEMC samples, this result is in accordance with the trend measured by the strain rate sweep and oscillatory tests, which attested that the yield values (Tab. 3) and the storage modulus (Fig. 4) increased with time and decreased as a result of polymer addition.

4 Conclusions

Different rheological behaviors of plain and HEMC-containing pastes were detected by rotational strain rate sweep, oscillatory shear and squeeze flow tests. The strain rate sweep indicated an increase of viscosity at high shear rates and decrease of yield stress and hysteresis area as a result of HEMC addition. The polymer caused reduction of both elastic and viscous components (G’ and G’’), as well as, a setting retarding effect, measured by oscillatory tests. For the pure paste a strain-hardening behavior, caused by friction between cement particles, was determined by squeeze flow, while a remarkable plastic deformation occurred for the HEMC samples. The lubricant nature of the polymer was only detected by the squeeze flow testing method, which allows the determination of viscosity and yield stress. However, as the change of strain rate is caused by the reducing gap (for tests conducted with the same displacement velocity), squeeze flow results may not be directly compared to rotational rheometry ones, but instead, be used as complementary rheological information.

Acknowledgements

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References

[1] B.H. Min, L. Erwin, H.M. Jennings, Rheological behavior of fresh cement paste as measured by squeeze flow. J. Mater. Sci. 29 (1994) 1374-1381

[2] J.F. Steffe, Rheological Methods in Food Process Engineering, Freeman Press, USA, 1996

[3] G.H. Meeten, Yield stress of structured fluids measured by squeeze flow, Rheol. Acta 39 (2000) 399-408

[4] N. Özkan, C. Oysu, B.J. Briscoe, I. Aydin, Rheological Analysis of Ceramic Pastes. J. Eur. Ceram. Soc. 19 (1999) 2883-2891

[5] J. Engmann, C. Servais, A.S. Burbidge, Squeeze flow theory and applications to rheometry: A review. J. Non-Newtonian Fluid Mech. 130 (2005) 149-175

[6] O.H. Campanella, M. Peleg, Squeezing Flow Viscosimetry of Peanut Butter, J. Food Sci. 52 (1) (1987) 180-184

[7] J. Pourchez , A. Peschard , P. Grosseau, R. Guyonnet, B. Guilhot, F. Valle. HPMC and HEMC influence on cement hydration. Cem Concr Res 36 (2006) 288 – 294

[8] M.A. Schultz, L.J. Struble, Use of oscillatory shear to study flow behavior of fresh cement paste. Cem Concr Res 23 (G) (1993) 273-282

[9] A. W. Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement paste. Cem Concr Res (31) (2001) 205-212

[10] L. Nachbauer, J.C. Mutin, A. Nonat, L. Choplin, Dynamic mode rheology of cement pastes, in: 2nd International RILEM Workshop on Hydration and Setting, Dijon, France, 1997, pp. 271-280

[11] H.A. Barnes, J.F. Hutton, F.R.S K. Walters, An Introduction to Rheology. 3ª ed. Elsevier Science Publishers B. V. Amsterdam. 1993, 199 p.

[12] A. Nonat, J.C. Mutin, X. Lecoq, S.P. Jiang, Physico-chemical parameters determining hydration and particle interactions during the setting of silicate cements. Solid State Ionics (1997) 923-930

[13] K.H. Khayat, Viscosity-Enhancing Admixtures for Cement-Based Materials - An Overview. Cem Concr Compos (20) (1998) 171-188

[14] H.J. Kong, S.G. Bike, V.C. Li, Electrosteric stabilization of concentrated cement suspensions imparted by strong anionic polyelectrolyte and a non-ionic polymer. Cem Concr Res 36 (5) (2006) 842-850

[15] K. Yoshioka, E. Tazawa, K. Kawai, T. Enohata, Adsorption characteristics of superplasticizers on cement component minerals. Cement and Concrete Research 32, 1507–1513, 2002.

[16] L. Nachbaur, P. Nkinamubanzi, A. Nonat, J. Mutin, Electrokinetic Properties which Control the Coagulation of Silicate Cement Suspensions during Early Age Hydration. J. Colloid and Interface Science 202 (2) (1998) 261-268

[17] J.J. Thomas, H.M. Jennings, A.J. Allen, The Surface Area of Cement Paste as Measured by Neutron Scattering: Evidence For Two C-S-H Morphologies. Cem Concr Res 28 (6) (1998) 897–905

[18] M.A. Schultz, Rheological studies of fresh cement pastes, Thesis, University of Illinois, 1991

[19] F.A. Cardoso, V.M. John, R.G. Pileggi, Squeeze Flow for Rheological Characterization of Cement-Based Mortars, Materials and Structures, submitted for publication (2006)