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Effect of HMEC on the consolidation of cement pastes: Isothermal calorimetry *versus* oscillatory rheometry

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ABSTRACT

Chemical admixtures increase the rheological complexity of cement pastes owing to their chemical and physical interactions with particles, which affects cement hydration and agglomeration kinetics. Using oscillatory rheometry and isothermal calorimetry, this article shows that the cellulose ether HMEC (hydroxymethyl ethylcellulose), widely used as a viscosity modifying agent in self-compacting concretes and dry-set mortars, displayed a steric dispersant barrier effect during the first 2 h of hydration associated to a cement retarding nature, consequently reducing the setting speed. However, despite this stabilization effect, the polymer increased the cohesion strength when comparing cement particles with the same hydration degree.

1. Introduction

Portland cements withstand chemical (dissolution and precipitation) and physical (flocculation and coagulation[1]) changes when in contact with water [1–4]. Such changes significantly affect the rheology of hydrating cementitious materials since the early ages, even during the induction period[2] [5,6], when the hydration reactions are still incipient. When chemical admixtures are present, the system becomes even more complex due to the physical–chemical interaction with the hydrating cement [7].

Cellulose ethers are widely used as viscosity modifying agents for the production of self-compacting concretes and dry set mortars, among other applications. The mechanism by which cellulose ethers affect the hydration of cement is only partially understood. It is known that the polymer increases the viscosity of the aqueous phase, retaining water in the system. Hydration kinetics may also be affected, resulting in longer induction and consolidation[3] times [8–12]. Adsorption of the polymer on the cement surfaces was reported in literature [13] as well as chemical interaction with metal ions [14]. However, the effect of such polymers on the early hydration and rheology of cement systems is not well understood.

The objective of this research is to evaluate the effect of HMEC (hydroxymethyl ethylcellulose) on the consolidation phenomenon of cement pastes. The rheologic behavior was evaluated using oscillatory rheometry. A correlation between the results from rheometry and isothermal calorimetry was attempted.

The dynamic mode rheology was used herein to study the mechanical properties of cement pastes from mixing through setting, because this technique has the ability to perform nondestructive measurements, providing useful information about the structure and forces acting inside the paste.

2. Experimental design, materials and methods

2.1. Materials

A limestone blended Portland cement (CPII-F 32 type containing 9.5% limestone, according to Brazilian standards) and the cellulose ether hydroxymethyl ethyl cellulose (HMEC) was used to prepare the cement pastes. The chemical and physical characteristics of the cement and polymer are presented in Tables 1 and 2, respectively. The contents of HMEC in the pastes were 0, 0.25, and 0.50% (cement weight basis). The mixing procedures were adapted to the different test methods.

2.2. Isothermal calorimetry

A JAF isothermal calorimeter (Wexham Developments) was used to assess the evolution of the heat of hydration of the cement pastes. Cement, polymers, and water were hand mixed for 3 min and then placed inside the equipment for the analysis. Water to cement ratio was 0.38 and the tests were performed at 25 °C, using 10 g samples.

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[1] Flocculation and coagulation are particle agglomerations that result from the combination of attractive (electrostatic and van der Waals) and repulsive forces. A coagulated or irreversible structure cannot be easily destroyed. Conversely, a flocculated system is week and reversible.

[2] During the induction period the overall hydration rate slows down significantly.

[3] Consolidation is considered herein as the transition from visco-elastic to elastic behavior, i.e., when the cement paste becomes a solid.

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Table 1
Cement characteristics.

Chemical characteristics (%)	Al_2O_3		4.28
	SiO_2		18.44
	Fe_2O_3		3.04
	CaO		63.38
	MgO		2.08
	SO_3		2.92
	Na_2O		0.09
	K_2O		0.74
	Free lime — CaO		2.43
	LO		5.10
	Insoluble residue		0.76
Bogue approximation	C_3S		45
	C_2S		19
	C_3A		6
	C_4AF		9
Physical characteristics	Specific gravity (g/cm^3)		2.97
	% passing sieve #325		96.8
	Specific surface area by Blaine method (m^2/kg)		330
	Initial and final setting times (min)		185, 285
	Compressive strength	3 days (MPa)	25.8
		7 days (MPa)	31.9
		28 days (MPa)	40.0

The length of the induction period was graphically obtained by the intersections of the horizontal base line with the extrapolations of the regression lines of the first heat peak (pre-induction period) and of the acceleration period, determining the beginning of the acceleration period (where the hydration reaction increases sharply) (see Fig. 1).

The degree of hydration ($\alpha(t)$) was determined from calorimetric curve as the ratio of heat evolved at a time ($Q(t)$) to the total (theoretical) heat of hydration of cement (Q_∞), according to Eq. (1) [15].

$$\alpha(t) = Q(t) / Q\infty \tag{1}$$

The total heat of hydration is the quantity of heat in joules per gram of non hydrated cement (J/g), evolved upon complete hydration. It was estimated from mineral composition (obtained from Bogue calculation, Table 1) as the relative sum of the heats of hydration of individual compounds (means value: 510 J/g for C_3S, 260 J/g for C_2S, 1100 J/g for C_3A and 410 J/g for C_4AF). Considering the tested cement, the total heat of hydration in this study is 381.8 J/g.

2.3. Rheometry

For the rheometry tests, the cement paste samples were mechanically mixed at 300 r.p.m., according to the following steps: (i) dry mixing cement and polymers; (ii) addition of dry materials to water within 180 s, keeping the mixer on; and (iii) mixing for 120 more seconds. The pastes were then placed in the rheometer.

Table 2
Characteristics of HMEC.

Protective colloid[a]	Glyoxal[b]
Substitution degree[a]	1.40–1.70
Mean molecular weight[a]	300,000 to 400,000 (g/mol)
Maximum particle size[a]	0.25 mm
Specific gravity of the powder[c]	1.28 g/cm^3
Viscosity[d]	40,000 mPa s
Ignited weight[e]	12%

[a] Information provided by the manufacturer.
[b] Organic compound, aldehyde-type, acidic, hygroscopic, and water soluble (pH = 2 in water).
[c] Determined by He picnometry.
[d] 2% solution at 20 °C, shearing rate 2.55 s^{-1}.
[e] Determined by thermogravimetry at 1000 °C under dynamic N_2 atmosphere; heating rate 10 °C/min.

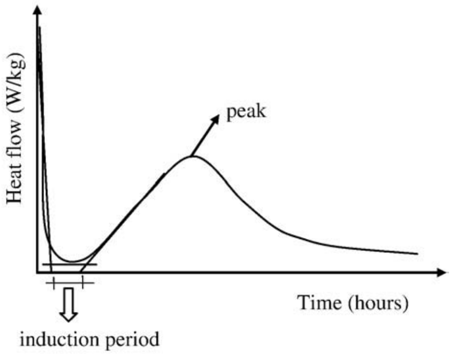

Fig. 1. Graphic determination the length of the induction period and peak temperature from the heat evolution curves.

The oscillatory tests were carried out using an AR 2000 TA Instruments parallel plates rheometer with 40 mm diameter plates. A texturized adhesive tape was sticked to the plates to avoid the sliding of the cement paste, as shown in Fig. 2. After mixing, the pastes were squeezed between the parallel plates until the gap was 1 mm and the tests were performed at 25 °C.

The oscillatory test is a method frequently used to evaluate the properties of fresh cement pastes, from mixing to setting [3,4,16–18]. It is a dynamic method capable of applying small deformation or low tension to the sample without causing its rupture. Deformation (γ) or tension (τ) is applied according to a sinusoidal curve, following the model expressed by Eqs. (2) and (3). The reactive tension to that effort is obtained by Eq. (3),

$$\gamma = \gamma_0 \times \cos \omega t \tag{2}$$

$$\tau = \tau_0 \times \cos(\omega t + \delta) \tag{3}$$

where ω is the angular speed, t is time, γ_0 is the maximum amplitude of deformation, and δ is the out-of-phase angle between tension and deformation. The limit behaviors of the materials are Hookean solid (in-phase tension and deformation, $\delta = 0$, i.e. $G^* = G'$, the response is purely elastic), and Newtonian fluid (out-of-phase tension and deformation, $\delta = 90°$, i.e. $G^* = iG''$, a purely viscous response). However, the vast majority of materials do not behave as ideal solids or liquids, but as a combination of both, i.e., they are viscoelastic ($0 < \delta < 90°$).

From Eqs. (2) and (3), G^* modulus, also called complex modulus, can be obtained by the ratio between tension and deformation (Eq. (4)). Because it is a complex number, it can be split in two components, which are the elastic (storage modulus, G') and the viscous (loss modulus, G'') components, expressed in Eqs. (5) and (6), respectively.

$$G^* = \tau / \gamma \tag{4}$$

$$G' = \tau_0 / \gamma_0 \cos \delta \tag{5}$$

$$G'' = \tau_0 / \gamma_0 \sin \delta \tag{6}$$

Because the objective of this research was to evaluate the consolidation of the cement paste, only the results of the elastic modulus G' are discussed for plain cement and HMEC-containing cement pastes.

To evaluate the viscoelasticity of suspensions, the measurements should be performed in the linear viscoelastic domain (LVD) of the curve, where G' does not depend on the applied deformation. Such region is limited by the critical strain (strain$_{\text{critical}}$) applied to the material that does not cause changes in its structure [3,4,16–18], which is determined by a strain sweep test (increased amplitude over