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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

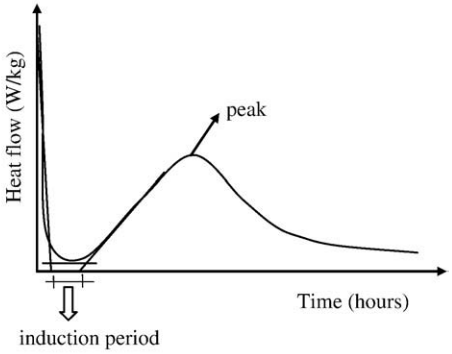

Fig. 1. Graphic determination the length of the induction period and peak temperature from the heat evolution curves.

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.

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

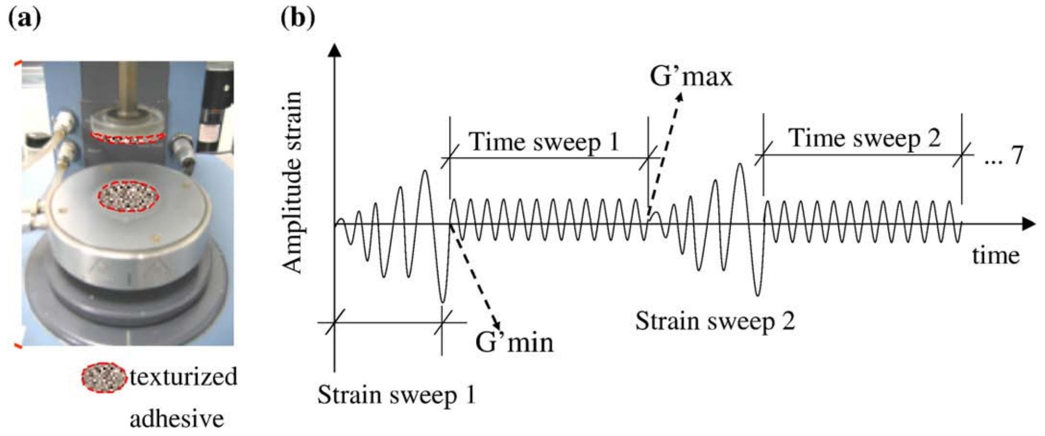

Fig. 2. a) Rough parallel plates of the rheometer AR2000; b) schematic drawing of the oscillatory test at constant deformation and frequency, intertwined with the deformation scanning test (two of seven full cycles shown). The G'min and G'max values for each time sweep test are indicated.

time, keeping frequency constant). All dynamic measurements were performed at an oscillatory frequency of 1 Hz, according to [16,18].

In this research, the critical strain was determined by increasing the amplitude from 10^{-5} to 10^{-1}. Usually, the critical strain is around 0.01% (10^{-4}), regardless the hydration time, as revealed by the literature [3,4,16,18] and preliminary tests.

In order to assure that all samples were in the same conditions before the tests, the strain sweep was performed first, followed by 30 min under oscillation at constant deformation and frequency, named time sweep. This sequence was repeated seven times, as illustrated in Fig. 2b, and was similar to that performed by Nachbaur et al. [3]. The strain sweep, where the strain exceeds the critical strain, destroys the structure of the paste; the time sweep enables to follow the evolution of the mechanical properties of the paste over time.

At last, the strain sweep allows the estimation of the yield stress (τ_0) using Eq. (7), proposed by Chen and Zukoski, quoted by [16].

$$\tau_0 = \text{strain}_{\text{critical}} * G' \qquad (7)$$

where G' is the storage modulus at the critical strain ($\text{strain}_{\text{critical}}$).

3. Results and discussion

3.1. Heat evolution

The incremental and cumulative curves of heat flow *versus* hydration time obtained from the isothermal calorimetry are shown in Fig. 3. The cellulose ether HMEC did not change the typical profile of the curve (Fig. 3a); however, it decreased the rate of heat evolution during the acceleration period, and decreased the maximum peak to 2.8 W/kg (0.25%) and 2.6 W/kg (0.50% HMEC), confirming the hydration delay phenomena reported in literature [19]. The polymer extended the induction period from 120 min (plain cement sample) to 210 and 285 min (0.25% and 0.50% HMEC, respectively). The total heat output after 4 h of hydration was reduced by up to 54%, further attesting literature reports [8,9,12,19,20], see Fig. 3b.

3.2. Critical strain

Fig. 4 shows that the critical strain of plain and HMEC-containing pastes was around 10^{-4} during the first 120 min (Fig. 4a), in agreement with previous studies [3,16,18]. After this first stage of hydration, the critical strain sharply increased due to the continuing cement hydration, confirming the formation of a structure able to withstand higher loads.

This behavior is a consequence of the agglomeration forces present in cement particles, which arises from the attractive electrostatic forces generated by the simultaneous occurrence of negatively and positively charged surfaces as a result of the contact with water. Calcium silicate phases (C_3S and C_2S) become negatively charged, while aluminate phases C_3A and C_4AF display positive charges [21]. In addition, van der Waals forces further increase the agglomeration strength of the cement particles thus resulting in rigid structure [1]. Both these surface agglomeration forces increase with hydration, given that hydrated products display higher surface areas [22].

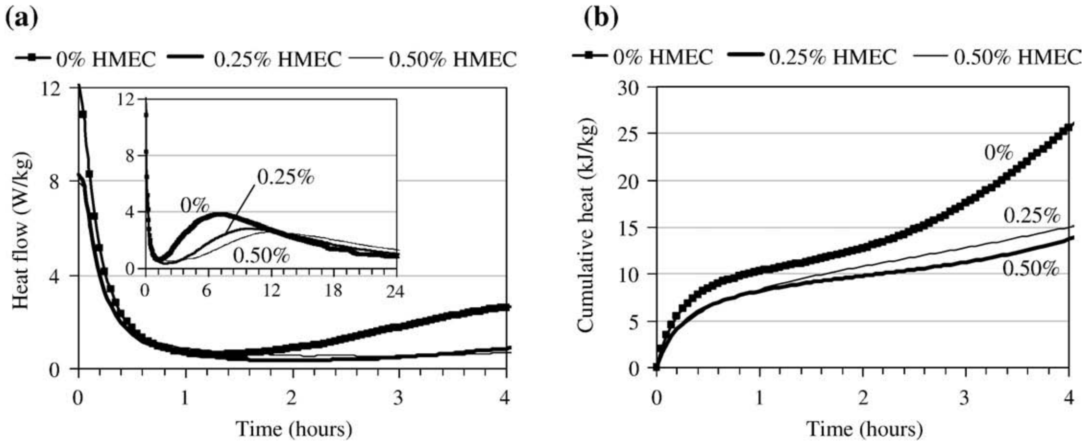

Fig. 3. Isothermal calorimetry curves of plain cement paste and pastes admixed with 0.25 and 0.50% HMEC after 4 h of hydration: (a) incremental curves (in the inset, the fittings of the 24 h) and (b) cumulative curves.

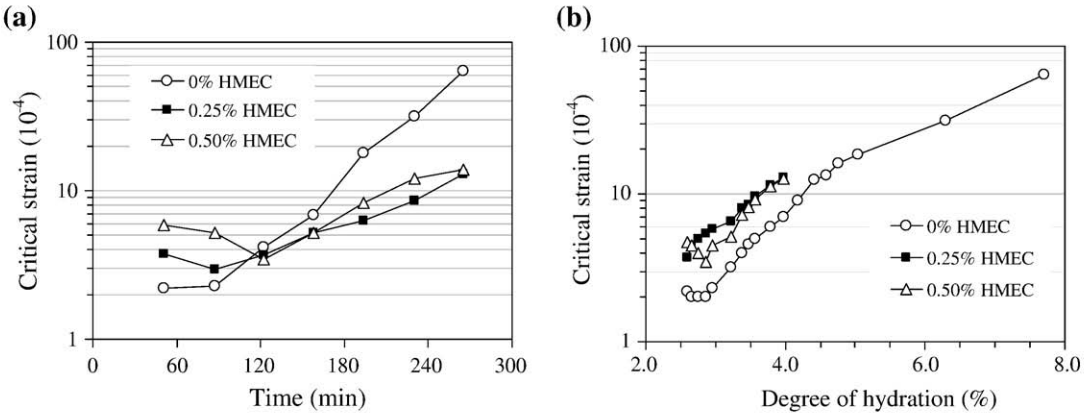

Fig. 4. Critical strains obtained from the scanning test with plain cement and HMEC-containing cement pastes over time (a) and over degree of hydration (b). Hydration degree of 2.6% corresponds to the second strain sweep for plain cement paste in 51 min of hydration, and 120 and 93 for 0.25 and 0.50 HMEC pastes, respectively.

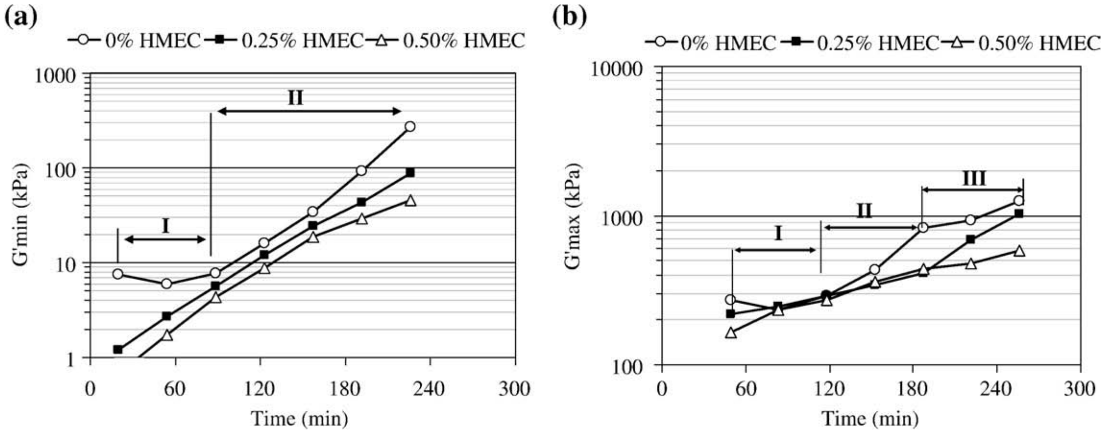

Fig. 5. Evolution of G' for plain cement and HMEC-containing samples: (a) G'min and (b) G'max. I, II, and III are denote regions of distinct behavior of plain cement paste.

Polymer addition increased the critical strain until approximately 90 min of hydration when compared to the plain cement paste, as shown in Fig. 4a. When HMEC is present in the system, van der Waals forces and hydrogen bonds are responsible for the formation of a three-dimensional gel structure, resulting in higher viscosity of the aqueous phase [9,23]. Given that, HMEC is partially adsorbed on the cement particle surfaces, the gel structure bridges the contact among cement particles, thus raising the critical strain.

After 120 min, however, the faster plain cement hydration increases the critical strain more rapidly than for the polymer added systems. This behavior is probably attributed to the enhancement of the attraction forces between hydrated products. This hypothesis is confirmed by comparing the critical strain and the degree of hydration calculated from the isothermal calorimetry curves according to Eq. (1). As observed in Fig. 4b, polymer-containing systems displayed higher critical strain than the plain cement for the same hydration degree. However, the HMEC retarding effect limited the hydration degree at most 4% in the first 4 h, whereas the plain cement reached almost 8%, thus resulting in higher critical strain levels.

3.3. Storage modulus (G')

The first time sweep test at constant deformation was started with a low value for G', named G′min, as shown in Fig. 5a. This is due to the dispersion of the cement particles caused by the strain sweep, exceeding the critical strain [3,4]. The continuous dissolution of the anhydrous cementitious phases increases the ionic strength in the system [24], causing the cement particles to re-agglomerate, increasing G' over time, so reaching G'max. The formation of a higher volume of hydrates, especially the high specific surface area C–S–H, also promotes the agglomeration due to the increase of van der Waals forces [Tattersall and Banfill cited by 18,25].

After each strain sweep test, a new G′min is obtained due to the rupture of the agglomerated structure, which agglomerates again

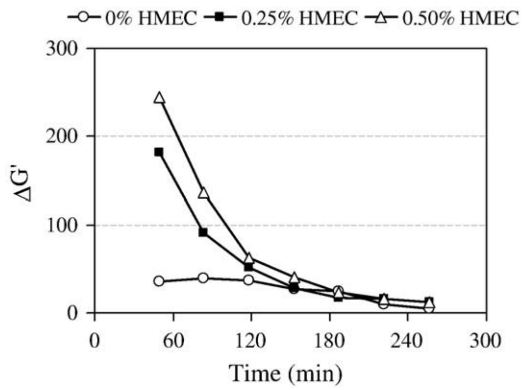

Fig. 6. Ratio between the elastic components at the beginning and end of each oscillatory test.

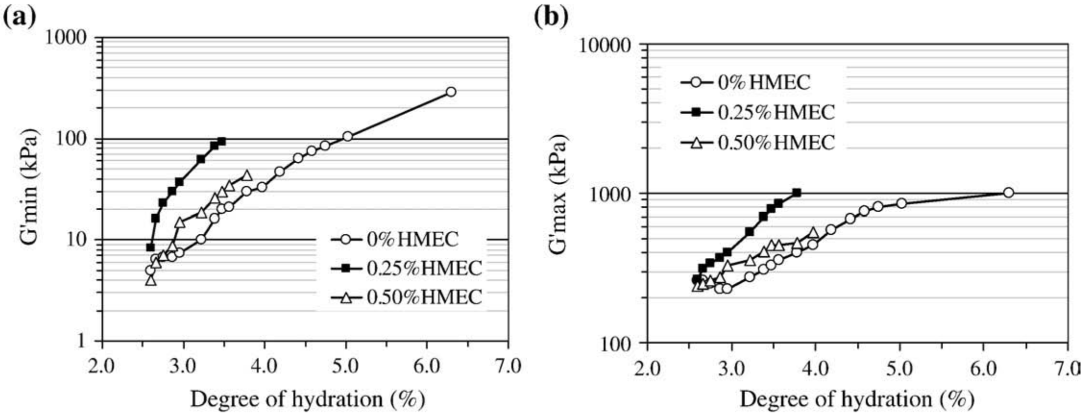

Fig. 7. Evolution of *G*′ with the same hydration degree for plain cement and HMEC-containing samples: (a) *G*′min and (b) *G*′max.

reaching *G*′max over time (see Fig. 5b). This behavior was observed for all the subsequent cycles. Both parameters increase over time, differing with those results obtained by Yang and Jennings [5].

G′max curve of the plain cement paste shows three distinct stages (Fig. 5b). During the first 120 min of hydration, there was a low rate of increase of *G*′max due to the slow hydration reactions and to the flocculation of the cement particles. This period corresponds to the induction period. The second stage of the curve shows a higher increase of *G*′max, i.e. more intense reagglomeration due to the increased specific surface area of cement particles as they hydrate. A hydration layer is reported to form on the surfaces of cement grains, including a layer of Al–Si rich gel, C–S–H, and AFt phases [22]. Furthermore, the anhydrous phases are still dissolving, increasing the ionic strength of the aqueous phase. As the hydration reactions continue, the agglomeration of the particles in the system is intensified, mainly C–S–H (at the end of the second stage), and the structure is formed by coagulated particles. At this point the acceleration period starts, as confirmed by calorimetry tests. After this point, the curve shows a smaller increase in *G*′max rate (third stage), which is probably due to the rupture of the coagulated irreversible structured paste.

HMEC-containing pastes exhibited similar behavior of *G*′max during the first four time sweeps steps. But, from the fifth cycle on, *G*′max was lower for the samples with HMEC content (Fig. 5b). The higher the polymer content, the lower the *G*′max values, thus attesting the retarding effect of HMEC.

On the other hand, G′min curve of the plain cement paste (see Fig. 5a) displayed only two distinct stages. G′min was stable during the first 90 min of hydration, but a steep increase of G′min was observed after this period. The measured parameter was high since the beginning of the test, thus indicating a flocculated structure, which was not totally dispersed during the strain sweep. The following increase of G′min attested that the strengthening of the coagulated structures promoted more stable and mechanically irreversible agglomerates.

G′min was lower when HMEC was added to the pastes (Fig. 5a). The cellulose ether adsorbed on the surface of cement particles [12] develops a steric barrier that reduces particles agglomeration. Moreover, the retarding action of HMEC resulted in smaller G′min increase ratios after 180 min when compared to the plain cement paste.

Considering the similar initial *G*′max profiles but lower G′min values for the polymer added systems, it is possible to infer an increase in the consolidation ratio due to the three-dimensional gel network generated by the HMEC, thus enhancing the reagglomeration rate. This behavior can be expressed by the ratio between the elastic components at each oscillatory test ($G'\text{max}/G'\text{min} = \Delta G'$), as shown in Fig. 6. Until the fourth test (120 min), the pastes with HMEC displayed higher $\Delta G'$ than the plain cement sample, due to the increased elastic component of the polymer containing sample. However, $\Delta G'$ values became similar for all samples after the fourth test due to both the hydration reactions and reagglomeration of particles.

The strengthening effect induced by HMEC addition was further confirmed by comparing the *G*′max and G′min profiles with cement hydration degree, as exhibited in Fig. 7. According to these results, both G′min (Fig. 7a) and *G*′max (Fig. 7b) are higher for the polymer-

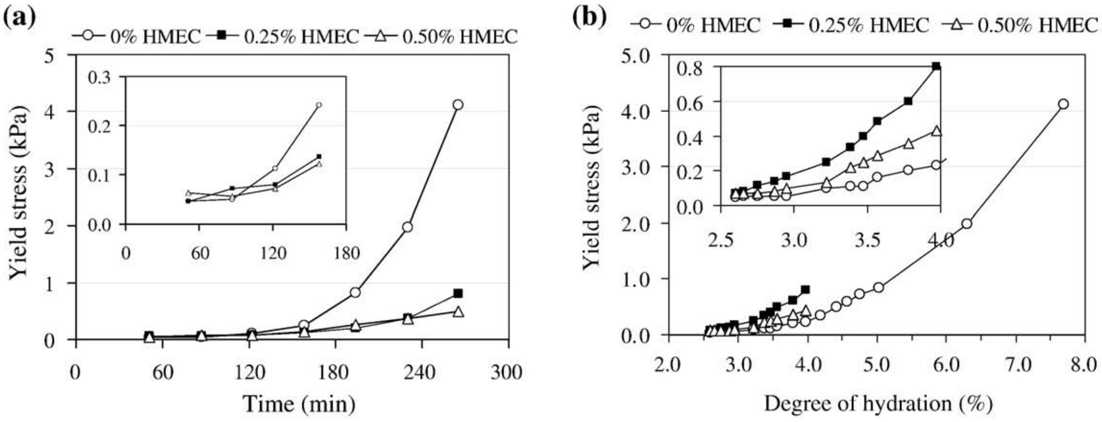

Fig. 8. Yield stress for plain cement and HMEC pastes: (a) over time and (b) degree of hydration.

containing systems when comparing similar hydration degree levels. However, G′min and *G*′max growth of the plain cement continued growing in time owing to its larger hydration degree.

3.3.1. Yield stress

The yield stress calculated by Eq. (7) can be obtained after determining the critical strain and its correspondent elastic component (*G*′). The yield stress can be used to evaluate the consolidation of cementitious materials, and can be correlated to the consistency and slump loss over time [26].

The yield stress of the pastes with HMEC is slightly higher than the plain cement paste until 120 min of hydration, as shown in Fig. 8a. The inflexion point is at 210 min for the 0.25% HMEC paste, and 300 min for the 0.50% of the polymer. These results confirm the retardation effect of HMEC. But this behavior changes when this property is observed at the same degree of hydration, see Fig. 8b, resulting in a positive effect of the polymer on the intrinsic yield stress.

4. Conclusions

- The rheology of cement pastes changes during the induction period, when the reactivity of the system is low. The rheologic changes are due to the agglomeration of the particles;
- The induction period was importantly extended with HMEC, as expected;
- The time sweep and strain sweep tests were shown to be effective and sensitive enough to investigate the consolidation of plain and HMEC-containing cement pastes, as well as to assess the transitions during flocculation/coagulation of the systems;
- The strain sweep test was proven to be a powerful tool to determine the critical strain over hydration time, the yield stress, and the estimation of initial setting time of the pastes;
- In the first hours of hydration, the HMEC increased the critical strain of the cement pastes measured with the strain sweep test when compared to the plain cement paste, probably acting as a steric barrier, besides the retardation effect. This phenomenon kept the cement particles dispersed after strain sweep. The higher the HMEC content, the higher and longer the steric effect because the adsorbed HMEC molecules onto the cement particles and on C–S–H enhancing the suspension stability due to steric repulsion;
- Due to this steric effect, the HMEC, after the strain sweep test, reduced the G′min, but, increased the storage modulus rate of the cement pastes, i.e. higher $\Delta G'$, due to the formation of the hydrogel, which is a three-dimensional network of the polymer in water. However, after the beginning of the acceleration period, *G*′max values of the plain cement paste are always greater than the pastes containing the polymer;
- The polymer contribution can be shown at the same degree of hydration; the results herein showed the positive effect of HMEC on the intrinsic critical strain, strength and yield stress of the hydrates formed.

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