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Effect of EVA on the fresh properties of cement paste

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ABSTRACT

The improved workability effect of latex in dry mortars has not been fully clarified. The purpose of this research was to investigate the influence of the EVA copolymer on the cement hydration and on the rheological properties of cement pastes. The results pointed to a minor influence of EVA on cement hydration and to a ball-bearing effect. In fact, the shear thinning behavior of reference paste at 15 min after mixing changed to shear thickening owing to the EVA addition. This behavior could be explained by the decrease in the interparticle separation distance as consequence of the solid content increase in case of shearing detachment of weakly adhered EVA particles from the cement particles surfaces. The expected EVA plasticizing effect was observed at 60 min. Such behavior points to the stabilization of EVA on the cement particles surfaces, thus resulting in a steric barrier effect.

1. Introduction

The polyethylene vinyl acetate (EVA) copolymer is a water-redispersible powder added to mortar and concrete to improve some properties such as fracture toughness, impermeability and bond strength using various substrates [1]. EVA can be added to anhydrous cement and aggregates before mixing with water, or it can be added as an aqueous latex dispersion.

There is a lack of agreement among researchers regarding the interactions between cement and polymeric particles. According to some authors, only physical interactions occur in the system [2–4], while others claim that there is the occurrence of both physical and chemical interactions [1,5–10].

Nonetheless, there is consensus that the EVA particles prolong the induction period and reduce the cement reaction rate in the acceleration period. The chemical explanation for the retardation effect of the polymer is the interaction between the polymer and Ca^{2+} ions, resulting in calcium acetate formation [1,4–6,8,9,11] reducing the CH precipitation [6,8], as measured at early ages by Betioli et al. [11]. The physical explanation for the retardation is the adsorption of EVA particles onto the surface of both anhydrous and hydrated cement, as observed by Silva and Monteiro [9] using soft X-ray microscopy.

The EVA effect on cement paste rheology is controversial. Some authors [1,7,12] report that EVA particles offer improvements over conventional cement mortar and concrete, allowing a reduction in the water/cement ratio for a given consistency. This effect is mainly interpreted in terms of improved consistency due to the ball-bearing effect provided by the polymer particles, the air entraining and the dispersing effect of surfactants in the polymer latexes. On the other hand, Atzeni et al. [13] have shown a considerable stiffening of cement paste using vinyl latex, increasing the yield stress and the apparent viscosity (ratio of stress to rate of strain). This behavior was attributed to a low mixing energy, which was not sufficient to disperse the system.

Therefore, the purpose of this study is to clarify the effect of EVA particles on cement hydration and on cement paste rheological behavior at early age. Isothermal calorimetry was employed to study the hydration kinetics and rotational rheometry to evaluate the EVA-modified pastes subjected to different shear rates.

2. Materials and methods

The effect of EVA (0%, 5% and 10% w/w) on the hydration and rheological behavior of commercial limestone blended cement pastes (0.38 water/cement) was measured by isothermal conduction calorimetry and rotational rheometry.

2.1. Materials

A limestone-blended Portland cement was used (CPII-F 32 type containing 9.5% limestone, according to Brazilian standard (NBR

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11578) and refers to Portland-limestone cement CEM II A-L, according to British standard (BS EN 197-1), and the chemical and physical characteristics are given in Tables 1 and 2.

The commercial polymers EVA water-redispersible powder (RE 5010N) was produced by Wacker Chemie AG and its characteristics are shown in Table 3. Redispersible powders based on EVA are the standard polymer most commonly used commercially in the modification of adhesive mortar for laying ceramic tiles [14].

EVA particles display spherical morphology due to the water-soluble protective colloidal polyvinyl alcohol (PVOH) on the latex surface [9]. The PVOH is one the most widely used polymers during EVA production, which stabilizes the EVA polymer emulsion. Normally, the PVOH content is between 5% and 15% by mass of the EVA water-redispersible powder [15,16]. According to Rottstegge et al. [16], the PVOH content in EVA (RE5010) is about 15%, by powder polymer mass, and, and, its hydrolysis degree is between 87% and 89%.

Table 1
Cement 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
CO_2	4.14
Free lime–CaO	2.43
Loss on ignition	5.10
Insoluble residue	0.76
C_3S^a	45
C_2S^a	19
C_3A^a	6
C_4AF^a	9

[a] Bogue approximation.

Table 2
Cement physical characteristics.

Specific gravity (g/cm^3)	2.97
% passing sieve #325 μm	96.8
BET surface area (m^2/g)	1.22
Initial and final setting times (min)	185, 285
Compressive strength (NBR 7215)[a]	
3 days (MPa)	25.8
7 days (MPa)	31.9
28 days (MPa)	40.0

[a] NBR 7215, Portland cement – determination of compressive strength, ABNT – Brazilian association for technical standards, São Paulo, Brazil (1997).

Table 3
Characteristics of EVA.

Source	Solids content[a]	98–100%
Manufacturer	Protective colloid[a]	Polyvinyl alcohol (PVA)
	Particle size[a]	Max. 4% over 400 μm
	Predominant particle size redispersion[a]	0.5–8 μm
	Minimum film forming temperature[a]	Approx. 4 °C
Laboratory measurement	Specific gravity[b]	1.27 g/cm^3
	Ash content[c]	12%

[a] Information provided by the manufacturer.

[b] Determined by Helium pycnometry.

[c] Determined by thermogravimetry at 1000 °C under dynamic N_2 atmosphere; heating rate 10 °C/min.

The cement and EVA particle size distributions were evaluated by laser diffraction (Mastersizer S long bed Ver. 2.19, Malvern Instruments Ltd.), as seen in Fig. 1. The cement and EVA suspension was diluted in deionized water (≈1 g/l) and dispersed by ultrasonic treatment. Fig. 1 shows the calculated particle size distribution for the cement/EVA mixtures considering the volumetric fraction of each constituent and well-dispersed particles.

The EVA contents in the mixtures were 5% and 10% by cement mass. The water/cement ratio was kept constant at 0.38, on a mass basis.

2.2. Isothermal calorimetry

A JAF calorimeter (Wexham Developments) was used to determine the heat of hydration of the cement pastes (J/g of cement). The cement, polymer and water were mixed by hand for 3 min and then placed into the equipment. The sample masses were approximately 10 g. The temperature of the water bath was 25 °C.

The length of the induction period, inclination of the acceleration curve and maximum peak heat flow were determined. The induction length was graphically obtained from the intersections of the horizontal base line with the regression line extrapolation at the first heat peak (pre-induction period) and in the acceleration period (see Fig. 2 and Ref. [17]).

2.3. Rheological characterization

The cement paste samples were mechanically mixed at 300 r.p.m. (IKA - RW 20), according to the following steps: (i) dry mixing of cement and polymers; (ii) addition of dry materials to the water within 180 s, keeping the mixer on; and (iii) mixing for 120 s. After mixing the pastes were immediately placed in the

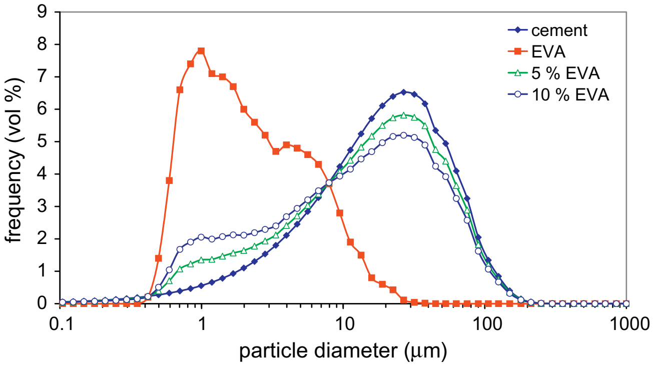

Fig. 1. Laser diffractometry discrete particle size distribution of cement and EVA dispersed in water, and estimated particle size distribution for 5% and 10% of EVA/cement mixtures, considering the volumetric fraction of each constituent and well-dispersed particles.

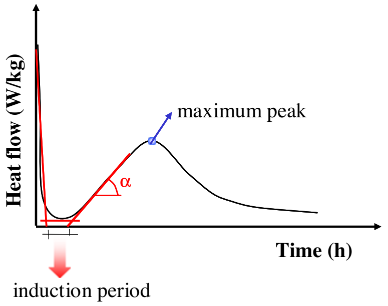

Fig. 2. Graphic determination of induction length and peak temperature from the heat evolution curve.

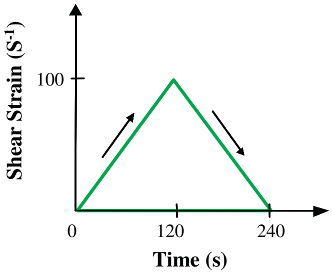

Fig. 3. Schematics drawing of the strain rate sweeps.

rheometer and squeezed between the parallel plates until the gap measured 1 mm and the excess paste was removed.

The rheological properties were investigated using a TA Instruments parallel-plate rheometer, model AR 2000, with 40 mm diameter plates. The temperature was kept constant at 25 °C by a Peltier plate. A rough-textured adhesive tape was stuck to the plates to avoid the slippage of the cement paste.

Rotational strain sweep tests were performed 15 and 60 min after the water–cement contact. For each test a new sample was used. This test consists of increasing the shear strain rate while measuring the resulting shear stress. The shear rate was first ramped from 0 to 100 s^{-1}, in 2 min, and immediately decelerated back to 0 s^{-1}, in an additional 2 min (see Fig. 3). The hysteresis area was calculated and the yield stress was determined by extrapolating the shear stress *vs* shear rate of the acceleration curve to zero.

3. Results and discussion

3.1. Calorimetry

The incremental and cumulative curves of heat flow *vs* hydration time obtained from the isothermal calorimetry of the cement reference paste and modified-cement pastes are shown in Fig. 4. The logarithmic scale was used to magnify the first hours of hydration.

The EVA had shown some effect in cement hydration. Its presence prolonged the induction period, which increased from 90 min for the reference paste to 100 and 120 min for 5% and 10% EVA, respectively. As can be seen in Fig. 4a, the acceleration period began at 100 min for the reference paste and at 120 min for 5% EVA and 150 min for 10% EVA. The maximum peak reduced from 3.8 W/kg for the reference paste to 2.8 W/kg for the modified ones. The major effect was detected in the heat evolution rate during the acceleration period, where the EVA polymer reduced this rate from 1.0 W/kg/h for the reference paste to 0.55 W/kg/h for the modified pastes.

Despite the heat rate reduction, the modified pastes showed higher heat flow than the reference one until 120 min (Fig. 4a), probably due the EVA alkaline hydrolysis reaction (Betioli et al. [11]). Fig. 4b showed that the total heat output until 72 h of hydration was not significantly reduced for the modified-cement pastes.

Therefore, the significant changes in the consistency observed during the induction period of reference cement paste or modified one could not be related only with hydration kinetics. In fact, physical and chemical aspects related to the surface characteristics of the EVA particles in the ionic environment of cementitious systems should also be considered, as discussed as follows.

3.2. Rheological characterization

The rheological measures were performed after 15 and 60 min of hydration, during the induction period, and the following results will be discussed for each time.

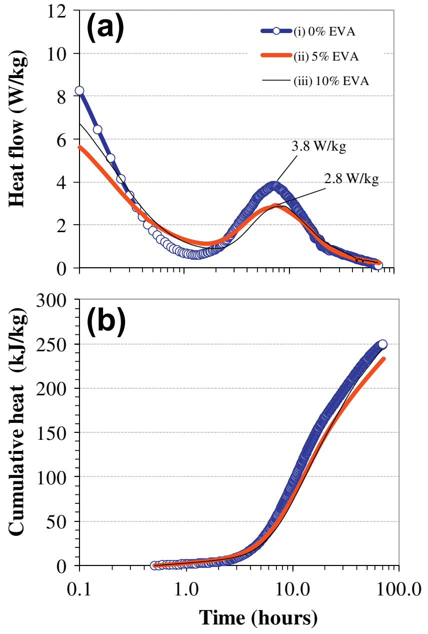

Fig. 4. Isothermal calorimetry curves of reference and admixed pastes with 5% and 10% of EVA and maximum peak (a) and cumulative heat (b), after 72 h of hydration.

3.2.1. 15 min

The rotational rheometry results (shear stress × shear rate curves) of the reference and EVA-modified pastes (5% and 10% EVA) for 15 min of hydration are shown in Fig. 5. A shear thinning behavior was observed for the reference paste hysteresis cycle (Fig. 5), which is typical behavior for agglomerated systems [18], where the shear stress reduces with shear rate increases. Another manner to demonstrate this behavior is through the apparent viscosity (shear stress/shear rate) reduction with shear rate increases, as can be seen in Fig. 6.

In Fig. 5, the acceleration curve (increasing shear rate) of the reference paste showed higher shear stress than the deceleration curve (decreasing shear rate), resulting in a hysteresis area of 13 kPa s^{-1} (Table 4). i.e., the desagglomeration rate is higher than the agglomeration rate, due to the cement particle agglomeration instability. The yield stress, determined by extrapolation of the acceleration curve to zero shear rate, was 440 Pa and its value was reduced by a factor of 8 in the deceleration curve due to the structural breakdown.

The flow curve profile of the mixtures containing 5% and 10% of EVA copolymer is different in the first 15 min of hydration compared to the reference paste, showing a shear thickening behavior profile with yield stress, as can be seen in Fig. 5a. Despite this shear thickening behavior, the apparent viscosity (Fig. 6a) was first reduced until to 40 s^{-1}, as a consequence of the rupture of the initial agglomerated structure.

In shear stress–strain curves (Fig. 5a) it is possible to observe two different stages: in the first one, in the acceleration curve up to 55 s^{-1}, the EVA-modified cement paste had lower shear stress than the reference paste, i.e., apparent viscosity reduction (Fig. 6); and in the second one, above this rate, this behavior was reversed, with the EVA-modified pastes showing a higher apparent viscosity than the reference one.

In the *first stage*, the smaller shear stress at low shear rates indicates an increase in the paste fluidity, probably due to the ball-bearing effect attributed to the ultra fine spherical EVA particles size distribution (Fig. 1). However, this would not account for the yield stress reduction by factors of 3 and 4 for the 5% and 10% EVA-modified paste (Table 4), since this parameter is determined

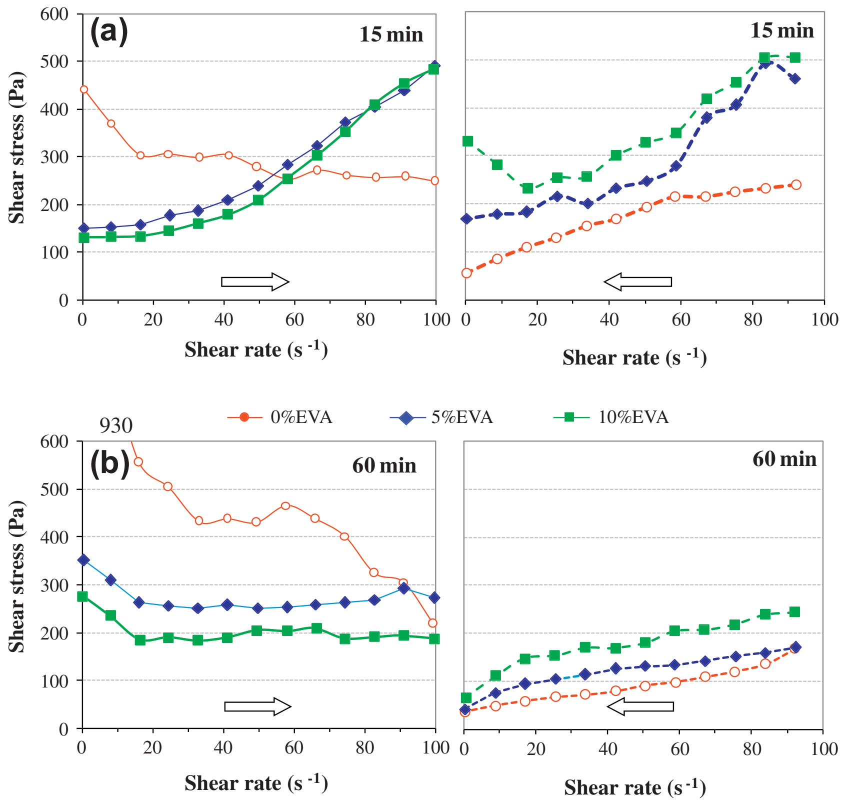

Fig. 5. Shear stress *vs* shear rate from strain rate sweep acceleration from 0 to 100 s^{-1} (⇨) and deceleration from 100 s^{-1} to 0 (⇦ hatched line), for reference and EVA-modified cement pastes with 5% and 10% EVA in 15 min (a) and 60 min (b) of hydration. Plotted at the same scale.

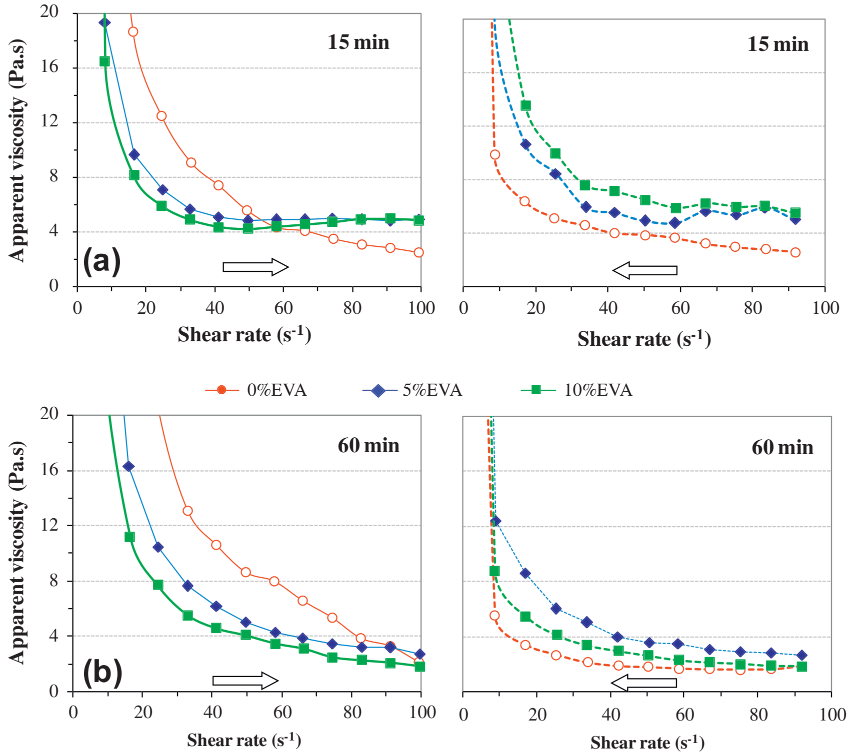

Fig. 6. Apparent viscosity *vs* shear rate from strain rate sweep acceleration from 0 to 100 s^{-1} (⇨) and deceleration from 100 s^{-1} to 0 (⇦ hatched line) for reference and EVA-modified cement pastes with 5% and 10% EVA after 15 min (a) and 60 min (b) of hydration. Note: apparent viscosity = shear stress/shear rate. Plotted at the same scale.

in the absence of flow, thus indicating that other EVA contributions must also be acting.

The EVA particles adsorption onto cement and hydrated products, observed by Silva and Monteiro [9], can contribute to that.

Table 4
Hysteresis area and yield stress values for reference and EVA-modified cement pastes.

Parameters	Reference paste		Paste with 5% EVA		Paste with 10% EVA	
	15 min	60 min	15 min	60 min	15 min	60 min
Hysteresis (kPa s^{-1})	13	40	0.02	10	−6.0	9
Yield stress (Pa)	440	930	150	350	130	280

This adsorption is induced by a positive charge, due to the PVOH coating layer with highly positive zeta potential at alkaline pH (170 mV in pH 12.5) measured in deionized water with KOH (ESA – 8000 form MATEC) and due to intermolecular interactions through hydrogen bonds between hydroxyl groups from PVOH and cement surfaces. This mechanism forms an electrosteric barrier which hinders the flocculation of the cement particles, i.e., it acts as a dispersion mechanism. Also, the presence of PVOH as a protective colloid can contribute to this EVA electrosteric effect, according to Trados [19] and So et al. [20].

The ball-bearing effect can only be verified when EVA particles move freely in the suspension. As the polymer adsorption hypothesis is still valid, the presence of free EVA in suspension depends on the amount of EVA exceeding the particles surface area and on the particles released from the surfaces (desorption) as the shear rate increases. Considering the average size of the EVA particles to be 1 μm (Fig. 1), the area coated by EVA particles would be 0.021 and 0.042 m^2 for 5% and 10% EVA, respectively, which is not sufficient to coat the 1.22 m^2/g cement surface area (Table 2).

This result suggests that there is no EVA excess in suspension, thus allowing the conclusion that ball bearing effect is first associated to the particles adhered to surfaces, which can be released from the cement surfaces due to the shearing flow.

In spite of the apparent dispersant effect of the EVA at low shear rates, in the *second stage* (>55 s^{-1}) the EVA induced shear thickening in the pastes, thus indicating that the ball-bearing effect was blocked at high shear rates (Fig. 5). This behavior, which is usually observed in suspensions with high solids concentration and short distance between particles where repulsive interactions are predominant [21,22], may indicate that the EVA desorption from cement particles surfaces during shear shortened the mean distance among the particles. Such distance was calculated by the interparticle separation distance (IPS) model proposed Funk and Dinger (1994) described in Eq. (1) and the results are shown in Table 5.

$$\mathrm{IPS} = (2/\mathrm{VSA}) \times [(1/\mathrm{Vs}) - (1/1 - P_0)] \tag{1}$$

where IPS is the interparticle spacing between particles (μm); VSA the volume specific surface area (m^2/cm^3); Vs the solid volume concentration (%); and P_0 is the minimum porosity for a dense packing.

The particle size distributions in Fig. 1 were calculated for 5% and 10% of EVA-modified pastes assuming that the polymer particles are released in suspension. Considering the dispersed EVA particles, the fines content increased along with the volume specific surface area (VSA), reducing the minimum porosity for a dense packing (P_0) and increasing the solid volume concentration (Vs) in Eq. (1) (Table 5). Therefore, the IPS was reduced respectively by almost 10% and 20% in the pastes modified with 5% and 10% EVA.

Table 5
Volume specific surface area (VSA), the minimum porosity for a dense packing (P_0), solid volume concentration (Vs), interparticle separation distance (IPS) of reference and EVA-modified cement pastes with 5% and 10% EVA.

Parameters	Reference paste	Paste with 5% EVA	Paste with 10% EVA
VSA (m^2/cm^3)	3.65	3.67	3.69
P_0	0.1267	0.0960	0.0791
Vs (%)	38.85	41.82	44.31
IPS (μm)	0.783	0.699	0.634

The IPS reduction also explains the modification in the hysteresis area at 15 min, which were reduced with 5% EVA and inverted to negative with 10% EVA addition (Table 4). The deceleration curve above the acceleration one points to an intensification in the agglomeration rate during deceleration for the cement/EVA systems. Such rheopexy could be an alternative explanation for the stiffening of cement paste reported by Atzeni et al. [13].

3.2.2. 60 min

Fig. 5b shows the results of the 60 min shear rate sweep tests. The reference paste shows a clear shear thinning behavior. The yield stress is two times higher than that for the 15 min test and the hysteresis area increases threefold (Table 4). However, the yield stress value on the deceleration curve remained constant during this time, providing evidence that during this time the structure is reversible. As the induction period (Fig. 4) is much longer than 60 min and therefore hydration plays a minor role, the increase in the yield stress and hysteresis area in the reference paste at 60 min can be largely explained by an increase in the agglomeration phenomenon [17].

The behavior of the EVA-modified cement pastes during the 60 min tests differed from that of the 15 min tests, as observed in Figs. 5b and 6b, in which the shear thickening is replaced by shear thinning, with larger hysteresis area when compared to 15 min, but with smaller hysteresis when compared to the plain cement paste (Table 4).

Silva and Monteiro [9] identified that EVA particles are readily recognizable by their spherical shape. However, the alkaline hydrolysis of EVA occurs in the high pH (around 12.3), the acetate group (CH_3COO^-) interacts with aluminum and calcium ions and polymeric particles are adsorbed onto cement surface [9]. In that case, these particles cannot be free to act as the ball-bearing effect, but still acting as an electrosteric barrier onto cement particles surfaces.

4. Conclusions

Significant rheological changes were observed in EVA-modified cement pastes, which could be associated to physical and surface phenomena, since the latex EVA showed a minor effect on cement hydration during the induction period. The EVA reduced yield stress and viscosity of cement pastes at low shear rates. This workability improvement reveals a combined dispersant and ball-bearing effect of this admixture during the first minutes of hydration. However, the EVA-modified pastes were shear thickening at 15 min of hydration, in contrast with the shear thinning profile of the reference. This behavior resulted from the EVA desorption from the cement surfaces at intense shear, thus increasing the amount of solid particles in suspension and reducing the mean distance among particles. After 60 min of hydration, a pronounced plasticizing effect was observed with yield stress, apparent viscosity and hysteresis area reduction. This behavior indicates the strengthening of the EVA adhesion onto the cement particles surfaces thus stabilizing a polymeric electrosteric barrier around the cement particles due to the blockage of the globule liberation into the suspension.

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