



## Behaviour of a starch as a viscosity modifier for aerial lime-based mortars

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### ABSTRACT

Different dosages of a commercialized potato starch were added to aerial lime-based mortars in order to check its efficiency as a rheological modifier. Several fresh state properties of the mortars were studied: consistency, density, air content, water retention capacity, setting time and evolution when applied on support. The effect of the starch on  $\zeta$ -potential of the lime particle surface as well as the particle size distribution and viscosity changes in lime pastes were also assessed in order to elucidate the action mechanism of the polymer. The behaviour of this starch polymer was found to be strongly dosage-dependent: it acted as a thickener when the incorporated dosage was up to 0.30% of lime weight; conversely, above that dosage, it behaved as a plasticizer. The thickening effect took place because polymer molecules were adsorbed onto lime particles acting as a flocculant, as confirmed by zeta-potential and particle size distribution results. For large amounts of polymer, steric hindrance and electrostatic repulsive forces appeared, leading to a dispersion mechanism which explained the plasticizing effect as well as the fresh mortar behaviour.

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### 1. Introduction

Starches and starch derivatives have been widely described as rheology-modifying admixtures (Leeman & Winnefeld, 2007; Ouyang, Jiang, Qiu, Yang, & Pang, 2009; Peschard, Govin, Grosseau, Guilhot, & Guyonnet, 2004; Rixom & Mailvaganam, 1999). The role they play in mortars is not easily predictable, as there are many factors affecting the influence that a polymer exerts on a mixture, such as: (i) the type and properties of the binder; (ii) the amount of mixing water; (iii) the mixing process; (iv) the experimental procedures and (v) the presence and properties of additives (Papo & Piani, 2004).

The molecular weight of a starch seems to be a critical point affecting its behaviour: high-molecular-weight polymers tend to agglomerate and produce a thickening effect on the mortars, while low molecular weight polymers can easily be adsorbed on the binder particles' surface, generating steric repulsions (i.e. a dispersing effect) which lead to lower viscosities (Ouyang et al., 2009; Vieira, Klemm, Einfeldt, & Albrecht, 2005).

The thickening action of starches and their derivatives (ethers and esters) can be understood by considering the similarity between these molecules and cellulose derivatives, which are the most common products used as viscosity-enhancing admixtures

(VEAs) or water-retaining agents, as reported by Paiva, Esteves, Cachim, and Ferreira (2009), Pourchez, Govin et al. (2006), and Pourchez, Peschard et al. (2006). Amongst all the derivatives, hydroxypropyl-methyl-cellulose (HPMC) and hydroxyethyl-methyl-cellulose (HEMC) are the most widely used (Paiva et al., 2009). In general, some of these water-retaining products improve the homogeneity of the mixture, enhance its workability and reduce segregation amongst the components of the mortar. They have also been proved to act as set-retarders (Peschard et al., 2006). Furthermore, they improve some of the properties in the hardened state (Jolicoeur & Simard, 1998; Paiva, Silva, Labrincha, & Ferreira, 2006; Paiva et al., 2009).

This kind of additive is able to fix water in the structure, reducing the amount of free water in the mixture and producing an increase in viscosity. Furthermore, their lateral chains can suffer an intertwining process that contributes to further increase the viscosity (Paiva et al., 2006). However, the mechanism of set-retarding action of these additives is still not clear, although there are several widespread hypotheses which assume that the water-retaining agent or some of its degradation products could be adsorbed on the cement particles (hydrated and/or anhydrous phases), hindering contact between the binder and the water, thus retarding the hydration reaction (Jolicoeur & Simard, 1998; Pourchez, Govin et al., 2006; Pourchez, Peschard et al., 2006). Some authors accept that this adsorption takes place through a process in which organic molecules (such as this kind of admixture) fix metallic ions by complexing or chelating, calcium being the most important such ion (Pourchez, Govin et al., 2006).

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However, as Paiva et al. reported (Paiva et al., 2006), HPMC could also act as a water-reducing agent, showing that polymers present a complex dosage-dependent behaviour. They determined the plastic viscosity and the yield stress of cement mortars with different amounts of HPMC, observing that, when the dosage of additive was lower than 0.08% – of the total dried mortar weight – it produced a plastifying effect. From that dosage to 0.25%, the polymer acted as a thickener. They found an explanation based on two factors: (i) samples with low amounts of HPMC presented high entrapped air content, which could lead to higher plasticity; (ii) the mixing process could disaggregate the entanglement of the chains, producing an alignment with the flow direction which reduced viscosity (Paiva et al., 2006).

In connection with the use of starch and starch derivatives, Lee-man and Winnefeld (2007) added a starch derivative to cement mortars and concretes with a super plasticizer, noticing that rheological properties of mortars were scarcely modified, while some properties of concrete were affected: the slump in flow table test and the compactability of the material decreased. Therefore, the starch derivative acted as a thickener in this case.

Glenn, Miller, and Orts (1998) prepared lightweight concretes with starch aquagels as admixtures. These additives were selected because they were able to absorb a large amount of water that, once in the concrete matrix, could easily be caught by the cement. As a result, the polymer suffered a shrinkage process which generated voids and made it possible to reduce the density of the hardened material. The behaviour of the polymer was typical of water retainers.

The dispersing effect of starch derivatives has been reported in many studies. In these cases, these additives have been presented as water-reducing agents or superplasticizers, as quoted by Glenn et al. (1998), Ouyang et al. (2009), Peschard et al. (2004), Vieira et al. (2005) and Zhang, Ju, Zhang, He, and Yang (2007), Zhang, Ju, Zhang, and Yang (2007), and Zhang, Ju, Zhang, and Yang (2008).

Water-reducing agents or plasticizers are additives which make it possible to reduce the water content of a mixture without modifying its consistency, or to improve the workability without varying the amount of mixing water (Papo & Piani, 2004). Most of the conventional water reducers are condensation products of formaldehyde (such as naphthalene sulphonated formaldehyde condensates and sulphonated melamine formaldehyde condensates) or polymer compounds like polycarboxylate, as reported by Peng, Qu, Zhang, Chen, and Wan (2005), Vieira et al. (2005), Zhang, Ju, Zhang, He et al. (2007), and Zhang et al. (2007, 2008). The first ones (formaldehyde derivatives) are high-molecular-weight products that, when dissolved in water, generate high-molecular-weight anions that can be adsorbed on the particle surface, leading to mutual repulsion of individual particles and to a reduction in the inter-particle friction. This dispersion avoids the flocculation of the particles, thus reducing the amount of water required to get a set consistency (Peng et al., 2005; Seabra, Paiva, Labrincha, & Ferreira, 2009; Zhang, Ju, Zhang, He et al., 2007). The second group of water reducers (polycarboxylates) avoids flocculation by means of a combination of electrostatic repulsive force and steric hindrance, due to their comb-shape (Peng et al., 2005; Zhang, Ju, Zhang, He et al., 2007). Formaldehyde derivatives and polycarboxylate-type plasticizers are not biodegradable, and may release formaldehyde into environment, leading to undesirable effects. Some previous works have suggested the use of starch ethers as water-reducing agents, in order to avoid any environmental problem (Vieira et al., 2005; Zhang, Ju, Zhang, He et al., 2007; Zhang et al., 2008).

Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007) studied the effect of starch sulphonate in cement pastes, concluding that it showed a more powerful water-reducing action than traditional naphthalene sulphonated formaldehyde condensates because, in the case of the starch ether, a strong steric hindrance was the main

dispersing mechanism. Vieira et al. (2005) obtained sulphoethyl starches with lower molecular weight than commercial ones, and reported that the effect of these products on some rheological properties of cement pastes (such as slump) was the same or even better than that of polycarboxylate ethers. According to these authors, commercialized starch and cellulose ethers show such a high molecular weight that their efficiency as dispersants becomes reduced, leading to a thickening effect. Peschard et al. (2004) studied the performance of five different powder polysaccharides in cement pastes, and found that the starch ether was the most effective in prolonging the setting time.

Some investigations have been carried out on lime-based materials with water-retaining agents and plasticizers, but so far no research has focused on the incorporation of starch in the mixtures. Seabra et al. (2009) studied the influence of some admixtures on the rheological behaviour of lime mortars. They concluded that HPMC initially exerted a thickening effect on the mixtures but, after some shaking time, this tendency was reversed, due to excessive entry of air. They also incorporated a sulphonated melamine formaldehyde superplasticizer in the mixtures, reporting an increase in the initial and final slump, a considerable increase in the yield stress and a decrease in the torque value of the mortars. Fortes-Revilla, Martinez-Remirez, and Blanco-Varela (2006) incorporated a polycarboxylate polyoxyethylene to a slaked lime-metakaolin mortar, and obtained significant improvements: (i) setting time was reduced; (ii) the amount of calcite was higher than the one of the control mortar without additive; (iii) the porosity level was lower and (iv) maximum mechanical strengths were larger and reached in a shorter time.

The rationale of the present study is that the water-reducing action of starches could be specially desirable in lime-based mortars, as these materials harden through two mechanisms: (i) loss of excess water and subsequent compaction of the material and (ii) the carbonation process, which starts during the first steps of setting and can last several years. If the amount of mixing water is larger, the loss of its excess becomes slower, and also the excess of water prevents CO<sub>2</sub> from gaining access to the mortar, thus slowing down the carbonation process. On the other hand, the thickening effect of starch is supposed to enhance the workability and to give non-sag and anti-slip properties to the mixtures, improving the pump ability in spray-on mortars and producing a thickening effect which makes it possible to reduce the number of repair cycles, which means a major advantage in repair work that must be completed in a short period of time (Rixom & Mailvaganam, 1999). The indicated properties would also be desirable to improve the performance of lime-based renders.

The aim of the present paper is to study the influence of a commercialized potato starch on different properties of lime-based mortars. The behaviour of different polymer dosages is assessed and related to a different mechanism of action. Several fresh state properties of the mortars are studied, in order to check the efficiency of the product as a rheology-modifier: consistency, density, air content, water retention capacity, setting time and evolution when applied on supports are reported. Experimental research on the effect of the starch on  $\zeta$ -potential of lime particles surface as well as the particle size distribution and viscosity changes in lime pastes are also conducted in order to elucidate the action mechanism. The dosage of the polymer was found to be critical for showing either thickening effect or dispersing action.

## 2. Materials

An aerial commercial lime and a pure limestone aggregate were used to prepare the mortars. The lime (class CL 90-S according to Spanish and European standard (UNE 459-1, 2001) was supplied

by Calinsa (Navarra). The aggregate was supplied by Caleras de Lis-kar (grupo HORMASA), and was a calcareous type. Materials characterization as well as their grain size distribution were previously reported (Izaguirre, Lanas, & Alvarez, 2009). The selected binder: aggregate ratio (B:Ag) was 1:1, by volume. This decision was taken according to previous data (Lanas & Alvarez, 2003; Lanas, Perez Bernal, Bello, & Alvarez, 2006). Volume proportions were converted into weight in order to avoid any imprecise measurements. Seven different dried mixtures were prepared by mixing 341.7 g of lime and 1286.9 g of aggregate. One of them was composed only of these two main components, and was taken as a control mortar. A commercialized potato starch (PS) was incorporated into the other six mixtures, using a different dosage in each case. The dosages tested were 0.03%, 0.06%, 0.15%, 0.30%, 0.50%, and 0.80% of the total dried mortar's weight, and samples were named from PS-1 to PS-6. All of these dosages are in line with previously used dosages of traditional water reducers and starches, as reported by Fortes-Revilla et al. (2006), Glenn et al. (1998), Seabra, Labrincha, and Ferreira (2007), Seabra et al. (2009), Vieira et al. (2005), and Zhang et al. (2008) and include a wide range in order to study the influence of the dosage of additive in the properties of mortars. The polymer was obtained from a supplier (OPAGEL CMT®, AVEBE) that describes it as a natural modified potato starch, with around 80% of amylopectin and 20% of amylose. Furthermore, pure soluble starch (Merck, Product No. 101252) was analysed in order to compare it with the admixture. Fig. 1 shows the IR spectra of both products, showing the huge similarity between them. Little modification, if any, was performed on natural potato starch with respect to functional groups to obtain the additive. Simultaneous determination of carbon and sulphur carried out by means of a LECO CS-125 showed for the potato starch from AVEBE a 39.71% of C and 0.92% of S, while the reference starch (Merck) showed very similar amount of C (39.17%) and 0% of sulphur. The results indicated that the potato starch used in the present work was modified to a certain extent, probably by introducing sulphate groups in the polymer structure. The scarce amount of these groups was proved by the low percentage of sulphur (0.92%) and by the lack of the absorption bands related to the asymmetric and symmetric stretching vibration of  $\text{SO}_2$  at  $1400$  and  $1254\text{ cm}^{-1}$  in the IR spectrum (Zhang, Ju, Zhang, He et al., 2007).

In order to obtain more information about the polymer characteristics, the molecular weight distribution of a very diluted solution with 0.02% of potato starch in water was obtained by means of dynamic light scattering (DLS). A simple cumulant analysis, which gives size information at a particular angle, was used (Chiou, Fellows, Gilbert, & Fitzgerald, 2005). The obtained hydrodynamic radius was 214 nm. This result matched the one previously reported by Roger, Bello-Perez, and Colonna (1999) for low amylose starch, and confirmed the information given by the supplier about the low amount of amylose in the polymer.

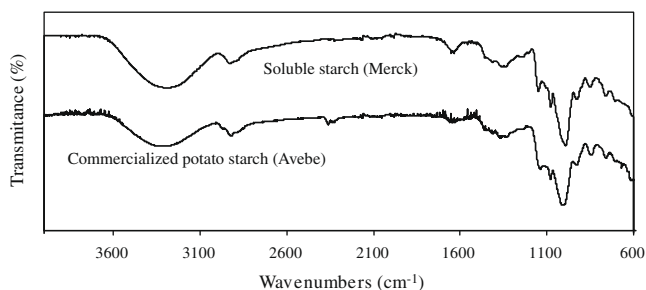


Fig. 1. IR spectra of commercialized potato starch from AVEBE and soluble starch from Merck.

### 3. Methods

#### 3.1. Mortar preparation

The amount of water was set according to the criterion of achieving a workable reference material, which is supposed to be related to the slump value obtained during the flow table test. The required amount of water to have a slump of  $160 \pm 10$  mm for the reference mortar was 410 mL. This value allowed good workability while avoiding an excess of water which would be damaging for mechanical strengths (Lanas & Alvarez, 2003). As the tested additive modified the rheology of the mixtures, the workability of mortars with PS was different from that of the reference material when the same amount of mixing water was incorporated, thus modifying the flow table test results.

Lime, aggregate and PS, if necessary, were blended for 5 min using a solid mixer BL-8-CA (Lleal S.A.). Water was then added and mixed for 90 s at low speed, in a Proeti ETI 26.0072 mixer. Mortars settled for 10 min before being tested, to let the additive take effect. Straight afterwards, fresh state properties were determined as described below.

#### 3.2. Fresh mixtures

##### 3.2.1. Fresh state mortar behaviour

For the fresh state of mortars, the following properties were studied according to the quoted standardized methods: consistency, through the flow table test, by measuring the slump (UNE 1015-3, 2000); density and air content, both data being recorded using a receptacle of  $1\text{ dm}^3$  previously weighed, which, after being filled with fresh mortar, was weighed again to obtain the density (UNE 1015-6, 1999). In a specific device, the entrained air was removed and replaced by a measurable amount of introduced water, which allowed us to determine the air content (UNE 1015-7, 1999); water retention capacity, determined by weighing absorbent materials placed on the fresh sample before and after 5 min of contact under pressure (UNE 83-816-93, 1993); and setting time, obtained from a specific device provided with a bradawl, which pushed the fresh sample until the strength exerted to introduce it into the sample was larger than 15 N (UNE 1015-9, 2000). The evolution of the mortars when applied on support was assessed. This last test consisted of spreading a 15 mm layer of mortar on a brick and observing any developments.

##### 3.2.2. $\zeta$ -Potential

Specific mixtures of lime, water, and additive were prepared to assess the viscosity,  $\zeta$ -potential and the particle size distribution, with a view to elucidating the mechanism through which the polymer acts.

The determination of  $\zeta$ -potential of solid-liquid interface permitted us to study the dispersing action of an additive, as the adsorption of the admixture on the solid surface of binder modifies this property, as stated by Papo and Piani (2004), Zhang, Ju, Zhang, He et al. (2007), and Zhang et al. (2007, 2008). Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007, 2008) studied the dispersing mechanism of starch sulphonate, carboxymethyl starch and a starch succinate half ester as water-reducing agents for cement, and observed that an increase in the polymer content led to a decrease in the  $\zeta$ -potential of the mixtures. They concluded that the adsorption of the admixture changed the charge distribution of the double-electrical layer on the cement surface, due to electrical and steric repulsive forces.

Following the method proposed by Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007, 2008), solutions with different concentrations of PS were prepared (from 0% to 1.4% w/w), and lime

was added with a solute/liquid ratio of 0.0025. After 5 min of stirring, the mixtures were separated by centrifuge, and the supernatants were analysed using a Zeta Potential Analyzer ZETA PLUS (Brookhaven Instruments Corporation, New York, USA). The average of ten measurements was regarded as the  $\zeta$ -potential of the lime particles.

### 3.2.3. Particle size distribution

As mentioned in Section 1 of this paper, thickeners are able to fix water on their structure and suffer an intertwining process, the consequence being an increase in viscosity (Paiva et al., 2006). Fixation of water and entanglement of chains should produce agglomerates, and particle size distribution of mixtures should change as a result, as mentioned by Chiou et al. (2005), Khayat (1998), Roger et al. (1999), and Saric-Coric, Khayat, and Tagnit-Hamou (2003).

Three grams of lime was added to 15 g of solutions with different amounts of PS in water (from 0% to 1.4% w/w), the resulting PS/lime ratios ranging from 0% to 7% w/w. The particle size distribution of these samples was determined using a Malvern Mastersizer (Malvern Instruments, Ltd., UK).

### 3.2.4. Apparent viscosity

The role of a thickener in a mixture consists of increasing the apparent viscosity, while a plasticizer is supposed to produce a decrease in this property, as quoted by Paiva et al. (2006), Papo and Piani (2004), Sobisch and Lerche (2008), and Vieira et al. (2005). Lime pastes were prepared by mixing 10 g of lime, 10 g of water and different amounts of the potato starch (PS percentages in relation to lime weight of 0%, 0.03%, 0.06%, 0.15%, 0.30%, 0.50%, and 0.80%), and their viscosities were determined using a HAAKE Viscotester VT 550, with a programme of rotation speeds increasing from 0 to 50 s<sup>-1</sup> during 90 s and then decreasing from 50 to 0 s<sup>-1</sup> in the same time.

## 4. Results and discussion

### 4.1. Fresh state mortar behaviour

In the present study, the reference mortar was prepared with the required amount of water in order to reach the set value during the flow table test. When PS was incorporated in dosages from 0.03% to 0.30%, lower results of slump were obtained, the effect being more important for higher amounts of admixture. However, when the dosage of 0.50% was used, a change in the behaviour of the material occurred: the fluidity became higher than the three previous ones and the workability was better, thus marking a critical point. The highest dosage followed the same trend, showing the highest slump values (Fig. 2). Analysing these results, it can be said that PS behaved as a thickener for dosages until 0.30%, and started to plasticize the mortars above that value.

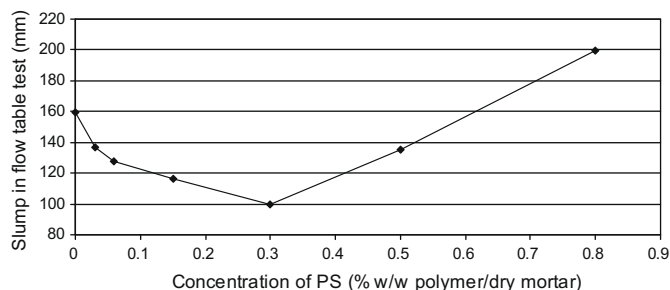


Fig. 2. Slump results in flow table test vs. concentration of potato starch.

As Fig. 3 shows, the incorporation of PS always led to an increase in the air content of the mortars. The percentages of entrained air are comparable to those obtained by Vieira et al. (2005) in cement mortars with starch derivatives. In fact, water-soluble synthetic and natural organic polymers classified as viscosity-enhancing admixtures (VEAs) have inherent surfactant properties that lower the surface tension of the aqueous phase of the paste, giving rise to air entrainment (Khayat, 1998; Seabra et al., 2009). This air entrainment could explain, broadly speaking, the decrease in the density of the mortars (Fig. 4).

Regarding the water retention ability, PS-5 and PS-6 showed a considerably greater water retention capacity, the highest dosage leading to a value of 99.6% (Fig. 5). This water-retaining behaviour can be explained on the grounds that the structure of starches is very similar to that of cellulose derivatives (the most widespread water-retaining agents) (Paiva et al., 2009). Functional hydrophilic groups in the starch molecules would be able to bind water molecules by means of hydrogen bonds. Nevertheless, only the highest amounts of PS led to higher water retentions than the control mortar, which suggests that the polymer behaves in a dosage-dependent manner.

The aforementioned water retention ability can be easily related to the setting time changes (Fig. 6). The large water retention capacity showed by PS-5 and PS-6 mortars could explain the delay in setting time, due to the fact that lime-based mortars must lose the

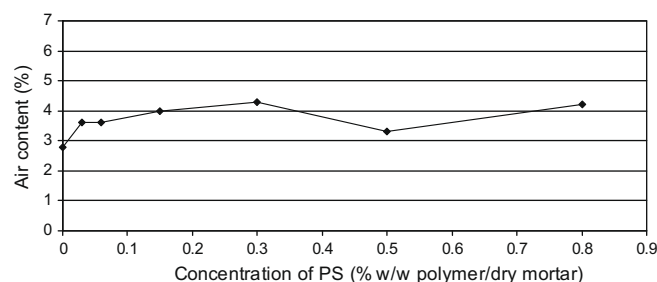


Fig. 3. Air content of mortars vs. concentration of potato starch.

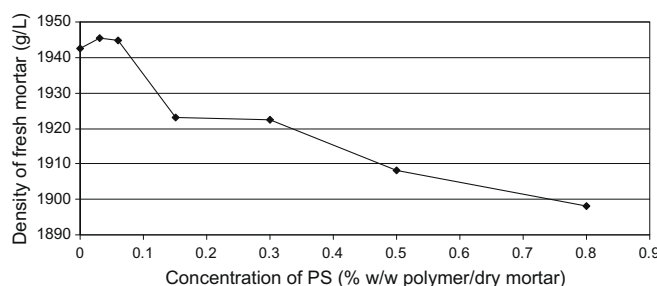


Fig. 4. Density of the fresh mixtures vs. concentration of potato starch.

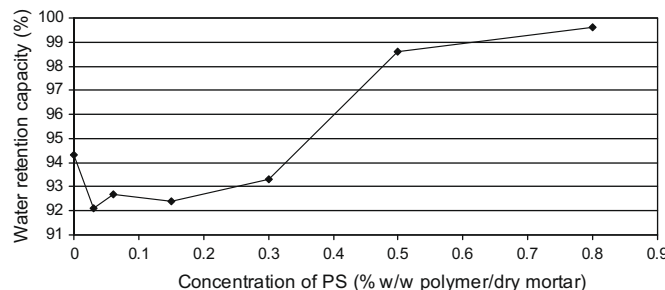
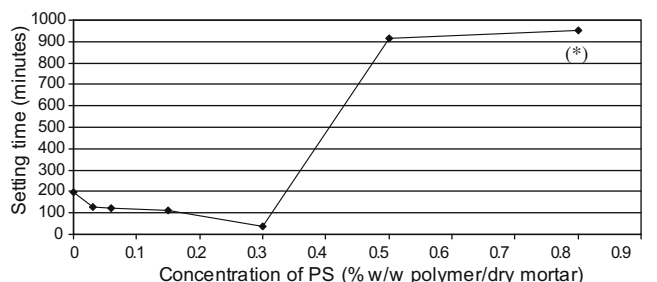


Fig. 5. Water retention capacity of the mortars vs. concentration of potato starch.





(\*) Value > 950 minutes, it could not be exactly measured because only a superficial layer hardened while the bulk of the mortar stood fresh.

Fig. 6. Setting time of mortars vs. concentration of potato starch.

excess water as a first step in the setting process. In spite of having the same amount of water, PS modified the setting time of the mortars, which showed its efficiency as a rheological modifier.

Fig. 7 shows the appearance of the layers of mortar 30 min after their application on bricks. The selected bricks had a very high water-absorption coefficient, in order to accelerate the evolution of mortars.

The control mortar showed a large number of macroscopic fissures, produced because of the high water-absorption coefficient of brick. When the potato starch was incorporated, the mortar presented no cracks, but the adherence was clearly affected by the dosage. As the amount of additive increased to 0.30%, the coherence of the mortar and its adherence to the brick's surface decreased, with a fall in PS-4. This behaviour fitted perfectly with the thickening effect observed in the flow table test and with the moderate water retention capacity of the mixtures. PS-5, which proved a workable and coherent material with high water retention capacity, permitted good adherence. The highest dosage led to a mortar that was too liquid, which made it impossible to get the brick up, because it slipped.

#### 4.2. Discussion on the action mechanism of the polymer

$\zeta$ -Potential data of solid–liquid interface of samples with different amounts of PS (Fig. 8) were collected in order to elucidate any

interaction between the polymer and the lime particle surface. Hydroxyl groups of the starch molecules should be ionized at the strong alkaline pH of the lime solution. The adsorption of the polymer onto the lime particles would change their zeta-potential, shifting it towards more negative results. It can be observed that the sample without PS showed the more positive value of  $\zeta$ -potential (39.93 mV) and the addition of the starch led to a reduction in this value, thus indicating an adsorption of the admixture on the lime surface. These results are in line with those reported by Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007, 2008) from  $\zeta$ -potential of cement particles with starch ethers added.

Fig. 9 shows the particle size distribution of lime pastes containing different amounts of PS (from 0% to 7% in relation to the lime weight). It can be seen that lime paste without additive (0% PS sample) presented two main peaks: a small one corresponding to particles between 0.1 and 1  $\mu\text{m}$  and a larger one between 10 and 100  $\mu\text{m}$ . The paste with 1% of potato starch (its ratio PS/lime was equivalent to an intermediate dosage between PS-3 and PS-4 mortars) produced a considerable displacement of the main peak toward higher values (between 100 and 1000  $\mu\text{m}$ ) and a huge increase in its intensity, thus showing the flocculant action between particles produced by this additive. The formation of large-size particles could thus explain the thickening effect of the starch up to 0.30%: it produced a fluidity drop in the flow table test (Fig. 2) and lower adherences when applied on bricks (Fig. 7).

However, when PS was added in dosages above 2% of lime weight (equivalent to PS-5 mortar) the intensity of the peak between 100 and 1000  $\mu\text{m}$  underwent a dramatic decrease, and the distribution became wider and centred on smaller sizes (from 10 to 300  $\mu\text{m}$ ).

On the basis of the experimental results obtained in the present study, it is evident that potato starch acted as a thickener in lime-based mortars when it constituted up to 0.30% of the total dried mortar weight. This thickening behaviour with starch addition is clearly different to that reported by Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007, 2008) for different starch ethers in cement pastes. In those studies, starch ethers – in all the tested dosages – acted as dispersing agents, with deflocculant behaviour which gave rise to a plasticizing effect. Nevertheless, in the present research, for samples up to 0.30% of admixture, starch acted as a

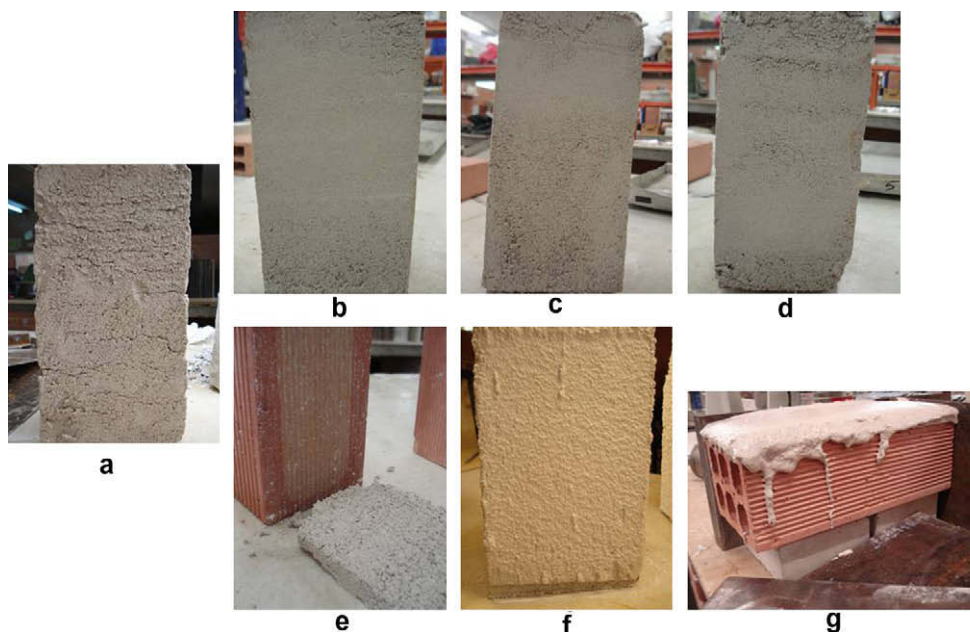


Fig. 7. Evolution of mortars on bricks: (a) REF; (b) PS-1; (c) PS-2, (d) PS-3, (e) PS-4, (f) PS-5, and (g) PS-6.

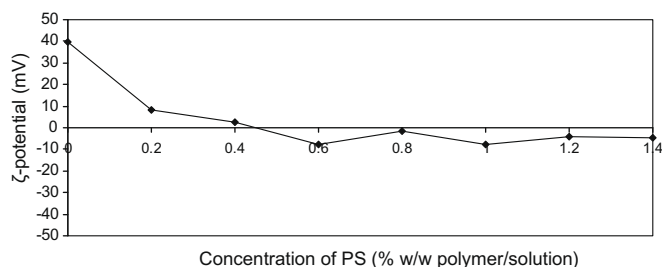


Fig. 8.  $\zeta$ -Potential of samples vs. concentration of potato starch.

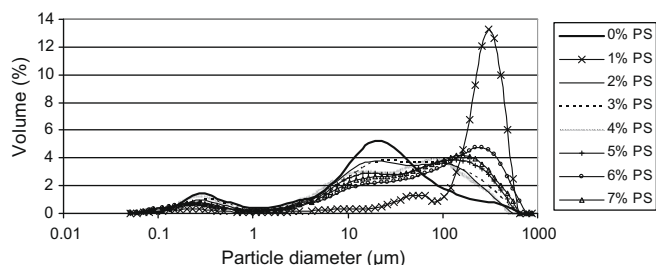


Fig. 9. Particle size distribution of lime pastes with different PS dosages (amounts of PS are expressed as percentages of lime weight).

flocculant agent, giving rise to interactions between lime particles and polymer molecules, thus explaining the  $\zeta$ -potential results, particle size distribution in lime pastes as well as the fresh state behaviour of modified mortars. Adsorption of the starch molecules on the lime particle surface may be caused by the hydrophilic functional groups, which act as “lime-anchoring” groups, just as functional groups in other polysaccharides have been reported to act in cement materials (Knaus & Bauer-Heim, 2003; Zhang, Ju, Zhang, He et al., 2007; Zhang et al., 2007, 2008).

When the dosage was larger than 0.30%, the behaviour changed and the product behaved as a plasticizer (Fig. 2). Particle size distribution showed a dramatic decrease in large particles for these samples, which suggests that the interaction between chains of polymer themselves and between lime particles and starch molecules were, at least, partially broken. Steric hindrance as well as electrostatic repulsions between chains might be generated due to the large amount of added polymer, resulting in dispersion of particles and, as a consequence, in a plasticizing effect. This dispersing mechanism could be similar to that proposed by Zhang, Ju, Zhang, He et al. (2007) and Zhang et al. (2007, 2008) to explain the effect of starch ethers in cement materials.

Mortars PS-5 and PS-6 thus corresponded to dosages of polymer in which it was executing a dispersing effect on the lime particles. The dispersion of lime, as well as the break of the linkages between additive chains and lime particles, could generate polymer molecules with many free sites and more dispersed lime particles where water could be fixed, thus explaining the high water retention capacity of those mortars.

In the end, viscosity measurements (Fig. 10) of lime pastes with different amounts of the tested starch showed a shear-thinning behaviour for the measured samples. This behaviour can be very useful for many practical functions (such as rendering, grouts, and shotcrete), because materials of pseudoplastic nature are supposed to resist sedimentation and sagging at rest but can be easily mixed, pumped and sprayed (Rixom & Mailvaganam, 1999; Yahia & Khayat, 2001). These materials are able to increase viscosity at low shear rates but show a reduction when great stress is applied (for example, when materials are pumped or sprayed during a “wet-mix” or “dry-mix” process) (Rixom & Mailvaganam, 1999).

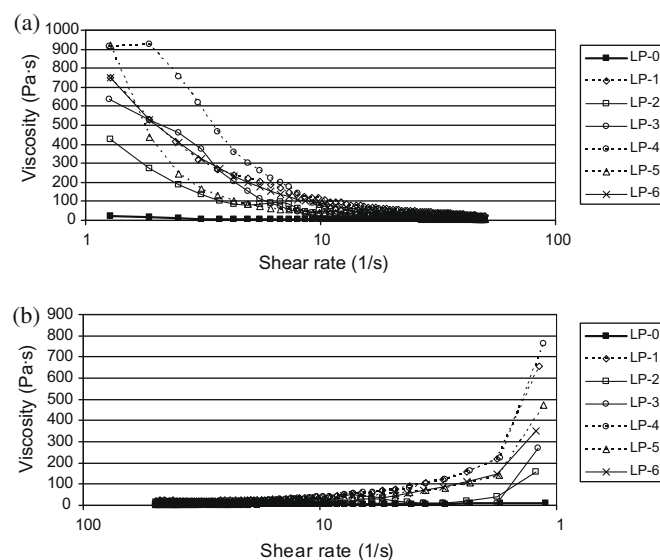


Fig. 10. Apparent viscosity of lime pastes (LP) without admixture (LP-0) and with increasing amounts of PS (from LP-1 to LP-6): (a) during increasing shear rate step; (b) during decreasing shear rate step.

When the stress is applied, linkages between polymer and lime particles may break, and linear chains of the polymer could align with the flow direction, thus causing a fall in viscosity. When the stress slows down, a recoagulation process could take place (Wallevik, 2009). In the samples studied, the recovery of viscosity when shear rate decreased was not complete, but was satisfactory in all the modified pastes (Fig. 10b).

On the other hand, although mortar fluidity (Fig. 2) and viscosity of lime pastes modified with starch addition are not directly related, there was a general trend: higher amounts of the tested starch led to higher apparent viscosity values up to 0.30% of PS. Differences between the mortar behaviour in terms of fluidity and paste viscosity could be related to both the effect of the aggregate (Gündüz, Bekar, & Sapci, 2007; Nehdi & Rahman, 2004; Seabra et al., 2009) and the slip phenomenon, which has been reported to take place when a coaxial cylinders model is used to obtain viscosity data (Nehdi & Rahman, 2004; Saak, Hamlin, & Shah, 2001).

## 5. Conclusions

A commercialized potato starch was tested as an additive for aerial lime-based mortars. Different dosages of the polymer were added to mortars and several properties at fresh state were studied in order to check their possible efficiency as a rheological modifier. Lime pastes with different amounts of polymer were also prepared to elucidate the action mechanism of the admixture.

The behaviour of the polymer was found to be strongly dosage-dependent. When up to 0.30% of lime weight was added, the potato starch acted as a flocculant agent, giving rise to interactions between lime particles and polymer molecules, proved by  $\zeta$ -potential measurements of the lime particles surface and particle size distributions of lime-starch suspensions. Adsorption of the starch molecules on the lime particle surface could be caused by the hydrophilic functional groups, which act as “lime-anchoring” groups. This thickening effect led to an increase in viscosity values and a decrease in workability and adherence of the material.

On the other hand, dosages of potato starch above 0.30% of lime weight produced a change in the behaviour of the polymer, which started to act as a plasticizer. Steric hindrance and electrostatic repulsions between chains might be generated due to the large

amount of added polymer, resulting in dispersion of particles and, as a consequence, a plasticizing effect, proved by particle size distribution results. Consequently, mortars became flowable and their adherence increased. Furthermore, their water retention capacity became greater, which could be related to the dispersion of lime and the break of linkages between additive chains and lime particles, which could generate many free sites where water could be fixed.

Both dosage-dependent effects produced by the tested polymer can be very useful for many practical application (such as rendering, grouts, and shotcrete), in which pseudoplasticity, adherence and sometimes thickening or plasticizing abilities of the mortars (depending on the application) are critical.

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