

# Effect of a biodegradable natural polymer on the properties of hardened lime-based mortars

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## Abstract

As an environmentally friendly and energy-saving alternative to cement-based materials and to some chemically obtained water-reducers, a commercialized starch was incorporated into aerial lime-based matrix. Five different dosages were tested in order to study the influence that the amount of additive exerted on the properties of the material. Density, shrinkage, water absorption through capillarity, water vapour permeability, mechanical strengths, porosity, pore size distribution, and durability in the face of freezing-thawing cycles were studied in the polymer modified mortars. The tested starch acted as a thickener for dosages up to 0.30%, and changed its behaviour for the largest dosage (0.50%): in that case it behaved as a plasticizer, dispersing the lime through the fresh mass and generating a more workable material. As a result, the matrix of the hardened mortar presented great coherence, owing to its large density and low porosity, characteristics which led to lower capillarity and permeability absorptions, better mechanical properties and improved durability.

## Resumen

Se estudió un almidón comercial incorporado a morteros de cal aérea. Este aditivo supone una alternativa, medioambientalmente más respetuosa y con menor costo energético, tanto a los materiales con base cemento como a algunos reductores de agua obtenidos por vía química. Se ensayaron cinco dosificaciones diferentes con el fin de analizar la influencia que la cantidad de aditivo tuvo sobre las propiedades del material. En los morteros modificados por la acción del polímero se determinaron densidad, retracción, absorción de agua por capilaridad, permeabilidad al vapor de agua, resistencias mecánicas, porosidad, distribución de tamaños de poro y durabilidad frente a ciclos de hielo-deshielo. El almidón utilizado actuó como espesante hasta la dosis de 0,30%, pero cambió su acción cuando se añadió en la dosis más alta (0,50%): en este último caso, se comportó como un plastificante, dispersando la cal a través de la mezcla en fresco, dando lugar a un material más trabajable. Como resultado, en la dosis 0,50%, la matriz del mortero endurecido presentó gran coherencia, debido a su mayor densidad y menor porosidad, características ambas que implicaron una menor capilaridad y permeabilidad, mejores resistencias mecánicas y una mejora en la durabilidad.

**Keywords:** mechanical properties; porosity; starch polymer; structural applications; lime mortar

## 1. Introduction

Restoration and maintenance of historic buildings has been reported to be a way to protect the environment as well as safeguard our Cultural Heritage.<sup>1</sup> An adequate choice of repair mortars is critical for the success of a restoration process, as the compatibility between the original materials and the new ones is essential.<sup>2,3</sup> Until the appearance of cement (in the mid-19<sup>th</sup> century), lime was the most widely used binder in construction, so lime-based materials constitute the best option for restoration work.<sup>1,2</sup>

Furthermore, the use of lime-based mortars is an environmentally friendly alternative<sup>4</sup>, not only for restoration work but also for new renders and grouts. The production of cement requires temperatures around 1450°C<sup>5</sup>, while lime is obtained from calcareous stone at ca. 900°C.<sup>6,7</sup> The lower energy consumption, together with a reduction in the emission of air-pollutants from the combustion process, makes the lime a more environmentally friendly product compared to cement.

Previous research has focused on the effect of starches and starch derivatives in cement-based materials, as they can act as rheology-modifying admixtures.<sup>8-15</sup> They have been shown to act as thickening agents<sup>9</sup> and also as water-reducers.<sup>10-15</sup> The use of starches as water-reducing agents could be especially desirable, as they are biodegradable and can be incorporated in the mixtures instead of traditional naphthalene sulphonated formaldehyde condensates (FDN) or polycarboxylate (PC)-type plasticizers. The addition of starches therefore contributes to reducing the environmental problems.<sup>10,13</sup>

Regarding the action mechanism of additives, many factors affecting the influence that a polymer exerts on a mixture have been reported, 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.<sup>16</sup> All these factors point to the difficulty of predicting the behaviour of the starches.

The molecular weight of a starch or any of its derivatives 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 derivatives can easily be adsorbed on the binder particles' surface, generating steric repulsions (i.e. a dispersing effect) which lead to lower viscosities.<sup>13,15</sup>

On the basis of the similarity between starches and cellulose derivatives, several effects of the starches have been clarified and tested, such as:

i) thickening behaviour, which allows use of starches as viscosity enhancing admixtures (VEA's);<sup>9</sup>

ii) closely related to this, a water-retaining effect, because these additives – with functional hydrophilic groups – are able to fix water in their 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;<sup>17</sup>

iii) a set-retarding ability,<sup>18</sup> even though the action mechanism of this process has so far not been fully clarified;<sup>19-21</sup>

iv) a dispersing effect on the cement particles, i.e. a plasticizing behaviour.<sup>10-15</sup> Many advantages regarding the use of starch ethers as water-reducing agents (instead of FDN or PC plasticizers) have been stated: reduction of environmental problems,<sup>10,13</sup> a more powerful water-reducing action<sup>13</sup> because a strong steric hindrance is the main dispersing mechanism,<sup>11</sup> and better rheological properties of cement pastes.<sup>13</sup>

As a result of the abovementioned increasing interest in lime mortars,<sup>1-3</sup> several pieces of research have addressed the behaviour of these lime mortars with water-retaining agents and plasticizers. Seabra et al.<sup>22</sup> 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 to 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.<sup>22</sup> Fortes-Revilla et al.<sup>23</sup> incorporated a polycarboxylate polyoxyethylene in a slaked lime-metakaolin mortar, and found a setting time reduction and larger, quicker maximum mechanical strengths.

Nevertheless, there is a gap in the literature concerning the behaviour of lime-based materials modified by starch addition. The thickening and dispersing effects of the starch mentioned above show conflicting behaviours that were reported to be strongly dose-dependent in a previous paper by our research group designed to investigate the effect of starch addition on the rheological properties of lime mortars.<sup>24</sup> The present study therefore focuses on the effect of a starch addition on the properties of a hardened lime matrix. The performance of the starch as well as the influence of the different dosages is evaluated by conducting analyses of density, shrinkage, water absorption capacity through capillarity, water vapour permeability and mechanical strengths. Any influence of the starch addition on the microstructure of the matrix has been assessed by means of pore size distribution obtained from mercury intrusion porosimetry data. Durability studies (freezing-thawing cycles) will also allow to draw conclusions about the enhancement of lime-based mortars through starch addition. The use of such a polymer-modified mortar would be a valuable option taking into account the environmental perspective, because i) lime turns out to be a low-cost binder (in terms of energy consumption and pollutants emission) and more suitable for repair work, and ii) starch is a natural, biodegradable polymer, and thus has clear advantages over other water-reducers.

## 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 standard<sup>25</sup>) was supplied by Calinsa (Navarra). The aggregate was supplied by Caleras de Liskar (grupo HORMASA), and was a calcareous type. The characteristics of the materials and their grain size distribution have previously been reported.<sup>26</sup> Mortars were prepared by mixing 341.7 g of the lime and 1286.9 g of the aggregate, amounting to a 1:1 volume ratio. Seven different dried mixtures were prepared. One of them was composed only of lime and aggregate, 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 proven dosages were 0.03, 0.06, 0.15, 0.30, 0.50, and 0.80% of the total dried mortar's weight, according to dosages of other water reducers and starches.<sup>9,10,13,14,22,23</sup> Samples were named from PS-1 to PS-6 according to the amount of additive. The polymer was obtained from a supplier (OPAGEL CMT® AVEBE) which describes it as a natural modified potato starch. A comparison between the admixture and a pure soluble starch (Merck, product number: 101252) was performed, showing a great similarity between the two (Fig. 1 depicts the IR spectra of both products). Little modification, if any, was introduced to the natural potato starch with respect to the functional groups to obtain the additive.

### 3. Methods

#### 3.1. Mortar preparation

A water/binder ratio of 1.2 was set, according to the criterion of achieving a workable reference material. This relation matched a slump value of  $160 \pm 10$  mm when the flow table test was executed. In order to assess any change due to the performance of the admixture, the same amount of mixing water was incorporated for all the samples, thus modifying the flow table results (Fig. 2). From these data, it can be seen that the starch addition up to 0.30% showed a thickening behaviour, while above that dosage, the admixture started acting as a plasticizer (with an increasing value of the slump).<sup>24</sup> Water retention capacities of the different mortars were also found to be related to the dosage of additive: only the highest dosages (where the PS acted as a plasticizer) led to larger water retention capacities (Fig. 2).<sup>24</sup>

Lime, aggregate and PS, if necessary, were blended for 5 minutes using a solid mixer BL-8-CA (Lleal S.A.). Water was then added and mixed for 90 seconds at low speed, in a Proeti ETI 26.0072 mixer. Mortars were moulded in prismatic 40x40x160 mm casts and demolded 5 days later.<sup>27</sup> Pastes were compacted in a specific device for 60 seconds. Curing was executed in laboratory conditions at room temperature for 28 days ( $RH 60 \pm 10\%$  and  $20 \pm 5^\circ C$ ). Three specimens were prepared for each mixture; hence, 18 specimens were tested.

#### 3.2. Determination of mortar properties

Analyses of density, shrinkage, water absorption through capillarity,<sup>28</sup> water vapour permeability,<sup>29</sup> open porosity, pore size distribution (by means of mercury intrusion porosimetry), and mechanical strengths<sup>27</sup> were carried out. Furthermore, durability was studied through freezing-thawing cycles.

##### 3.2.1. Density and shrinkage

Before the specimens were broken during the mechanical test, their length was measured with a gauge and the mass was set with a balance METTLER PC 4000, which allowed us to determine their density. On the basis of the length that the samples showed when they were demolded, shrinkage could be calculated.

##### 3.2.2. Water absorption capacity through capillarity and water vapour permeability

Samples used for the determination of water absorption capacity through capillarity were prepared in the same way as those for mechanical strengths tests. After 28 days of hardening in laboratory conditions at room temperature ( $RH 60 \pm 10\%$  and  $20 \pm 5^\circ C$ ), the four main surfaces of samples were covered with liquid paraffin to seal them. Once this had hardened, specimens were broken in two fragments, and these were immersed in water for 90 minutes. The difference between the initial mass, the mass after 10 minutes of immersion and the mass after 90 minutes made it possible to determine the capillarity coefficient.<sup>28</sup>

Special samples disk-shaped were prepared to study the water vapour permeability of mortars. Specimens hardened for 28 days in laboratory conditions at room temperature, and were then placed as lids on containers where a saturated solution of  $KNO_3$  was put. The mass lost in the course of 72 hours permitted to calculate the water vapour permeability of mortars.<sup>29</sup>

### 3.2.3. Mechanical strengths

The three-point flexural tests were carried out on the mortar specimens using a Frank/Controls 81565 compression machine at low rates of loading ( $1 \text{ kp}\cdot\text{s}^{-1}$ ). Flexural strength determination was performed on the Ibertest IB 32-112V01. Compressive strength tests were executed on the two fragments of each specimen resulting from the flexural tests. This was carried out on a Proeti ETI 26.0052, and the rate of loading was  $5 \text{ kp}\cdot\text{s}^{-1}$ .<sup>27</sup>

### 3.2.4. Pore structure

Open porosity was determined according to the water saturation test<sup>30</sup> with a hydrostatic balance. The pore size distribution test was performed by using a Micromeritics AutoPore IV 9500 with a pressure range between 0 and 207 MPa. Pressure, pore diameter and intrusion volume were automatically registered.

### 3.2.5. Durability: Freezing-thawing cycles

Owing to its better strength results, samples of PS-5 mortar were selected, prepared and subjected to durability cycles and compared to a control group. Mortars were prepared as explained above in 3.2.1. Curing was executed in laboratory conditions at room temperature over 56 days ( $\text{RH } 60 \pm 10\%$  and  $20 \pm 5^\circ\text{C}$ ), and after that, samples were subjected to several freezing-thawing cycles. They were immersed in water until complete saturation and then frozen in a freezer (CARAVELL 521-102) at  $(-10^\circ\text{C} \pm 2^\circ\text{C})$ . A total of ten specimens were prepared for each mixture; hence, 20 specimens were studied. Different testing days were set corresponding to 1, 4, 7, 10 and 14 complete cycles. Qualitative alteration according to a previously proposed criterion<sup>31</sup> and compressive strengths were studied. Two specimens of each mortar were tested at each point, and the reported results are an average of the two. Table 1 shows the characteristics of the set cycles.

## 4. Results and discussion

### 4.2.1. Density

As Table 2 shows, the density at hardened state was quite similar for all the mortars, although it was possible to identify a general trend: density decreased as the amount of PS increased. PS-5 sample was an exception, showing the highest density at hardened state. This fact matched with the visual evaluation of the samples (Fig. 3) and the change of fluidity behaviour (Fig. 2). The deflocculation that could be observed in the fresh mixture of PS-5 gave rise to a greater coherence in the mortar paste (Fig. 3 a)), avoiding gaps in the hardened mortar, thus increasing the density.

Hardened state properties of PS-6 mortar were not measured because it showed an excessively liquid nature which made it difficult to manipulate.

### 4.2.2. Shrinkage

As was expected for lime mortars, shrinkage coefficients were very high.<sup>32</sup> Owing to the presence of some water-absorbent component, some binding materials must be prepared with large amount of mixing water. Lime mortars can be quoted as an example of this kind of material. As a result of the large amount of water, these mortars undergo considerable shrinkage.<sup>33,34</sup> Following this tendency, the shrinkage coefficients of the mortars rose with the

amount of additive (Table 2), and this was especially important for PS-5, which was the mixture that showed the largest water retention capacity (Fig. 2).

Gleen et al.<sup>14</sup> studied the influence of two different starch ethers as additives for lightweight concrete. They found that the large water absorption capacity, which these polymers showed in themselves, allowed them to reduce the amount of mixing water. The additives kept the water in their structure, and once in the concrete matrix, they could be transferred to the cement, giving rise to a considerable shrinkage of the polymer. In the present study, PS-5 mortar contained a large amount of starch which was able to retain water and could act as described by Glenn et al.,<sup>14</sup> contributing to the outstanding shrinkage coefficient shown by this mixture.

#### **4.2.3. Water absorption capacity through capillarity**

Water absorption is an extremely important property for mortars, as they are usually exposed to environmental phenomena - such as rain - or in contact with elements that could be wet. As a consequence, an inappropriate mortar could become damaged and cause water movement inside the building structure, thus affecting and damaging other materials such as stones, through efflorescence phenomena.<sup>35</sup>

As Table 2 shows, the addition of the starch reduced the water absorption capacity of the mortars only when the amount of admixture was high: PS-4 and PS-5 mortars. The capillary sorptivity force (as a pressure difference) increases when the pore diameter drops.<sup>35</sup> Obviously, the amount of pores with small sizes also plays a relevant role. The great compaction of PS-5 mortar could explain its low water absorption capacity through capillarity, as the number of pores in this sample should be lower than those of other mixtures. PS-4-mortar showed an outstanding amount of large pores (Fig. 3, b) and c)). This fact would probably cause a decrease in the amount of capillary pores, giving rise to a capillary suction drop. Analysis of the pore structure of mortars (4.2.6) will help to confirm these assumptions.

#### **4.2.4. Water vapour permeability**

The permeability coefficient expresses the difficulty that water vapour molecules find when trying to pass through a mortar, so the lower the coefficient, the higher the permeability.

Table 2 shows the permeability coefficients for the studied mortars. It can be seen that the addition of PS resulted in a larger permeability level of the material up to 0.30%, while the highest dosage of admixture produced a huge decrease in this property. Mortars up to PS-4 showed lower coherence (Fig. 3, b) and c)), reflected in lower density results, while PS-5 behaved in the opposite way. This change in the material's coherence could explain the modification in water vapour permeability, as a more coherent material will put up more resistance to the molecules that pass through it.

#### **4.2.5. Mechanical properties**

Figure 4 shows the flexural and compressive strength results for the mortars studied after 28 days of curing. It can be observed that the addition of potato starch always led to an improvement in mechanical properties, except for sample PS-4. Furthermore, PS-5 showed a great increase in those properties.

Leemann et al.<sup>9</sup> tested different viscosity modifiers -starch derivative being one of them- and stated that all the cement mortars modified with this kind of admixture showed greater

mechanical strengths than the reference mortar, due to the better cement distribution through the mass. Fortes-Revilla et al.<sup>23</sup> concluded that a water reducer (based on polycarboxylate) improved the final mechanical properties of lime-metakaolin mortar, and allowed them to be reached in a shorter period of time. They found the lower porosity and the larger amount of calcite to be responsible for this behaviour.

The lower coherence of PS-4, caused by the excessively marked thickening effect of the admixture, led to a weaker material. On the other hand, the great compaction of PS-5 mortar produced a coherent structure with a much improved mechanical behaviour (Fig. 3, a)). The density of a mortar is supposed to be one of the most important factors affecting its mechanical performance: as the density increases, mechanical strengths improve.<sup>34</sup> The dispersing effect that the potato starch exerted when used in large dosage (0.50%) could explain the better coherence of PS-5 sample, due to the homogeneity of the obtained mixture, as the density values confirmed (Table 2). This behaviour matched the results obtained by Fortes-Revilla et al.<sup>23</sup>

The improvement in mechanical properties is a very important advance for lime-based mortars, due to the fact that the lower mechanical strengths that lime-based materials show – especially in comparison to the larger ones exhibited by cement mortars- is one of their main disadvantages.<sup>2,36</sup>

Figure 5 shows long-term strengths for the PS-5 sample, demonstrating that this sample presented better mechanical performance than the control mortar from the first week of setting, especially in the flexure test. After 28 days of setting, both flexural and compressive strengths were almost twice as much as the reference values. After one year of hardening, both flexural and compressive strength of PS-5 mortar were higher than the reference one. As a general observation, it can be said that final mechanical properties were reached in a considerable shorter period of time, and were also improved in long-term tests. The same conclusion was drawn by Fortes-Revilla et al.<sup>23</sup> when they incorporated a polycarboxylate-type water-reducing agent in lime mortars with metakaolin. They related this to the lower porosity and better carbonation of the samples. In the present study, the degree of carbonation was found to be similar for all the tested samples (results not shown), but calcite could be better distributed through the mass thanks to the better dispersion of the lime produced by the admixture, thus generating a more uniform structure with better mechanical properties.

#### 4.2.6. Pore structure

There are several factors affecting the porosity of a mortar, such as: the water/binder ratio, the properties of the binder and the aggregate, the curing conditions and the presence of admixtures.<sup>23,37</sup> In the present study, the dosage of potato starch is the only modification introduced in the studied mortars, so differences in the porosity level between them must be explained in terms of the additive effect.

Open porosity results for hardened mortars are shown in Table 2. As can be observed, the addition of PS always led to a lower porosity level than the reference, except for PS-4. The incorporation of the additive up to 0.30% produced a thickening action which led to a more tangled structure, thus decreasing the number of pores. The dosage of 0.30% thickened the fresh mixture so greatly and created such a large number of agglomerates that, when the mortar was moulded, it was scarcely flowable and could not be properly compacted, generating a large amount of voids (Fig. 3, b) and c)). The highest dosage (PS-5 sample) produced a change in the polymer behaviour, generating a dispersing effect which led to a more uniform and coherent matrix, and allowing the consolidation of a compact material,

with few number of pores (Fig. 3 a)). As a result, the porosity level of PS-5 mortar was the lowest.

Figure 6 shows the micro and meso-pore size distribution results for the studied mortars. The control material showed two important peaks: the first one was related to large pores (10  $\mu\text{m}$ ) and the second one –which was the main peak- related to pores around 1  $\mu\text{m}$ . Furthermore, it showed a certain population of pores at  $\sim 5 \mu\text{m}$  (seen as a shoulder of the main peak). The addition of PS always led to a decrease in the intruded volume of the 10  $\mu\text{m}$  peak, which could be related to the thickening action of the polymer: its flocculation effect led to a more tangled structure, and so a pore size reduction took place. It may be suggested that differences in pore size distribution between PS-5 and the other samples arose from the macro-porosity level instead of the meso and micro-porosity ranges, as the open porosity results confirmed.

Taking into account the porosity as well as pore size distribution, the lowest capillarity coefficients of PS-4 and PS-5 samples can be explained by the fact that these samples presented the lowest amount of pores up to 1  $\mu\text{m}$  (responsible for the water absorption through capillarity).

Mechanical properties have been widely reported to be strongly dependent on the porosity level of the mortars: as a general statement, the larger the porosity, the lower the mechanical strengths.<sup>2,23,37,38</sup> Figure 7 presents the correlation between compressive strength and open porosity of mortars, showing that the differences in open porosity, within the experimental limits of the present study, might easily serve to explain the observed mechanical behaviour.

#### **4.2.7. Durability: freezing-thawing cycles**

Table 3 shows the degree of alteration of the mortars after they were subjected to several freezing-thawing cycles. The specimens did not last long enough to be tested at all the set times.

The reference material was completely destroyed after 6 freezing-thawing cycles, and showed signs of deterioration from the first steps (Fig. 8). PS-5 mortar showed much better performance: it did not show any crack during the first steps, and only some samples were visually affected after four cycles. Samples were destroyed during the eighth cycle.

Figure 9 presents the compressive strength results for the tested materials after they had been subjected to several freezing-thawing cycles. It can be observed that mechanical behaviour of PS-5 mortar was considerably better than that of the reference mortar.

The improvement in durability found for PS-5 mortar could be explained by considering its lower water absorption capacity through capillarity as well as its lower open porosity. As the pore structure of the material hindered the water intake, freezing and thawing processes affected the mortar in a less aggressive way, allowing to obtain better results in the durability test. The better performance of the modified lime mortar subjected to freezing-thawing cycles has been reported to be a relevant characteristic for repair mortar in restoration work.<sup>39</sup>

## **5. Conclusions**

A commercialized starch (with several environmental advantages compared to FDN and PC plasticizers) was tested as an additive for aerial lime-based mortars. Different dosages of the polymer were added to mortars and several properties at hardened state were studied in order to test their influence on the final material properties.



The behaviour of the admixture was found to be strongly dosage-dependent: it behaved as a thickener when the dosage was less than 0.30% of total dry mortar weight, generating a tangled fresh mass which led to a less porous hardened material. When 0.30% of starch was added, the large amount of polymer generated such a great amount of agglomerates that the fresh mortar became scarcely workable and could not be properly compacted. As a result, the porosity level of the hardened matrix increased, thus damaging the mechanical strengths. The highest dosage of starch (0.50%) produced a change in the behaviour: it exerted a dispersing effect which led to a more uniform and coherent matrix, consolidating a compact material with a small number of pores. Owing to its dense structure, this mortar was found to have a very satisfactory performance: low water absorption capacity through capillarity and water vapour permeability, much improved mechanical strengths since the first days of setting and better durability results when subjected to freezing-thawing cycles. In addition, the final mechanical properties were reached sooner, which constitutes a great advantage for lime-based mortars.

The improvements described could be very useful to obtain appropriate lime-based mortars to apply in restoration work as well as for new building purposes. Some of the main disadvantages presented by lime materials (such as low mechanical strengths and the length of time required to reach them) can be resolved by the incorporation of the tested biodegradable additive, leading to a final product which can be produced in a more environmentally respectful way than cement-based materials, and which potentially presents less long-term danger to the environment.

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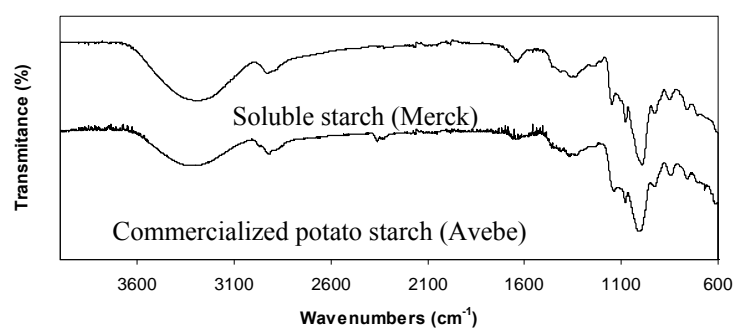
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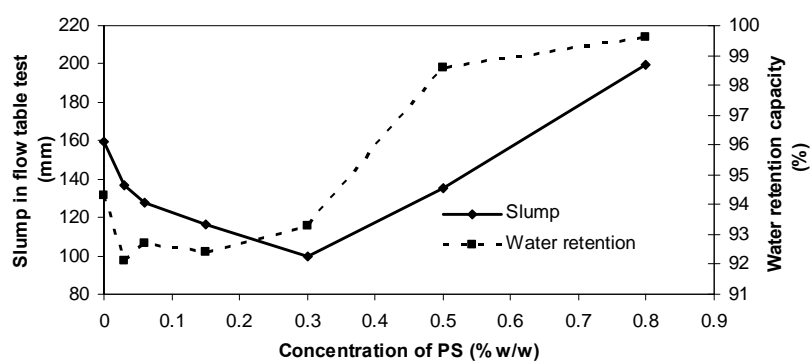
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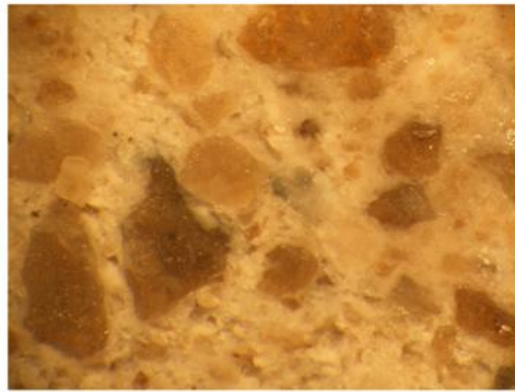
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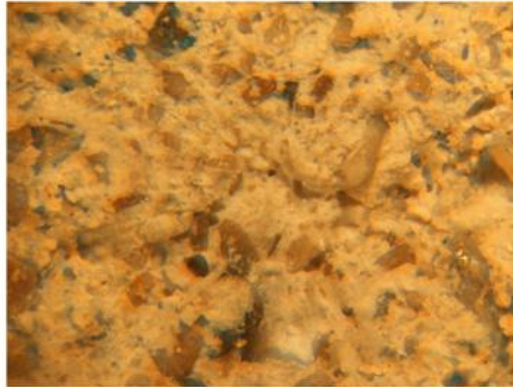
**Figure 1.** IR spectra of commercialized potato starch from Avebe and soluble starch from Merck.



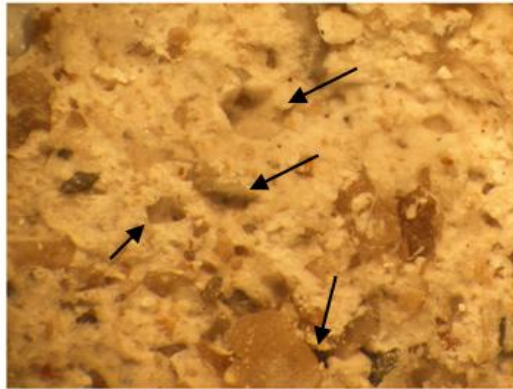
**Figure 2.** Slump results in flow table test and water retention capacity vs. concentration of potato starch.



a)



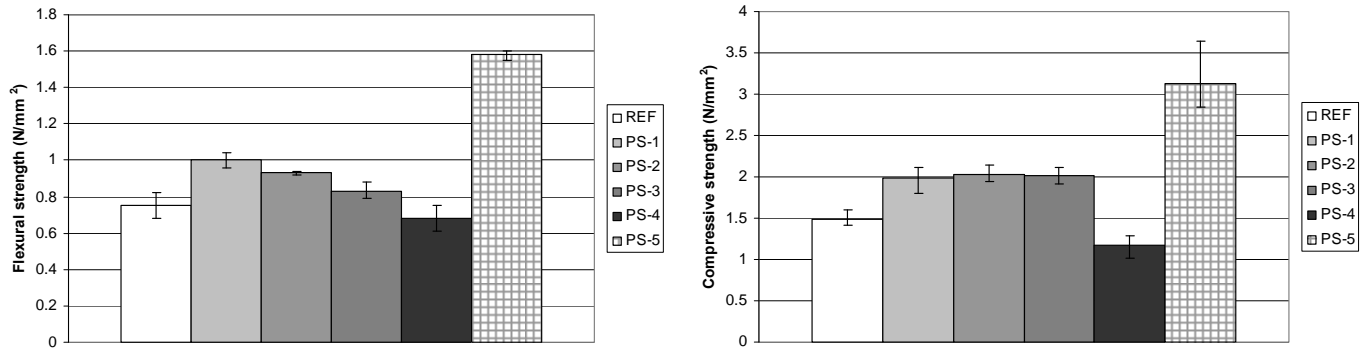
b)



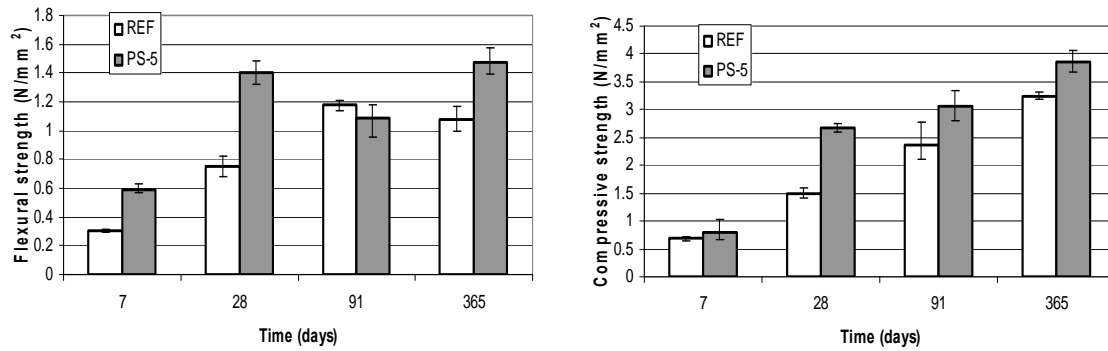
c)

**Figure 3.** Fragments of hardened mortars: a) PS-5 sample with a magnification of 16, showing large coherence and scarce porosity; b) PS-4 mortar with a magnification of 16, showing a less coherent matrix, with larger amount of pores and less integrated aggregate particles; c) PS-4 mortar with a magnification of 25, where some visible pores have been marked and some aggregate grains are clearly disaggregated.

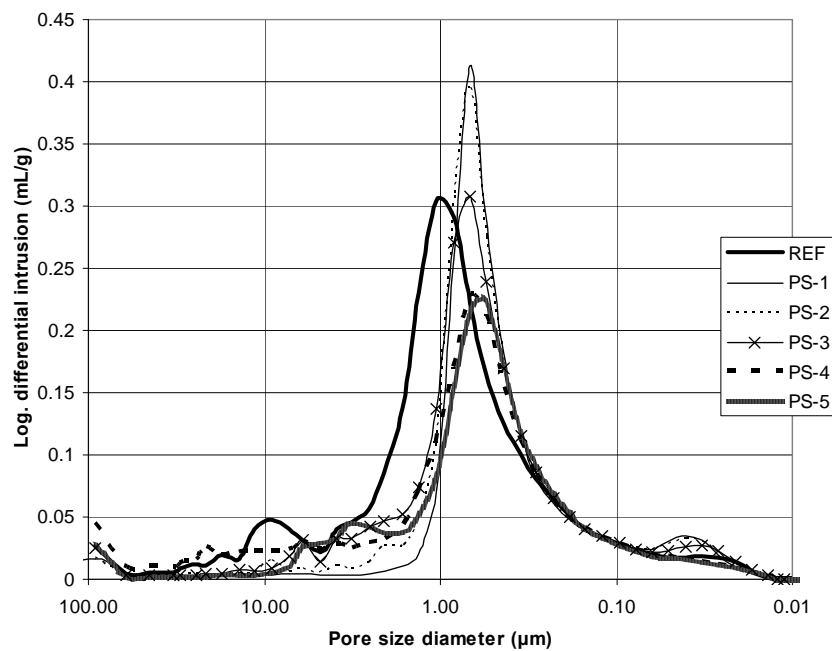
a)



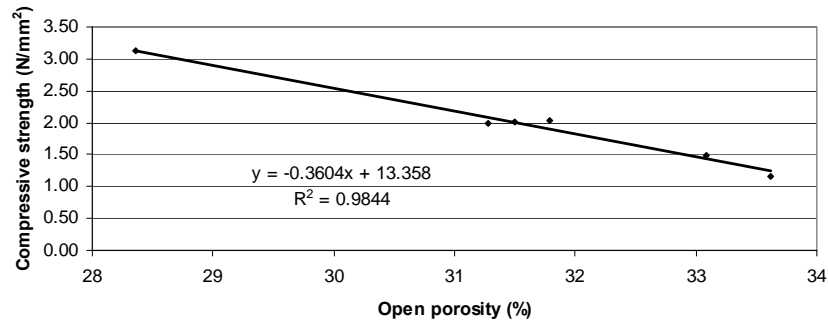
**Figure 4.** Flexural and compressive strengths after 28 days of hardening for the tested mortars (error bars are included).



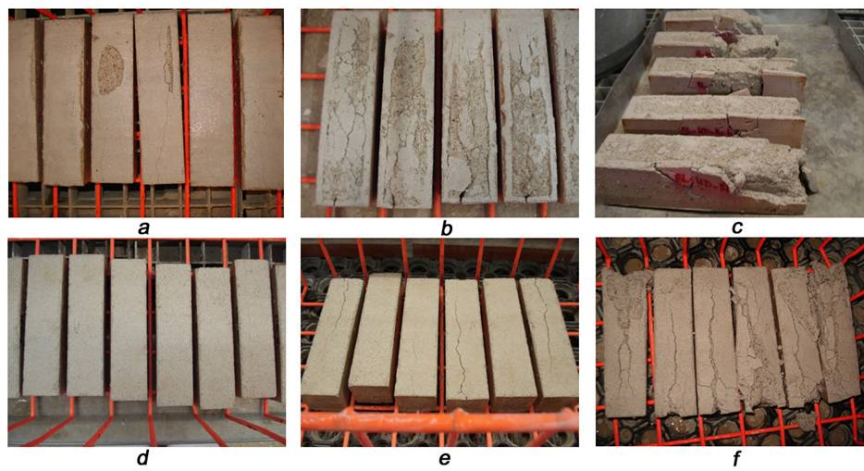
**Figure 5.** Flexural and compressive strengths of PS-5 mortar and a reference sample vs. time (error bars are included).



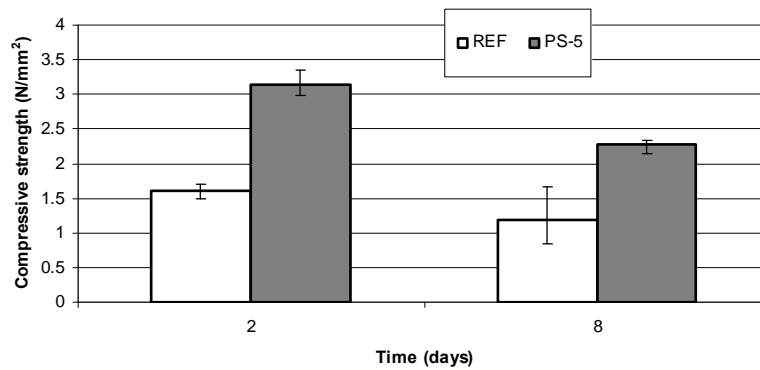
**Figure 6.** Pore size distribution of the studied mortars.



**Figure 7.** Open porosity-compressive strength relationship for the studied mortars.



**Figure 8.** Tested specimens after freezing-thawing cycles; a) REF samples after 1 cycle; b) REF samples after 4 cycles, with evidences of alteration; c) REF samples after 6 cycles, totally destroyed; d) PS-5 specimens after 1 cycle; e) PS-5 specimens after 4 cycles, with few superficial cracks; f) destroyed PS-5 specimens during eighth cycle.



**Figure 9.** Compressive strength of mortars after freezing-thawing cycles (error bars are included).

Cycle duration	Steps	Temperature	Water immersion	Time
48 hours	Step 1	Room temperature	Yes	24 hours
	Step 2	-10°C ± 2°C	No	24 hours

**Table 1.** Freezing-thawing cycles.

	Density (g/mL)	Shrinkage coefficient (mm/m)	Capillarity coefficient (kg/m <sup>2</sup> ·min <sup>1/2</sup> )	Permeability coefficient	Open porosity (%)
<b>REF</b>	1.67	13.59	2.36	16.6	33.08
<b>PS-1</b>	1.60	13.33	2.52	12.5	31.28
<b>PS-2</b>	1.63	14.79	2.50	13.0	31.79
<b>PS-3</b>	1.61	16.35	2.36	11.8	31.50
<b>PS-4</b>	1.46	17.08	1.45	12.7	33.62
<b>PS-5</b>	1.68	25.63	1.85	19.1	28.36

**Table 2.** Density, shrinkage, capillarity and permeability coefficients and open porosity at hardened state of the studied mortars.

	Alteration degree		
	1 cycle	4 cycles	7 cycles
<b>REF</b>	0	4	-
<b>PS-5</b>	0	1-2	4-5

Equivalences of the alteration degrees:

0: Without alteration.

1: Slightly altered, some small (thin and short) cracks on the surface of the specimens.

2: Altered, several cracks (like spider's web) and deeper.

3: Very altered, several deep cracks and swelling of the specimen.

4: High degree of alteration, large and deep cracks, large swelling of the specimen including a partial weight loss.

5: Completely altered, the specimen is practically destroyed, only little pieces of it are kept.

**Table 3.** Qualitative evaluation of the mortars during freezing-thawing cycles.