

INFLUENCE OF POLYMER ADDITIVES ON ADHERENCE AFTER IMMERSION IN WATER

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ABSTRACT

With the constant increase of the ceramic tiles demand in wet areas of the buildings, there has been concern about the durability of the ceramic system, especially in façades. It is known that the bond strength between adhesive mortars and ceramic tiles decreases when the system is saturated in water, phenomenon that might be related to changes in the polymeric phase of the mortar when under long contact with water. Due to the “wall effect” that the ceramic tiles induce when in contact with fresh mortar, especially the porcelain tile, there is the formation of thick layer of polymeric phase in the interface mortar/ceramic tile which is said to be the major responsible for the adhesion. Aiming to evaluate the effect of the water on the adhesion between porcelain tile and adhesive mortars in the hardened state, polymer-modified mortars were prepared with the polymers HEC (hydroxyethyl cellulose) and EVA [poly(ethylene-co-vinyl acetate)] in different contents (HEC: 0, 0.5 and 1%; and EVA: 0, 10 and 20% of the weight of cement). The mortars were applied on the back surface of the porcelain tile, then subjected to different exposition conditions and tested as to bond strength. The results showed reduction of the bond strength between some mortars and the tiles when the system was saturated with water, however the effect is partially reversible after drying. The results are correlated with the water absorption and dimensional changes tests results.

1. INTRODUCTION

Ceramic tile adhesives are modified with polymers to improve some properties in the fresh and hardened states. Cellulose ethers, such as hydroxyethyl cellulose – HEC, are employed because of their excellent water retention capacity and to the improvement of the rheology of these mortars. Vinyl latex, such as poly(ethylene-co-vinyl acetate) – EVA, are added to improve the hardened mortar performance, mainly flexibility and bond strength.

The better adherence of latex-modified mortars is attributed to the formation of a thin polymeric film at the interface with the ceramic tile, especially with low water absorption ceramic. This film usually results in a better impermeability and in the hindrance of cracks caused by tensile and shear stresses. However, it has been stated that these materials have poor water resistance, i.e., they can be negatively affected if they are wet or if they are exposed to high humidity conditions^[1,2]. Fritze^[3] and Jenni^[4] have observed lower mechanical and bond strengths of polymer-modified mortars under wetting.

The concern is more evident when low water absorption ceramic tiles are employed, such as porcelain. The pore solution of the fresh mortar is not able to penetrate into the tile's body, hindering the mechanism of adhesion. Moreover, there is an accumulation of water at the interface, and the formation of a thin transition zone with a high water/cement ratio^[5]. The polymers are dissolved or dispersed in the aqueous phase of the mortar; when the mortar hardens and dries, there is the formation of the polymeric film at the interface, and this film is said to assure the adhesion of the mortar to the tile^[6].

It has been hypothesized that the mortar sensitivity to water might be due to changes in the polymeric phase after a long contact with water, such as disaggregation, softness, weakness and/or expansion of the polymeric phase could be the responsible for the observed behaviour^[1,4]. Fowkes says that the decay of mechanical strength in wet conditions can be attributed to the polymer interaction preferentially with water due to an acid-base association, which is stronger than the Van der Waals forces that act in the polymer-cement interface. There would be a competition between water molecules and cement matrix for the polymer^[7].

In order to investigate the behaviour of the bond strength between polymer modified mortars and porcelain ceramic tiles, mortars specimens were prepared with different contents of the cellulose ether HEC (hydroxyethyl cellulose) and the copolymer EVA [poly(ethylene-co-vinyl acetate)]. The specimens were subjected to a wetting and drying cycle, and were tested to determine the bond strength. The results were correlated with the water absorption and dimensional changes of the specimens. The data presented herein are part of the Masters thesis developed by OLIVEIRA^[8].

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1. MATERIALS

Portland cement (type CPII-F 32 according to Brazilian standard NBR 11578/91), fine sand of aeolian origin, deionized water, the cellulose ether hydroxyethyl cellulose (HEC), and the EVA copolymer [poly(ethylene-co-vinyl acetate)] were used to prepare the mortars. Tables 1, 2 and 3 present the material's characteristics.

Cement:sand ratio of 1:3 was used to prepare the mortars (in weight basis). The water/cement ratio was kept constant at 0.76. The contents of HEC and EVA were 0, 0.5, 1% and 0, 10, 20%, respectively, in cement weight basis. Nine different mortars were studied.

CHEMICAL ANALYSIS (%)										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	CO ₂	LOI	Insoluble
17.40	4.62	2.62	59.93	5.96	3.22	0.19	1.07	3.94	4.80	1.35
PHYSICAL AND MECHANICAL CHARACTERISTICS										
Setting time (min)		Water for 255±10mm flow table	Blaine surface area (cm²/g)	#200(%)	#325(%)	Compressive strength (MPa)				
Initial	Final					3 days	7 days	28 days		
275	345	26.69	3381	3.10	13.02	27.79	31.24	39.00		

*CPII-F 32 is a normal Portland cement with up to 10% of finely ground limestone, in according with a Brazilian standard NBR 11578/91

Table 1. Characteristics of Portland cement CPII-F 32*

PARTICLE SIZE DISTRIBUTION - NBR 7217/87	SIEVE SIZE (mm)	% RETAINED	
		INDIVIDUAL	CUMULATIVE
	0.6	0.03	0.03
	0.3	1.03	1.06
	0.15	71.81	72.87
	0.075	27.02	99.89
	<0.075	0.11	100.00
FINENESS MODULUS - NBR 7217/87		0.74	
UNIT WEIGHT - NBR 7251/82		1.51 kg/dm ³	
SPECIFIC GRAVITY - NBR 6508/84		2.64 kg/dm ³	
POWDERED MATERIALS - NBR 7219/87		0.81%	

Table 2. Physical characteristics of sand

EVA	
Solids content (thermogravimetry) ^a	99±1%
Ash content (30min at 1000°C) ^a	7.63%
Apparent density of the powder (mercury intrusion porosimetry) ^a	1.34g/cm ³
Specific gravity (NBR 6474/84)	1.24g/cm ³
Particle size (laser granulometry in ethanol) ^a	11% above 250µm
Protective colloid ^b	Poly(vinyl alcohol)
Glass transition temperature-Tg (DSC - differential scanning calorimetry) ^a	11.2°C
Minimum film forming temperature ^b	Approximately 4°C
HEC	
Ash content (30min at 1000°C) ^a	2.47%
Apparent density of the powder (mercury intrusion porosimetry) ^a	1.57g/cm ³
Specific gravity (NBR 6474/84)	1.41g/cm ³
Particle size (laser granulometry in ethanol) ^a	6% above 250µm
Glass transition temperature -Tg (DSC - differential scanning calorimetry) ^a	-5,34°C
Melting peak (DSC - differential scanning calorimetry) ^a	100.42°C
Molecular weight ^b	1,900,000
Polymerization degree ^b	7,600
Viscosity (2% aqueous solution) ^b	100,000 mPa.s

^a SILVA, D.A.^[9] ^b characteristics informed by the polymer manufacturer

Table 3. Physical characteristics of EVA and HEC polymers

The bond strength of the mortars to 425 x 425 x 9mm porcelain ceramic tiles was tested. The water absorption of the tiles was 0.04% and moisture expansion was 0.00 mm/m, according to the results of the tests described by the Brazilian standards NBR 13818/97 and ABNT Project 02.002.100-003/96, respectively.

The mortars were mixed in a low speed mechanical mixer, according the following procedure: (i) mixing of the dry materials (cement, sand and polymers) for 120 seconds; (ii) pouring the dry mixture on the water, for 30 seconds, and mixing for 60 seconds; (iii) interruption of the mechanical mixing, when the mixture was manually stirred with a spatula for 60 seconds; (iv) mechanical mixing for 60 seconds; (v) mortar rest for 15 minutes, covered by a humid cloth to avoid the evaporation of water; (vi) mechanical mixing for 15 seconds.

The temperature and relative humidity in the laboratory were kept constant at 23°C and 65%, respectively.

2.2. BOND STRENGTH TEST

A single layered mortar, 6mm thick was applied on the back side of the porcelain ceramic tiles, followed by the application of a 0.08 kgf/cm² load for 30 seconds to promote the penetration of the mortar in the surface porosity of the tile. In order to study the effect of the wetting and drying on the bond strength between the mortars and the tiles, the samples were subjected to the conditions shown in Table 4.

Condition	Elapsed time		
	23°C and 75% RH (lab)	Wetting (under water)	Drying at 23°C and 75% RH (lab)
1	56 days*	-	-
2	46 days*	10 days	-
3	46 days*	10 days	16 days

* including 7 days in the moulds

Table 4. Exposure conditions of specimens

In order to evaluate the effect of saturation time on the bond strength of mortars containing 0.5% HEC, the samples were subjected to different, increased times of immersion, as described in Table 5.

Condition	Elapsed time		
	23°C and 75% RH (lab)	Wetting (under water)	Drying at 23°C and 75% RH (lab)
2.1	46 days*	14 days	-
2.2	46 days*	21 days	-
2.3	46 days*	28 days	-
2.4	46 days*	14 days	16 days
2.5	46 days*	21 days	16 days
2.6	46 days*	28 days	16 days

* including 7 days in the moulds

Table 5. Further exposure conditions of mortars containing 0.5% HEC and 0, 10 and 20% EVA.

After being exposed to the conditions described in Tables 4 and 5, the bond strength between mortars and tiles was determined with the pull-out method, adapting the recommendations of Brazilian standard NBR 14084/98 test method. Ten circular sections (50 mm diameter) were sawn in the mortar layer for each combination, as shown in Figure 1. Steel disks were glued to the mortar with epoxy resin, in order to allow the load application at 250 N/s. The results were statistically analyzed using the analysis of variance method (ANOVA).

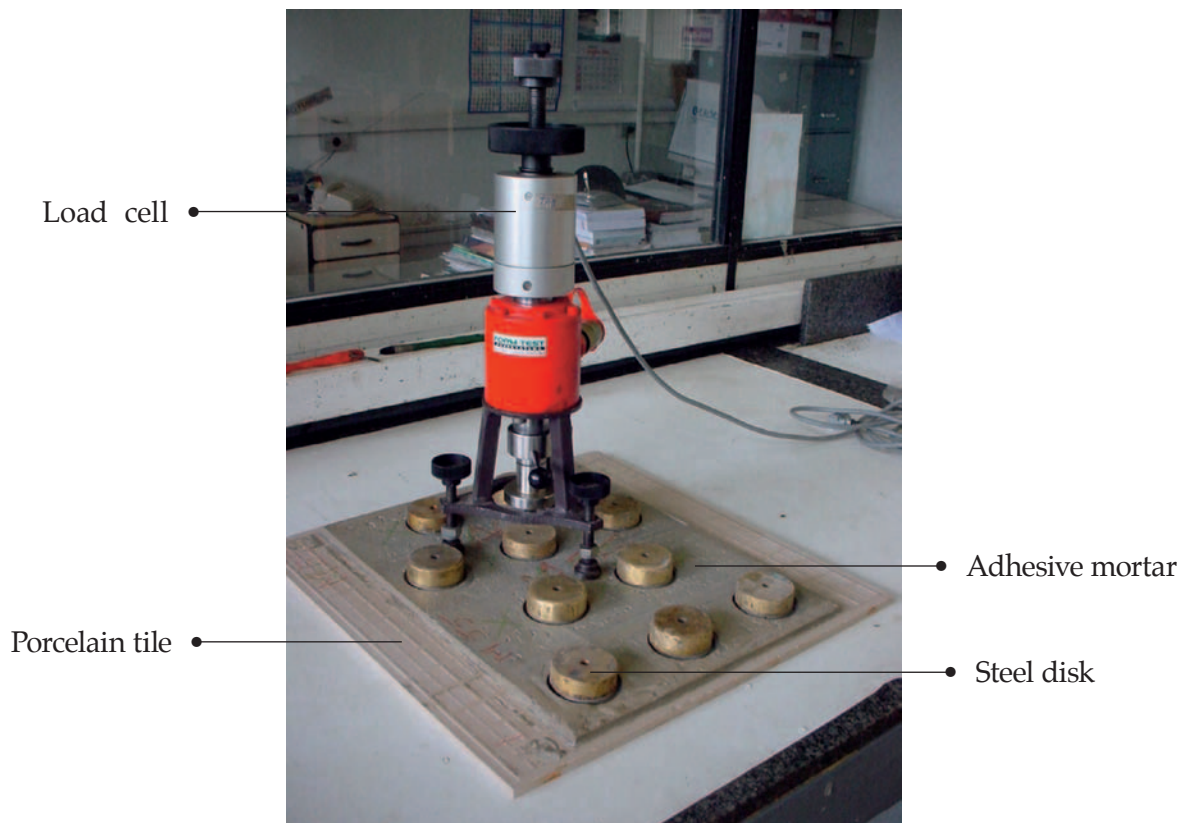


Figure 1. Bond strength test equipment

2.3. WATER ABSORPTION AND DIMENSIONAL TESTS

Water absorption tests were performed in prismatic mortar specimens (10 x 40 x 160mm) during the wetting period of Condition 2 (Table 4). The 46 days-old specimens were weighed just before the immersion in calcium hydroxide saturated water, and then at each day during the 10 days of immersion. The final weight, i.e., the weight obtained after the wetting period was registered and expressed in percentage (%) of the initial weight of the specimen. Six specimens for each mortar were tested, the average results being presented herein.

The dimensional (length) changes of the mortars exposed to the wetting period were evaluated on prismatic specimens (10 x 60 x 240mm), during the same Condition 2. The distances between two small steel disks (demec points) glued to the specimens surface at their borders were measured with a mechanical extensometer (demec-gauge). The measurements were performed just before the immersion in the calcium hydroxide saturated water and then at each day until the end of the immersion period.

Four specimens were investigated for each mortar. The average results are presented in this article.

3. RESULTS AND DISCUSSION

Figure 2 shows the influence of the exposure conditions on the bond strength of mortars. It can be seen that the highest bond strength was obtained for EVA-modified mortars, while mortars containing only HEC show the lowest results, regardless of the exposure condition. EVA addition increased the bond strength of HEC mortars, probably due to the film formation at the mortar/tile interface^[1], evidencing the efficacy of the latex on the adherence with porcelain tiles, as expected. It must be also considered that EVA-modified mortars are more fluid in the fresh state, being able to better wet the tile surface when compared to the rest of the mortars. We expect that this effect may improve the bond strength of the mortar to the tile, although experiments considering the rheology of the mortars should be performed in order to verify this hypothesis.

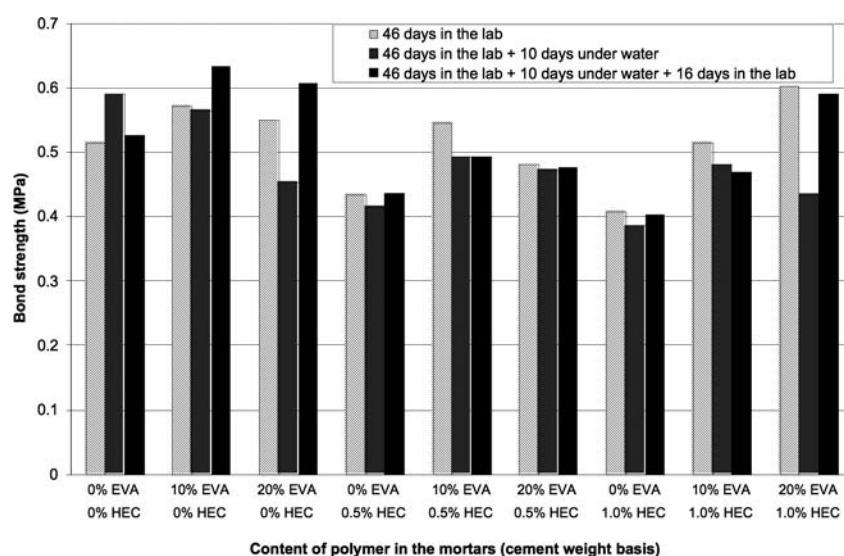


Figure 2. Effect of the exposure condition and the polymer content on the bond strength of Portland cement mortars to porcelain tiles

Indeed, the effect of HEC depends on the EVA content, as can be seen in Figure 3. In mortars with no or low content of the copolymer (10%), HEC reduces the bond strength, regardless of its content and the exposure condition. In the presence of higher contents of EVA, high contents of HEC (1%) seem to invert the effect, increasing the bond strength for mortars not saturated with water.

The isolated effect of EVA addition was the increase of the bond strength in samples subjected to 56 days in the laboratory (Condition 1) and the decrease of the strength under water (Condition 2). In mortars with the cellulose ether, EVA addition resulted in higher bond strengths, regardless of the HEC content and the exposure condition. The decrease of the bond strengths of samples kept under water was still observed, but in less intensity. Thus, the interaction of HEC and EVA contents seems to play an important role on bond strength of the mortars to the porcelain tiles.

It is important to emphasize that all the polymer-modified mortars (with HEC and/or EVA) suffered a reduction of the bond strength when under water, while the mortar with

no polymer addition was the only one that showed higher bond strength when saturated. EVA-modified mortars show the highest decreases of strength after 10 days under water. In the worst scenario, the bond strength under water was as low as 72% of the initial strength (after 46 days in the lab), for the mortar with 1% HEC and 20% EVA. However, Figure 2 shows that the performance decay of most of the mortars is almost completely reversible after drying, leading even to higher strengths when compared to the initial values. The mortar with 0.5% HEC and 10% EVA showed the worst recovery of the initial strength: the final value (after the wetting and drying cycle) was 90% of the initial strength.

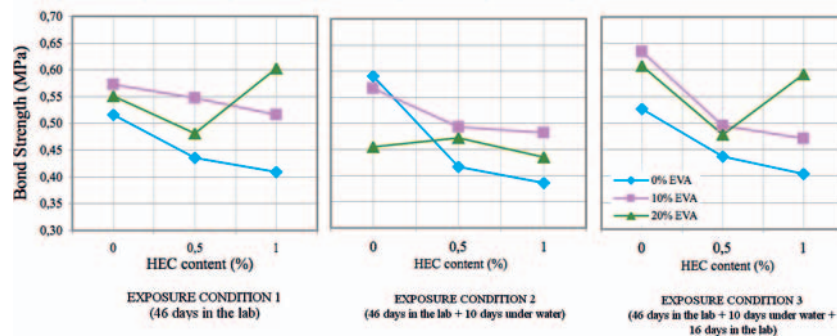


Figure 3. Effect of EVA and HEC contents on the bond strength of the mortars to porcelain tiles when subjected to the different conditions.

Figure 4 plots the ratio between the bond strength obtained during the immersion of mortars with 0.5% of HEC and 0, 10 and 20% of EVA, and the bond strength obtained after 46 days of cure in the lab, immediately before the immersion. The tests were performed after 10, 14, 21 and 28 days of immersion. As can be seen in the figure, the bond strength of EVA-modified mortars decreased when immersed in water, regardless of the immersion period. The lowest strength value was 60% of the initial one (obtained immediately before the immersion), and was detected after 2 weeks of immersion. Contrarily, the mortar with only HEC reached higher bond strengths to the porcelain tiles after 21 days under water.

Figure 5 shows the effect of drying the same samples of Figure 4. The figure shows the ratio between the strength obtained after drying the samples for 16 days and the strengths obtained in each immersion time. It can be seen that the mortars with only HEC did not suffer remarkable changes on the bond strength, while a tendency for a better recovery of the initial strength was observed for mortars with EVA, for longer periods of immersion.

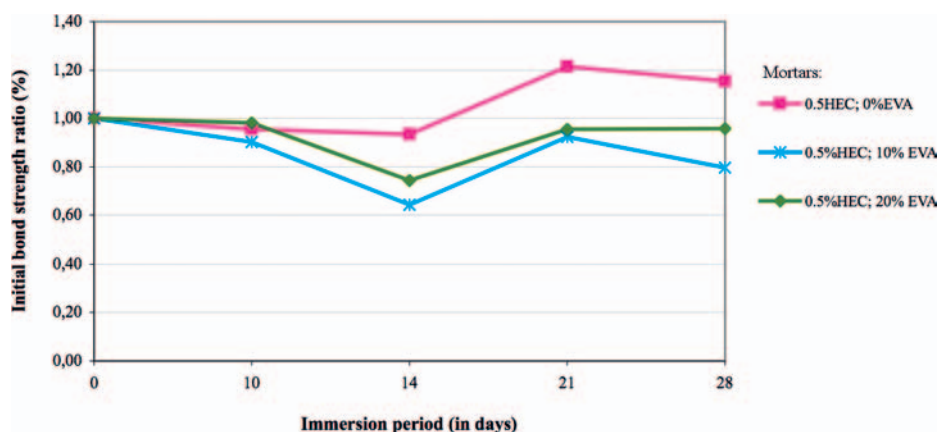


Figure 4. Bond strength ratio of mortars with 0.5% of HEC after being kept under water for 10, 14, 21, and 28 days.

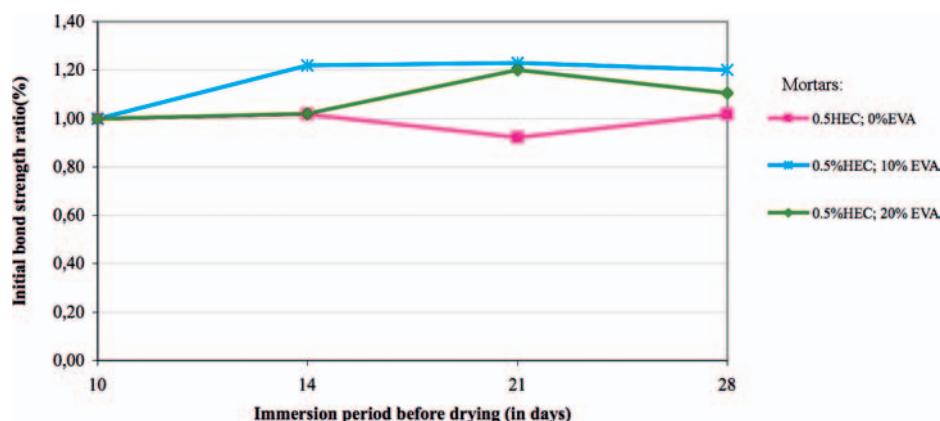


Figure 5. Bond strength ratio of mortars with 0.5% of HEC dried for 16 days after being kept under water for 10, 14, 21, and 28 days.

Figure 6 shows the results of the water absorption tests as a function of the polymer contents. It can be seen that the mortars modified only with HEC have the highest water absorption: the higher the HEC content, the higher is the absorption. The EVA copolymer increases the water absorption of mortars without HEC, but the effect is much slighter. Interestingly, EVA clearly reduces the water absorption of the mortars when HEC is present.

From these results, it can be concluded that HEC changes the capillary pores of the cement matrix, allowing higher water penetration. The cellulose ether indeed increases the amount of capillary pores in cement pastes, as evidenced by Silva et al. (10). However, the possibility of a physical interaction of HEC with water cannot be discarded. It is likely to occur due to the well known hydrophilic character of the cellulose ethers, which adsorb water and swell, forming a hydrogel or even a solution, depending on the water and polymer availabilities and the elapsed time. We speculate whether such a hydrogel would form in the cement matrix pores of mortars containing HEC. Further tests on water absorption and permeability of HEC modified cement mortars should be carried out in order to confirm our speculation.

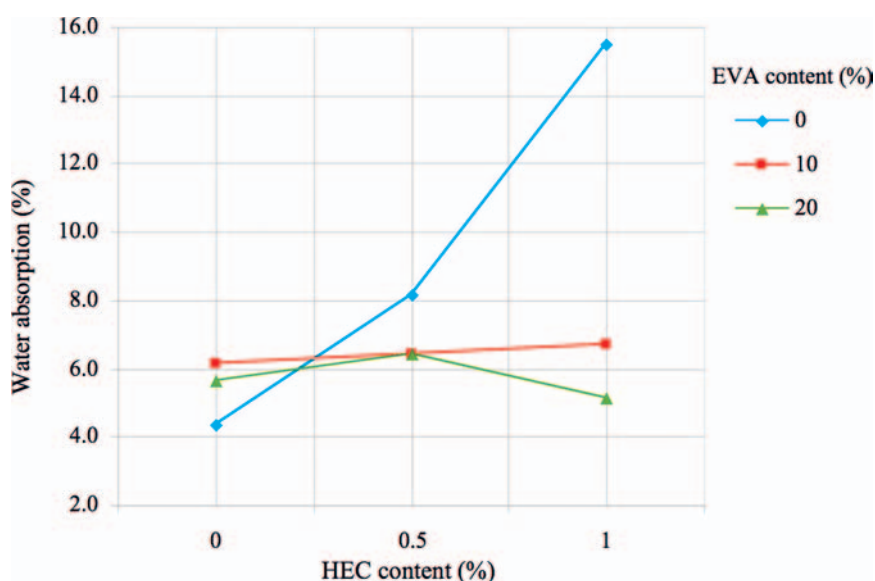


Figure 6. Water absorption of the mortars in the end of the immersion period

Even being highly water absorbent, the strengths of the HEC-modified mortars are not substantially affected by the immersion in water, which might be an evidence of the preferred location of HEC in the pores of the hydrated cement matrix whose swelling and hydrogel formation upon water absorption would not significantly affect the bond strength. Contrarily, EVA modified mortars showed a tendency to lose strength under water, even though the water absorption for such mortars is low, as shown in Figure 6. The apparently contradictory results might be due to a penetration of water mainly at the interface mortar/ceramic tile, which is said to be the main responsible for the adherence due to a large amount of polymer phase and film.

Figure 7 shows the specific length of the mortars samples during the 10 days of immersion. The specific value was calculated by the division of the length of the specimens after the 10 days of immersion by their length just before the immersion, when they were 46 days old. It can be seen that all the mortars expanded when kept under water, because the specific length values are all positive, as expected.

Both EVA and HEC cause the swelling of the mortars. However, EVA has a stronger effect, being able to increase the expansion almost five times, when compared to the reference mortar. HEC also causes the expansion of the mortars with no EVA. However, it is clear from the figure that the effect of HEC on the specific length of the mortars depends on the EVA content and vice versa. HEC seems to play a major effect, because the higher the HEC content, the more similar are the values of the specific length, regardless of the EVA content.

Figures 6 and 7 show that, although EVA was able to reduce the water absorption of the mortars, it caused increased swelling as much as HEC allows. The possibility of swelling of the polymer phase, which would lead to the swelling of the whole specimen or only the swelling of its surface, where the water is able to reach, cannot be discarded. The cellulose ether causes both the water penetration in the mortar and the swelling of the mortar specimens. The swelling of the mortars with HEC might be due to both the swelling of the polymeric phase and the water adsorption in small pores ($\phi < 50$ nm) of the mortar, which are the pores responsible for the dimensional changes of the hydrated cement when there is a local change in the water content.

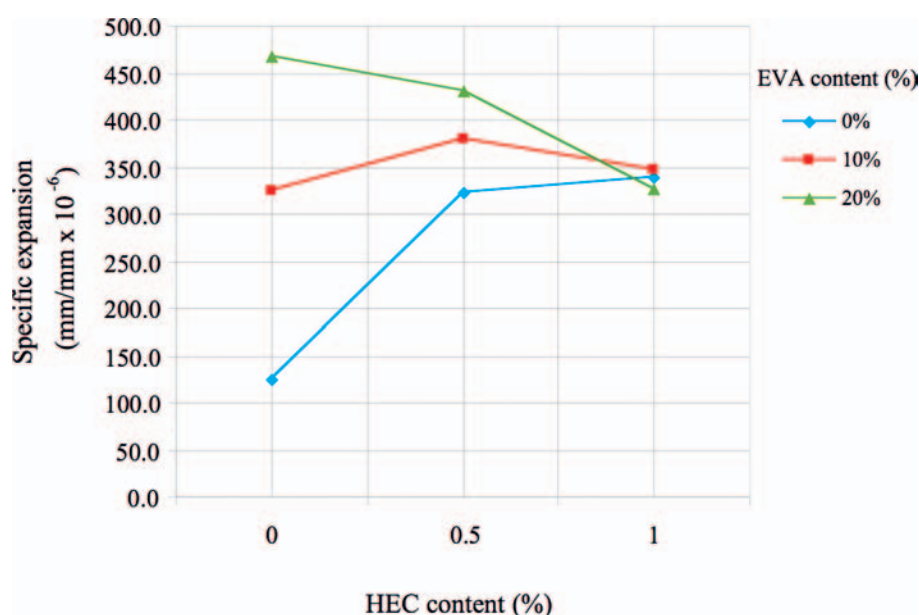


Figure 7. Effect of the polymers on the specific expansion occurred during the immersion period

4. CONCLUSIONS

The results of bond strength tests show that EVA is responsible for an increase of 10% on bond strength to porcelain tile, while the HEC-modified mortars reached the lowest strengths, reducing them up to 21%. EVA-modified mortars showed a higher sensitivity to water immersion, leading to a decrease of 28% on bond strength of mortars modified with 20% of EVA. However, the phenomenon seems to be almost completely reversible after 16 days of drying. Some EVA modified mortars showed final bond strengths even higher than the initial values, while the reference mortar (with no polymers) showed the same initial and final bond strengths to the tile. This behaviour leads the authors to conclude that EVA indeed weakens the mortar under water, but the recovery is clear after drying, probably due to the continuous hydration of the cement during the immersion. Such hypothesis is viable because it has been proven that EVA retards the hydration reactions^[11].

The effect of EVA on the water absorption and swelling of the mortars is intriguing, being dependent on the HEC content. The copolymer increases the swelling of the specimens after 10 days underwater, but slightly increases or even reduces the water absorption of the mortars. We speculate whether expansion of the mortars could be a result of a swelling of the polymeric phase due to the contact with water. HEC, on the other hand, sharply increases the water absorption, but the swelling is not so expressive. Further work should be carried out in order to understand the behaviour of the polymeric phase of HEC and EVA mortars under water.

5. ACKNOWLEDGMENTS

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