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Effect of Wetting and Drying on the Behavior of Polymer-Modified Cement Materials

Efeito da Saturação e Secagem no Comportamento de Materiais Cimentícios Modificados com Polímeros

J. DE OLIVEIRA [A]
D. A. SILVA [B]
L. A. GÓMEZ [C]

Abstract

Polymer-modified mortars and concretes have been widely used as construction materials since 1960. However, it has been reported that these materials show lower strengths when saturated in water or when submitted to high humidity conditions. In an attempt to understand this behavior, the present study evaluated mortars modified with hydroxyethyl cellulose (HEC) and poly(ethylene-co-vinyl acetate) - EVA - during wetting and drying. The results have shown that the mechanical strengths (especially flexural tensile and bond strengths) of the mortars are affected by the water absorption. However, this phenomenon seems to be partially or completely reversible.

Keywords: mechanical behavior; polymer-modified cement-based material; water immersion; drying.

Resumo

Argamassas e concretos modificados com polímeros vêm sendo amplamente utilizados como materiais de construção desde 1960. No entanto, há indicações de perda de resistência mecânica desses materiais quando saturados em água ou submetidos a elevadas umidades. Com o intuito de compreender este comportamento, o presente estudo avaliou argamassas modificadas com hidroxietil celulose (HEC) e copolímero acetato de vinila/etileno (EVA), durante saturação em água e secagem. Os resultados mostram que as resistências mecânicas (especialmente a resistência à tração na flexão e a aderência) das argamassas são afetadas pela absorção de água. Entretanto, este fenômeno parece ser parcial ou totalmente reversível.

Palavras-chave: comportamento mecânico; materiais à base de cimento modificados com polímeros; saturação e secagem.

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[a] Juliana de Oliveira is a PhD student at the Department of Civil Engineering, Federal University of Santa Catarina, Brazil. She receveid her BS (2001) and her MS (2004) from the same university.

[b] Denise A. Silva is an Assistant Professor of Civil Engineering at the Federal University of Santa Catarina, Brazil. She received her BS (1989) and ME (1993) from the Federal University of Rio Grande do Sul, and her Ph.D. (2001) from the Federal University of Santa Catarina at Florianopolis, Brazil. She recently developed a post-doctoral research at the University of California at Berkeley (2004).

[c] Luis Alberto Gómez is an Assistant Professor of Civil Engineering at the Federal University of Santa Catarina, Brazil. He received his MEE (1985) from NUFFIC, Holland and his Ph.D. (2000) from the Federal University of Santa Catarina, Brazil.

1 Introduction

The polymers are responsible for modifying some properties of cement-based materials, such as durability, impermeability, abrasion-erosion resistance, flexibility and bond strength. Nowadays, polymer-modified cement-based materials are widely used as repair materials for the reinforced concrete structures due to their compatibility with the base concrete, on overlays of bridges and parking decks and as adhesive mortars for ceramic tile installation (1,2).

The properties of polymer-modified mortars and concretes depend, basically, on the co-matrix, where the polymer and the cement gel matrix are homogeneized (3). The characteristics of this co-matrix depend of the content and type of polymer, which can be classified into: latexes or polymeric dispersions, redispersible powders, water-soluble polymers and liquid polymers (4).

The drainage of water from the systems modified with polymeric latexes, along with the cement hydration, leads to the formation of a thin film or membrane (3). This film usually results in a better impermeability of the composite and in the hindrance of cracks caused by tensile stresses. The better adherence of polymer-modified mortars and concretes is attributed to the formation of the polymeric film at the interface with other materials. 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 (3,5). Fritze (6) and Jenni (7) have observed lower mechanical and bond strengths of polymer-modified mortars under wetting. It has been hypothesized that such sensitiveness to water can be due to changes in the polymeric phase after a long contact with water. Changes such as disaggregation, softness, weakness and/or expansion of the polymeric phase could be the responsible for the observed behavior.

Polymeric latexes and cellulose ethers are widely used polymers in Brazil and in many countries. Together, they are used to produce mortars for ceramic tiles installation. Separately, they are often studied and used to produce self-compacting concretes, macro defect free cements, and repair mortars.

In order to investigate the water resistance of polymer modified cement-based materials, mortar 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 single wetting-drying cycle and were tested in compression, tensile, flexure, and bond strength. The results where correlated with the water absorption and dimensional changes of the specimens. The data presented herein are part of the master dissertation recently concluded by OLIVEIRA (8).

2 Experimental Procedure

2.1 Materials

The research was performed on mortars containing portland cement (type CPII-F 32 according to Brazilian standard NBR 5732/91), fine sand of aeolian origin, deionized water, the cellulose ether hydroxyethyl cellulose (HEC), and the copolymer poly (ethylene–co-vinyl acetate) (EVA). Tables 1, 2 and 3 present the materials characteristics.

Table 1 -- Characteristics of portland cement CPII-F 32*

Chemical analysis (%)										
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	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 (cm^2/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 15% of finely ground limestone, in according with a Brazilian standard NBR 11578/91.*

The proportions of the materials used to prepare the mortars was 1:3 (cement:sand, in mass basis). The w/c was kept constant at 0,76. The contents of HEC e EVA were 0, 0.5, 1% and 0, 10, 20%, respectively, in cement mass basis. Thus, nine different mortars where studied.

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 over deionizead water, for 30 seconds, and mixing for 60 seconds; (iii) interruption of the mechanical mixing, when the mixture was manually stirred with a spatule for 60 seconds; (iv) mechanical mixing for 60 seconds; (v) mortar resting for 15 minutes, covered by a humid cloth or plastic to avoid the evaporation of water; (vii) mechanical mixing for 15 seconds. The temperature and relative humidity in the laboratory were approximately 23ºC and 65%, respectively.

Table 2 -- Physical characteristics of sand

	Sieve size (mm)	**% Retained**	
		Individual	**Cumulative**
Particle size distribution - NBR 7217/87	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 3 -- Physical characteristics of EVA and HEC polymers

EVA	
Solids content (thermogravimetry)[a]	99±1%
Ash content (30min at 1000ºC)[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]	11.2ºC
Minimum film forming temperature[b]	Approximately 4ºC
HEC	
Ash content (30min at 1000ºC)[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]	-5,34ºC
Melting peak (DSC - differential scanning calorimetry)[a]	100.42ºC
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*

2.2 Exposition conditions

In order to evaluate the effect of the wetting-and-drying cycle on the behavior of the polymer-modified mortars, they were exposed to three different conditions:

1. 56 days in laboratory* (23ºC and 75% RH) + 0 days immersed;
2. 46 days in laboratory* + 10 days immersed;
3. 46 days in laboratory* + 10 days immersed + 16 days in laboratory.

** including 7 days in the moulds*

Physical and mechanical tests where performed after exposition of the specimens to the abovementioned conditions, as described in 2.3 and 2.4, respectively.

2.3 Physical tests

Water absorption tests by mass measurements were performed in prismatic specimens (surface area/volume ratio = 2.4) exposed to the condition (2). The 46 days-old specimens were weighted just before the immersion in the lime water, and then each day, during the 10 days of immersion. The mass change after the wetting period was registered and expressed in percentage (%) of the initial mass of the specimen. Six specimens for each mortar were tested, and the average results are presented.

In order to evaluate the dimensional (length) stability of the mortars exposed to the wetting period, prismatic specimens (10 x 60 x 240mm) were exposed to the same condition (2), and the distances between two small steel discs (demec points) glued to the specimens surface at each extremity were measured with the mechanical extensometer (demec-gauge). The measurements were performed just before the immersion in the lime water and then every day until the end of such period. Four specimens were studied for each mortar, and the average result is presented.

2.4 Mechanical tests

In order to evaluate the mechanical strengths of the mortars, cylindrical (50 mm diameter and 100 mm height) and prismatic (10 x 40 x 160 mm) specimens where coat. The cylindrical specimens were tested in compression and splitting tension, according to the Brazilian standards NBR 7215/96 and 7222/94, respectively (10,11). They were moulded in four layers and a spatule was used to compact the layers. To reduce the air entrapment due to the sticky behavior of the fresh mortars, a vibration was applied in the end of the moulding process by the contact of the moulds with an engine vibrating at 3425 r.p.m. for 30 seconds. The prismatic specimens were moulded into a single layer that received 30 spatule strikes, and the vibration at the end of the moulding process.

The flexural test was a three-point bend test, i.e., two supports and a load being applied in the center of the span. The load was applied at a constant rate of 0,1mm/min. Further details on the method were described elsewhere (12).

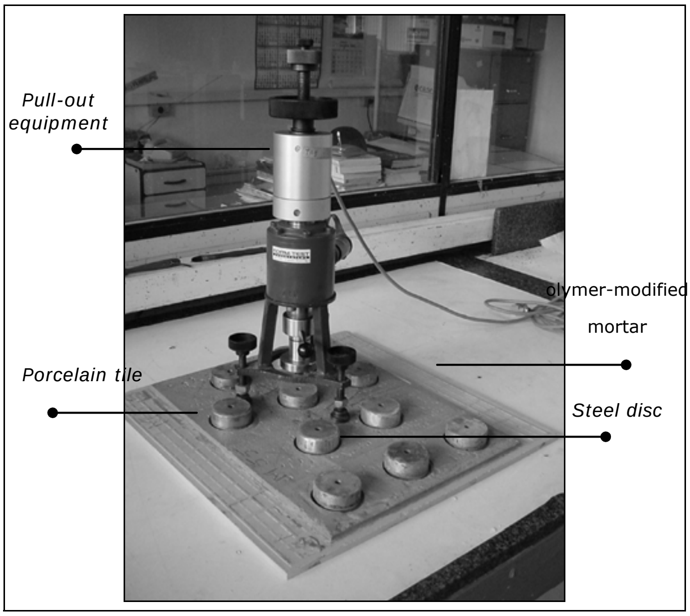

Figure 1 - Bond strength test equipment.

The flexural tensile strength is obtained through the classic equation (Eq.1) from the solid mechanics theory, where σ is the flexural tensile strength (MPa), P is the applied load (N), L is the span between the supports (mm), b is the largest dimension of the transversal section of the specimen (mm) and h is the height of specimen (mm).

$$\sigma = \frac{1,5PL}{bh^2} \qquad (1)$$

The bond strength of the mortars was tested against a porcelain ceramic tile, because of the tendency to the film formation at the interface between polymeric mortars and low water absorption materials. The tiles employed have water absorption 0,04%, and moisture expansion 0,00 mm/m, determined according the Brazilian standards NBR 13818/97 and ABNT Project 02.002.100-003/96, respectively. A 6 mm thick, single layered mortar was applied on the back side of the tiles, followed by the application of a load around 0,08 kgf/cm² for 30 seconds. After the exposition to wetting and drying, the mortars where tested by the pull-out method, as shown in Fig. 1. The mortar was cutted in several circular sections (50mm diameter) and steel disks were glued to the mortar with an epoxy resin, in order to allow the load application.

Three or four specimens for each mortar where submitted to compression, tension and flexural tests. For the determination of the bond strength, ten specimens were tested for each mortar. The results were statistically analyzed by the analysis of variance method (ANOVA).

3 Results and Discussion

3.1 Compressive and splitting tensile strength

The analysis of variance of the compressive and splitting tensile strengths has shown that the wetting and drying significantly affects the results.

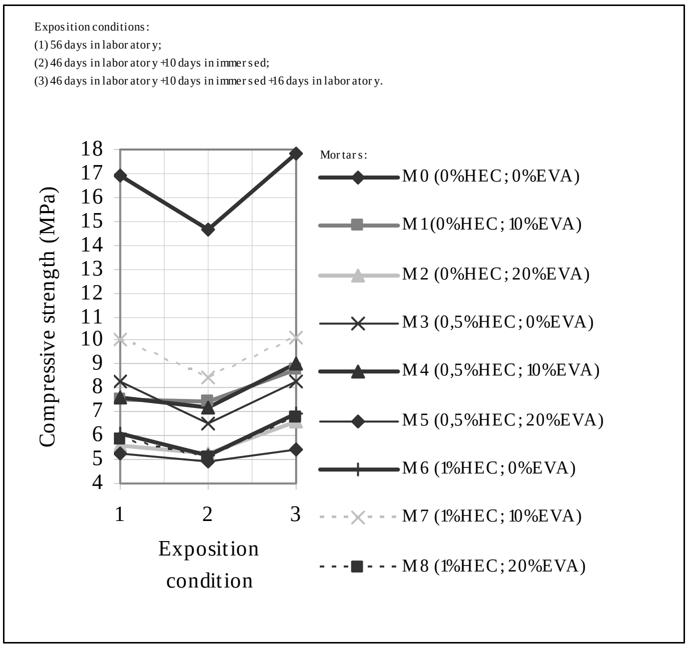

Figure 2 - Effect of the exposure condition and the polymer content on the compressive strength of the mortars

As can be seen in Fig. 2, besides the lower compressive strengths of the polymer-modified mortars, there is a tendency for a decrease of the strength when the specimens are immersed in lime water for 10 days, i.e., from condition 1 to condition 2, regardless the polymer content. The drying of the specimens for 16 days (condition 3) totally recovers the mechanical resistance of the mortars. Because of the reversibility of the phenomenon, the changes in the strengths can be attributed to the effect exerted by the surface tension of the water on the capillaries of the hydrated cement matrix. Furthermore, no evidence of a sharper strength reduction was observed for the polymer-modified mortars. Thus, from the compression tests, it is not clear if the presence of the polymers has provided any water sensitivity to the mortars.

Fig. 3 shows the graph for the splitting tensile test results. The tendencies are similar to the compression test, although they are slighter. Thus, it is not possible to conclude, from such results, whether the polymer-modified mortars are water sensitive or not.

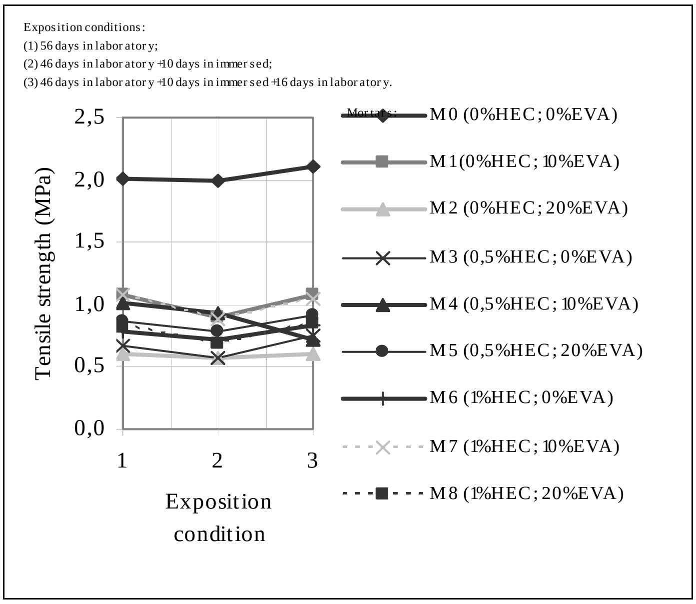

Figure 3 - Effect of the exposure condition and the polymer content on the splitting tensile strength of the mortars

3.2 Flexural tensile strength

The immersion of the specimens in the lime water, as well as their drying, is a significant factor to influence the tensile strength of the mortars in flexure, according to the ANOVA results. Fig. 4 shows the effects of the exposure conditions and polymer content on the results. As expected, the higher flexural tensile strength was obtained for the reference mortar, i.e., the mortar with no polymer addition (M0). However, on contrary to the compression test, the flexural strength of the reference mortar was not decreased by the wetting. All the polymer-modified mortars, on the other hand, have shown a sharp strength reduction on wetting (condition 2) followed by a partial or strength recovery on drying (condition 3).

It has been stated that the polymers have strong effect on the flexural behavior of mortars and concretes, due to their deposition and film formation on the surfaces of aggregates and hydrating cement particles, which would affect the bond between such particles and the cement matrix (13,14). Assuming such statement, the results shown in Fig. 4 indicate a sensitivity of the polymer-modified mortars to the higher water content during their immersion, because of the different behavior of the reference and the polymeric mortars.

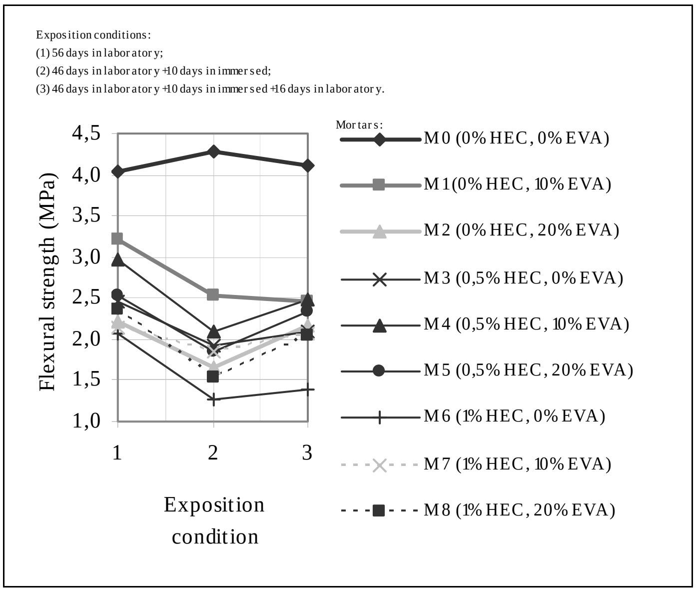

Figure 4 - Effect of the exposure condition and the polymer content on the flexural strength of the mortars

3.3 Bond strength

The bond strength of the mortars to the porcelain tiles is significantly affected by the wetting-and-drying cycle as well, according to the ANOVA results. Fig. 5 shows the influence of the exposure conditions and the polymer content on such property. It can be seen that the lowest bond strengths were determined for HEC-modified mortars, regardless the exposure condition. As expected, EVA addition increases the bond strength of HEC mortars, due to the film formation at the mortar/tile interface.

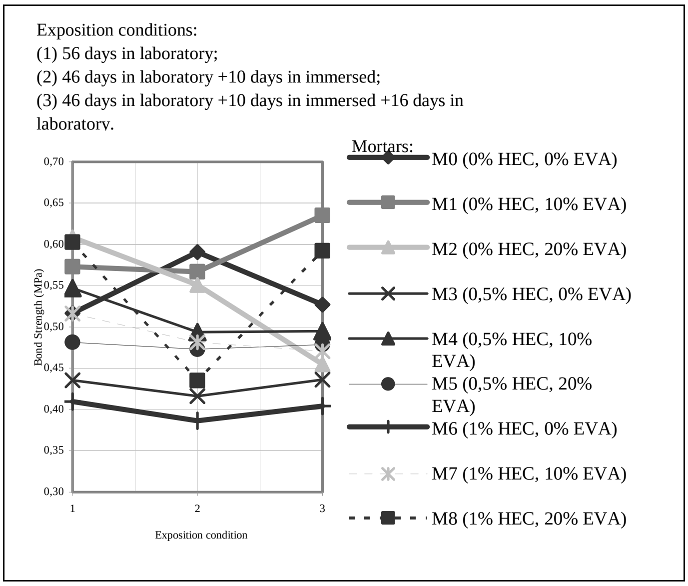

Figure 5 - Effect of the exposure condition and the polymer content on the bond strength of the mortars to porcelain tiles

The authors of this paper have hypothesized that the polymeric phase could be negatively affected by the contact with water. Because of the polymeric film formation at the mortar/tile interface, it would be expected that the effect of water immersion would be more evidenced by the bond strength tests. Besides the fact that only the reference mortar (M0) has shown higher bond strength when wetted, no other evidence was found to support our hypothesis. However, although it was possible to run the ANOVA, the dispersion of the results is high, as can be seen in Fig. 5. Thus, we conclude that further bond strength tests by a different technique are needed in order to confirm the water resistance of the EVA and HEC modified mortars.

3.4 Water absorption

Fig. 6 shows the results of the water absorption tests in function of the polymers 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 does not have such strong effect. However, it clearly reduces the water absorption of the HEC mortars.

From these results, it can be concluded that HEC either changes the capillary pores of the cement matrix, allowing higher water penetration, or physically interacts with water. The latest statement 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 in the cement matrix pores. EVA seems to change this behavior, decreasing the amount and rate of water absorption.

Even being highly water absorbent, the strengths of the HEC-modified mortars are not substantially affected by the immersion in water. Thus, it can be concluded that the polymeric phase is mainly located in the pores of the hydrated cement matrix and do not significantly affect the strength of the mortar upon contact with water. The polymer-cement composite phases, if they exist, are either water resistant or occur in a small amount.

3.5 Underwater length stability

Fig. 7 shows specific length changes occurred during the immersion (for 10 days) of the specimens. The specific expansion was calculated by the division of the length of the specimens just after the immersion by their length just before the immersion, when they were 46 days-old.

Both EVA and HEC increase the swelling of the mortars, as seen in the figure. However, EVA has a stronger effect, being able to increase the expansion almost five times, when compared to the reference mortar. Although causing higher expansion in mortars with no or low amount of EVA, HEC seems to regulate the effect of the copolymer, reducing its swelling ability. The higher the HEC content, the higher the regulation ability of the cellulose ether.

From the comparison of the Figs. 6 and 7, it can be seen that even EVA copolymer being able to reduce the water absorption of the mortars, increases their swelling. The opposite effect is observed for the cellulose ether: HEC causes high water absorption by the mortar, but the swelling is not as strong. From such results, we conclude that HEC increases the capillary pores of the mortars, resulting in high water absorption. The higher swelling of the mortars with HEC can be due to both the swelling of the polymeric phase and the water adsorption in the small pores (ø < 50 nm) of the mortar. Thus, HEC might cause the increase of the pore volume in such diameter range. EVA, on the other hand, decreases the water absorption, but increases the expansion of the immersed mortars, leading to the assumption that the polymeric phase swells causing the swelling of the whole specimen or only the swelling of its surface, where the water is able to reach.

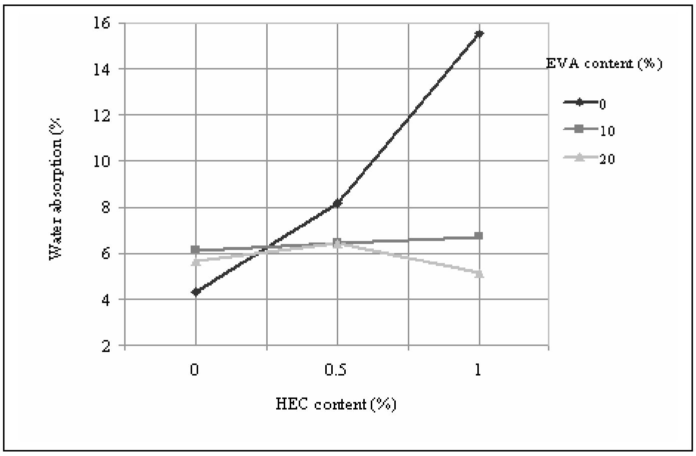

Figure 6 - Water absorption of the mortars in the end of the immersion period

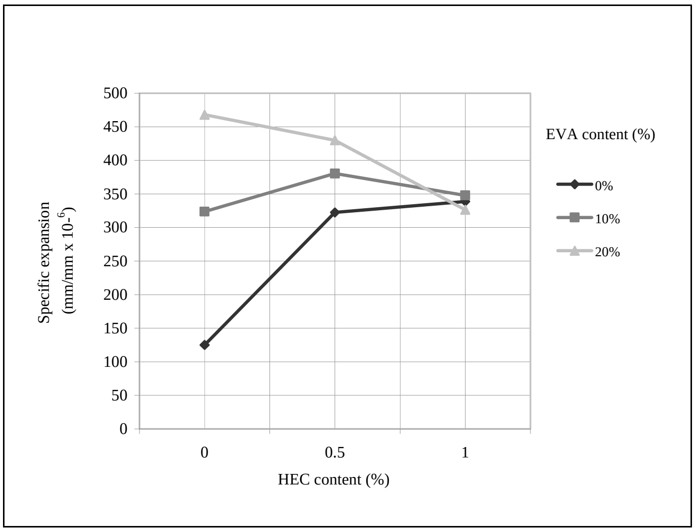

Figure 7 - Effect of the polymers on the specific expansion occurred during the immersion period

4 Conclusions

The study of the behavior of EVA and HEC modified mortars have shown that their immersion in water is able to reduce only slightly the compressive and splitting tensile strengths of the mortars, while the reduction of the flexural tensile strength is expressive. Total recovery of the strength after the drying of the specimens was not observed. From the bond strength tests, it was evidenced that EVA is responsible for an increase of the bond strength to porcelain tile, while the opposite was observed for the cellulose effect. EVA-modified mortars have shown a higher sensitivity to water immersion, indicating that the polymeric phase or an eventual cement-polymer composite phase is affected by the contact with water. The phenomenon seems to be partially or completely reversible after drying.

The effect of EVA on the water absorption and swelling of the mortars is intriguing. The copolymer increases the swelling of the specimens after 10 days underwater, but slightly increases or reduces the water absorption of the mortars. The results indicate the expansion of the mortars might be a result of a superficial 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. Thus, we conclude that the cellulose ether increases the volume of capillary pores in the mortars, being also able to swell, causing the overall expansion of the specimens.

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