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Physico-chemical characterization of EVA-modified mortar and porcelain tiles interfaces

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ABSTRACT

EVA (poly(ethylene-co-vinyl acetate)) redispersable powders with different contents of copolymers were tested in order to evaluate their effects on the complex interactions developed at mortar/tile interface. EVA addition has increased the bond strength almost 40% when compared with unmodified mortar. Based on EVA hydrolysis, a novel method named as 'Extension of Hydrolysis (EH)' was suggested to monitor the reaction mechanism which occurred during the interface layer formation. Thus, higher EH values were related to a significant improvement of adhesion at interface observed as a changing on the failure mode from mostly cohesion to adhesion. Calculated EH parameter of 2.64 was associated with a cohesive component of rupture in the mortar of 50% while for an EH of 0.92, the rupture in the mortar was only 7%. The enhancement on adhesion was attributed to the hybrid ceramic–polymer interface formed based on hydrogen-bonds between silanol groups from tile surface and hydroxyl groups from hydrolyzed EVA.

1. Introduction

Polymers have been used as property modifiers of Portland cement systems for several years [1,2] where the first detailed publication on polymer modified mortars (PMM) and concretes (PMC) was issued in 1953 [3]. Since then, polymers have been added to mortars and concretes to enhance some properties such as workability, water retention, impermeability, flexural and adhesive strength, and deformability [1]. The ability of improving bond strength between ceramic tiles and mortar are crucial to the long term stability, durability and reliability of the ceramic tiles systems that use the direct adhered method. The interfaces between ceramic tiles and Portland cement mortar are derived from several physical and chemical phenomena that take place when they are formed. For instance, ceramic tile water absorption influences the migration of pore solution to the tile porosity allowing the precipitation of cement hydrates inside the pores and promoting a mechanical anchoring [4]. In systems that comprise tiles with high water absorption (>6 wt.%) and polymer modified mortars, a general improvement of mortar properties and the formation of a continuous polymer film at the interface are added to the mechanical interlocking improving the bond strength at tile/mortar interface [1,2,5]. The decrease of ceramic tiles water absorption (porcelain tiles → 0 wt.%) implies a high water to cement (w/c) ratio at the interface due to bleeding and wall effects [6–10] which results in a transition area of higher porosity favoring the precipitation of $Ca(OH)_2$ crystals near the interface [6,11]. Both aspects reduce the adherence resistance of the system. The addition of a polymer modifier in mortars usually reduces bleeding and cement flocculated state effects improving the cohesion of the mortar and the adhesion at the interface [12,13]. Among several alternatives of polymers available in the market, poly(ethylene-co-vinyl acetate) or EVA has been the standard choice as polymer in the dry-set mortar because it can be broadly found as redispersable powder and excellent compatibility with cement-base systems. Nevertheless, the physico-chemical and microstructural features of polymer modified mortar/porcelain tile interface are not totally understood and a more in-depth investigation is required.

Thus, the aim of this research was to evaluate the physico-chemical mechanism of interface formation between porcelain tiles and EVA modified mortar and also to conduct extensive characterization of its properties.

2. Experimental procedure

2.1. Materials

Portland cement type CPII-F 32 (Cimento Cauê) according to the Brazilian Standard NBR 11578/91 and quartz sand were used to prepare the mortars and pastes. The composition and properties of the cement are summarized in Table 1. Two commercial EVA redispersible powders were selected, with characteristics as presented in Table 2. The choice of these EVA powders was driven by their different contents of acetate groups (and consequently ethylene) in the copolymer. Also these products were technically recommended by the manufacturers (Rohm and Haas Química and Wacker Chemie) to

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Table 1
Chemical properties of Portland cement CPII-F 32.

Chemical composition	% Weight
SiO_2	18.6
Al_2O_3	4.4
Fe_2O_3	2.9
CaO	62.6
MgO	3.0
SO_3	2.4
Na_2O	0.1
K_2O	0.9
CO_2	4.3
Free CaO (lime)	1.3
Loss on ignition	4.8
Insoluble residue	0.7
Major phases (Bogue)[a]	
$C_3S–3CaO\cdot SiO_2$	46.5
$C_2S–2CaO\cdot SiO_2$	20.0
$C_4AF–4CaO\cdot Al_2O_3\cdot Fe_2O_3$	9.7
$C_3A–3CaO\cdot Al_2O_3$	6.0
$CaCO_3$	9.8

[a] Modified Bogue calculation as recommended by Taylor [14].

be used in dry-set mortar. Commercial porcelain ceramic tiles with water absorption less than 0.5% were selected as substrate for mortar application.

2.2. Sample preparation of polymer modified mortars for mechanical and interface formation analyses

Mortars were mixed with mass ratio of cement:sand 1:1.7 and 0.60 water to cement ratio. The actual EVA copolymer contents in the mixtures were 5%, 10%, and 15% by cement weight. These amounts were corrected due to the % solids and to the presence of inorganic compounds in the copolymer powder measured by the ash content. Seven different mortar samples were obtained as detailed in Table 3. Mortar samples were prepared in a low speed mechanical mixer according to the procedure described in Fig. 1. In order to mimic the tile installation work, a single layer of 6 mm thick mortar was applied onto the backside of the porcelain ceramic tile, followed by the application of a 0.03 kgf/cm^2 (=3.0 kPa) load for 45 s to promote even spreading of mortar on tile surface. The samples were stored in a saturated humidity chamber for 23 days. Finally, samples were cured under laboratory environment conditions ($T = (25 \pm 5)$ °C and RH = (70 ± 10)%) for 5 days. These samples were later evaluated by mechanical pull-off tests.

Table 2
Characteristics of EVA redispersible polymer powder.

Properties		Values	
		EVA1	EVA2
Glass transition temperature — Tg		−12 °C	16 °C
% Mass of acetate in copolymer (% molar)		62% (35%)	87% (69%)
% Mass of ethylene in copolymer (% molar)		38% (65%)	13% (31%)
Minimum film formation temperature (MFFT) of redispersion		NA[a]	4 °C
Protective colloid		PVA[b]	PVA[b]
Anti-blocking agent		Calcite	Kaolinite
Particle size	As supplied	90 µm	Maximum of 4%> 400 µm
	After redispersion	NA[a]	0.5–8.0 µm
% Solids		99.7%	99.4%
% Ash		10.0%	10.1%

[a] NA = not available.
[b] PVA = Poly(vinyl alcohol).

Table 3
Mortar/pastes designation according to EVA type and polymer content.

Description of mortar/pastes	EVA	Copolymer to cement ratio (p/c) (%)
Ref	None	0
EVA1-5%	EVA1	5
EVA1-10%	EVA1	10
EVA1-15%	EVA1	15
EVA2-5%	EVA2	5
EVA2-10%	EVA2	10
EVA2-15%	EVA2	15

2.3. Mechanism and kinetics study of polymer modifier mortars reactions

2.3.1. pH Measurements

PMM samples were prepared in a similar process as previously described in Section 2.2 for monitoring the reaction at early stages. Thus, after 1 h from the first initial contact of cement-mixture (cement + sand + polymer) with water, mortar pore fluids were extracted by vacuum filtration using filter paper (2 µm) under inert nitrogen atmosphere. pH measurement of the just collected pore solution was conducted in a sequential dilution (1:10, 1:100, and 1:1000) using a pH-meter with a hydrogen-ion responsive electrode.

2.3.2. FTIR characterization — extension of hydrolysis

Cement paste samples (Table 3) were prepared for FTIR analysis. The anhydrous cement previously blended with polymer powder (p/c = 0% (reference), 5%, 10%, and 15%) was manually mixed with deionized water (w/c ratio of 0.60 wt.%) for 15 s followed by mechanical mixing for further 60 s. Then, the cement paste was kept still for 15 min covered by a humid cloth, mixed for another 15 s, and lastly cast into polyethylene (PE) flasks, sealed, and stored at laboratory conditions until the spectroscopic assays were conducted. Spectra were obtained for reference and modified pastes with 28 days of age in the range of 4000–400 cm^{-1}, in Diffuse Reflectance mode (DRIFTS, Perkin-Elmer, Paragon 1000). Prior to FTIR analysis, paste samples from each different evaluated age were demolded, crushed, sieved (200 mesh) and blended with KBr.

In the present research, a novel parameter named as “Extension of Hydrolysis (EH)” is suggested to correlate adherence results with EVA hydrolysis (Fig. 2) based on FTIR spectroscopy characterization method. EH values were evaluated through the FTIR spectra of Portland cement pastes modified with EVA. The carboxylate anion (COO^-), which presence is due to the alkaline hydrolysis of EVA [15,16], was quantified based on peak area ($A_{carboxylate}$) in the region

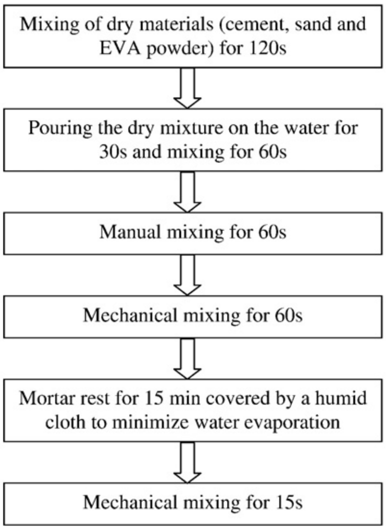

Fig. 1. Flowchart of mortar preparation and mixing procedure.

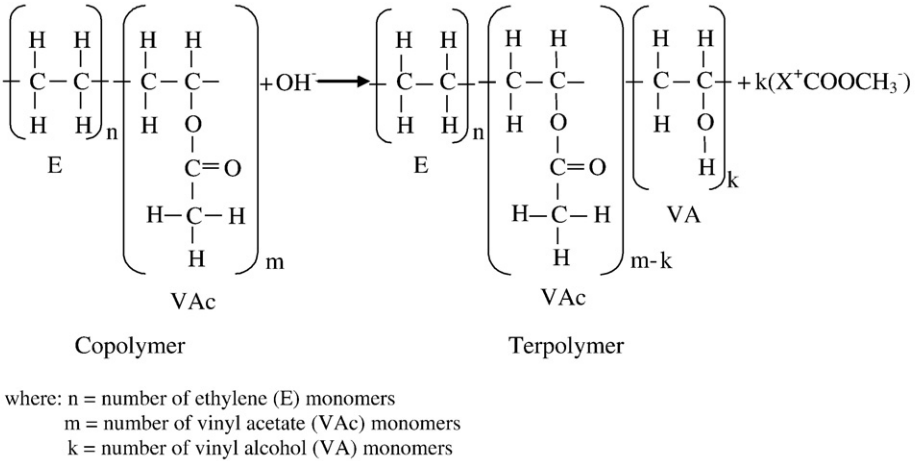

Fig. 2. Hydrolysis reaction from vinyl acetate units (VAc) to vinyl alcohol (VA) in EVA copolymer chain under alkaline medium.

of 1525–1610 cm^{-1}. Normalization was performed with the areas of the peaks centered at 1740 cm^{-1} (A_{1740}, in the range of 1720–1762 cm^{-1}) and 1240 cm^{-1} (A_{1240}, in the range of 1215–1270 cm^{-1}). The 1740 cm^{-1} and 1240 cm^{-1} vibrations are attributed to C═O and C–O vibrations of vinyl acetate units, respectively [16,17].

It is important to note that this analysis is possible because the carbonyl vibration in vinyl acetate monomer is different from its vibration in the ion carboxylate. The C═O stretch band at 1740 cm^{-1} in the EVA shifts to lower frequencies related to the ionization of the carboxylic structure due alkaline hydrolysis correspondent to the COO^{-} symmetric stretch at 1520–1610 cm^{-1} in the carboxylate [18]. In this sense the band at 1740 cm^{-1} from C═O is expected to reduce or even disappear during hydrolysis. On the other hand, the C–O vibration from EVA at about 1240 cm^{-1} is due to the ether structure (–C–O–C–) of vinyl acetate monomer that is broken in the saponificafion process [15–17]. So despite of the C–O structure is still present at carboxylate it is not associated with the ether structure that presents vibration in the range of 1275 to 1200 cm^{-1} [19]. Based on these explanations, the band C–O (C–O–C) should also reduce/disappear during hydrolysis.

In this sense, both bands, C═O and C–O from vinyl acetate are replaced by the vibrations associated with COO^{-} in the range of 1640–1550 cm^{-1}, as already identified as the symmetric stretch, and in the range of 1440–1340 cm^{-1}, due to the anti-symmetric stretch. As this last vibration is of medium intensity and it is overlapped with the hydrated cement paste peaks, the symmetric stretch (1640–1550 cm^{-1}, more specifically 1610–1520 cm^{-1}) was chosen to be used as a carboxylate formation reference.

Based on these reasons, EH was calculated for the two parameters showed in Eqs. (1) and (2) [20].

$$EH_{1740} = \frac{A_{\text{carboxylate}}}{A_{1740}} \tag{1}$$

$$EH_{1240} = \frac{A_{\text{carboxylate}}}{A_{1240}} \tag{2}$$

In both cases, the $A_{\text{carboxylate}}$ is increasing while the A_{1740} and A_{1240} are decreasing during hydrolysis. The global result indicates that higher de EH value, higher will be the extension of hydrolysis.

2.3.3. Characterization of adhesion mechanism and hybrid interface formation microstructure

Bond strength between mortar and tile was determined with pull-off method adapting the procedure described in the Brazilian Standard NBR 14084/04 test method, allowing the determination of adhesion in tension of the mortar to the porcelain tile. One day before the completion of the curing period, nine squared sections (length = 50 mm) were sawn in the mortar layer and metallic pull head plates were glued onto the glass tiles using epoxy adhesive. After 24 h of storage, each of these metallic plates was connected to the test machine for the direct pull-off tensile test. The bond strength was calculated by dividing the maximum load (the load carried by the specimens at failure) by the area of the bonded surface (50 × 50 mm^2).

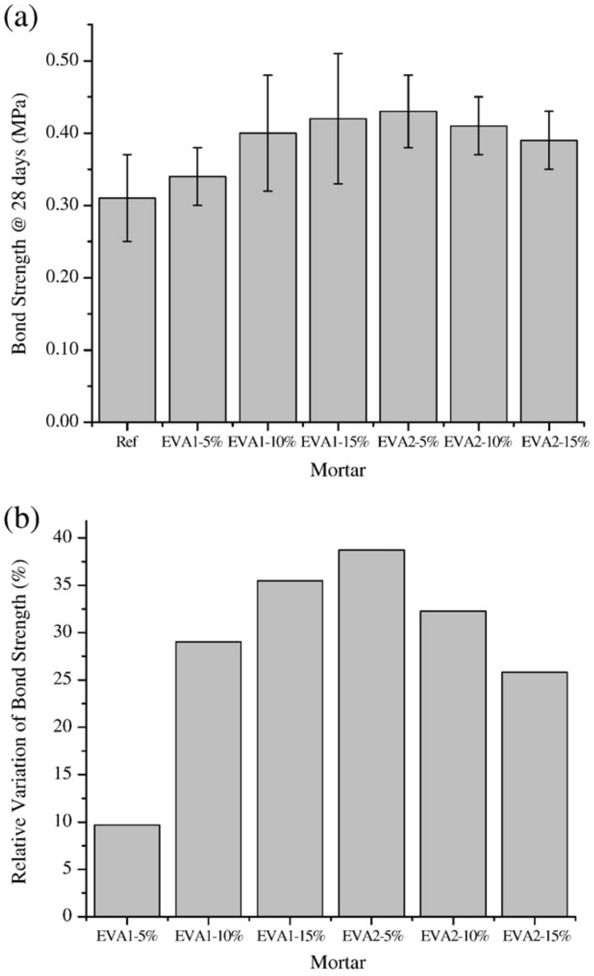

Fig. 3. (a) Effect of the polymer content on the bond strength of EVA modified Portland cement mortars to porcelain tile. (b) Variation of bond strength due to polymer modification.

After the adhesion tests, the cross-sections of the specimens were observed for failure modes analysis, which were sorted into the following two categories: a) cohesive failure in polymer modified mortar; or b) adhesive failure at the interface tile/polymer modified mortar. These two modes can occur simultaneously resulting on a combined effect. Scanning Electron Microscopy (SEM, Jeol JSM 6360LV) technique was used to assist on the evaluation of failure cross-section morphology and microstructural aspects of the surface. SEM images were taken from fractured surfaces at the mortar/tile interface. Prior to examination, sample surfaces were chemically etched with 3% hydrochloric acid (HCl) for 5 h followed by rinsing with deionized water. Acid etching dissolves the cement phases and hydrates, destroying the inorganic structure and leaving the polymer portion visible [21]. Then, samples were dried with moderate nitrogen-blow for 15 min, maintained in desiccator for 4 h. Finally, they were coated with a thin gold-sputtered film at low deposition rate, cooling the substrate and keeping the maximum distance between target and sample in order to avoid sample damage. Images of secondary electrons (SE) were obtained using an accelerating voltage of 15 kV.

3. Results and discussions

Fig. 3(a) shows the bond strength results obtained for the studied mortars, indicating that the addition of polymer improved the bond strength. Statistical analysis of tensile strength results (95% of confidence) indicated a significant increase of adherence for mortars EVA1-15%, EVA2-5%, EVA2-10% and EVA2-15% when compared to the reference (Ref) mortar. Mortar EVA1-10% has also presented an improvement of bond strength of almost 30% related to Reference. However, as adherence tests usually have broad standard deviations [20], the increase of pull-off results was not significant within 95% of confidence for the mortar EVA1-10%. Fig. 3(b) indicates the variation of bond strength due to mortar modification with different p/c ratios and EVA products (EVA1 and EVA2).

The bond strength values have showed different trends depending on EVA type and content. These relatively inconsistent results were also observed in literature that presents as a consensus only the improvement of adhesion with EVA polymer addition. Ohama [1] and Afridi et al.'s [22] experiments revealed that the higher the EVA admixture content, the higher the bond strength up to a limiting amount. Also the specimen failure mode was found to change considerably with the addition of EVA, from mostly interfacial failure for systems without EVA to a mixed-mode interfacial-cohesive failure of the mortar with addition of EVA. On the other hand, Silva et al. [23] and Pakusch et al. [24] have identified a trend on increasing the adherence strength as the polymer/cement ratio (p/c) decreases. Contradictory conclusions were presented by Utida et al. [25] that have measured similar values of interfacial resistance even after duplicating the EVA polymer amount.

Fig. 4 exhibits the failure mode distribution of polymer modified mortars in adhesion test in tension. The mode of rupture depended upon the EVA used and the polymer to cement ratio. EVA1 mortars and EVA2-15% mortar have showed almost simply adhesive failure at the interface tile/modified mortar (≥93%), quite similar to the reference. In EVA2-5% and EVA2-10% mortars, a mixture of cohesive failure in the polymer modified mortar and adhesive failure at interface was observed with the relative percentage of cohesive

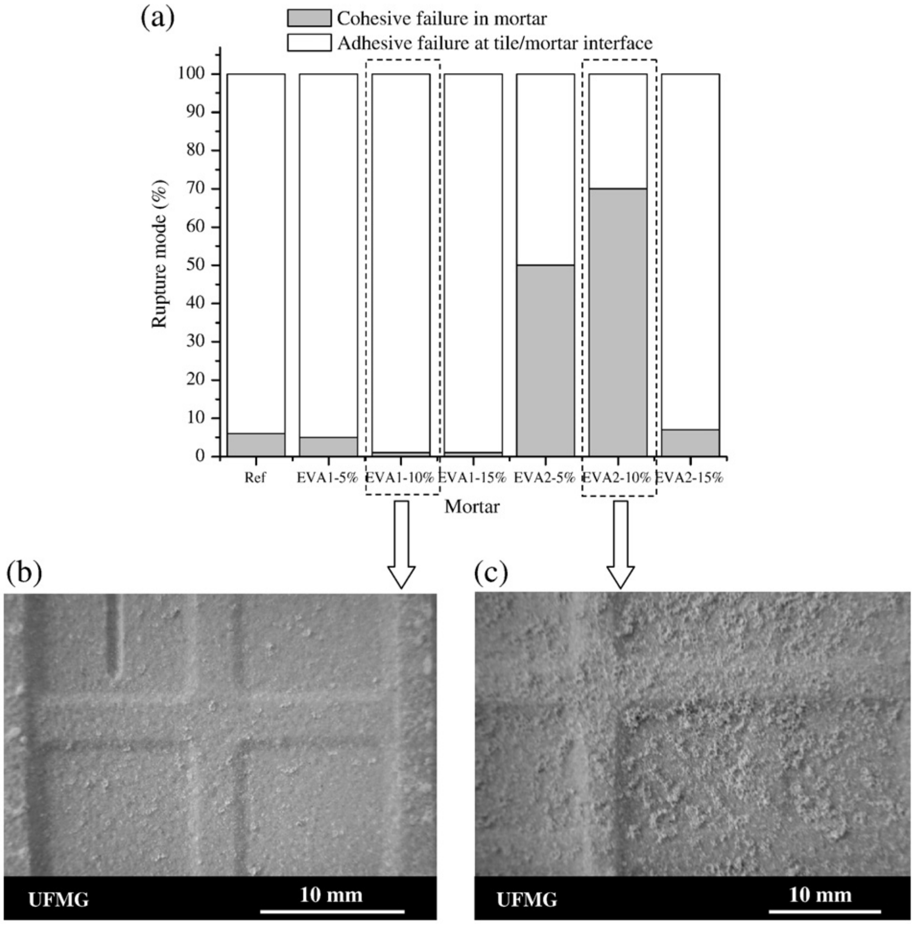

Fig. 4. Failure mode distribution of polymer modified mortars in adhesion test in tension.

failure in mortar increasing with a raise in p/c ratio. Hence, it can be stated that the bond strength between the porcelain tile and the mortar was higher than the mortar intrinsic resistance what is crucial for the use of adhered method for installation of ceramic tiles. In the study of several cases of tile systems failures, adhesive rupture between cladding and modified mortar was observed in 84% of the buildings [26]. This value was somehow expected because the modeling of ceramic tile covering behaviors reveals the highest shear stresses at tile/tile bed interface, when considering stresses caused by moisture expansion or thermal movements [27]. Based on the mode of rupture results, the improvement of interfacial bond was verified for EVA2 (higher content of acetate groups) at p/c ratios of 5% and 10%, the later performing better.

Scanning electron microscopy technique was selected in order to make an in-depth analysis. It is a very useful tool to show what phenomena may have occurred in the mortar matrix and at interfaces [28,29].

Fig. 5 shows the etched failure interfaces of mortar samples modified with EVA2 at various polymer–cement ratios in comparison with the non-etched surfaces. The acid etching has revealed non-continuous polymeric domains over the entire surface of rupture (Fig. 6). It is also noteworthy that even at relatively low p/c ratio of 5% it was already verified the presence of coherent polymer film at interface, quite similar to mortars samples with higher p/c ratios. Based on that, it is assumed that the tile/modified mortar interface is a hybrid matrix of two components (interphases): polymer and hydrated cement compounds. EVA latex films interweave cement hydrates forming a monolithic polymer–cement co-matrix structure at interface [2,21].

In order to understand the observed behavior of bond strength and rupture modes, some features of porcelain tiles and EVA polymers should be analyzed together. EVA latex is a copolymer of ethylene and vinyl acetate groups that do not present high chemical affinity with porcelain tile surface. Based on that, predominantly the weak van der Waals forces are expected to be developed at the tile–polymer modified mortar interface. However, when comparing EVA modified mortar to the unmodified mortar (Ref) an improvement of adhesion is expected related to the formation of a more cohesive porcelain tile/EVA interface. In mortars without polymers, it is usually observed that a porous layer extending away from the tile interface to the paste bulk while for the polymer-modified mortars, almost no porosity can be seen. This occurrence can be explained by wall effect and bleeding [6–10] that promote a higher effective water to cement ratio at interfacial zone resulting in the increased porosity, larger crystals of hydrated products and lower bond strength [9,10,31,32]. The addition of polymers to cement based materials alters the state of flocculation/

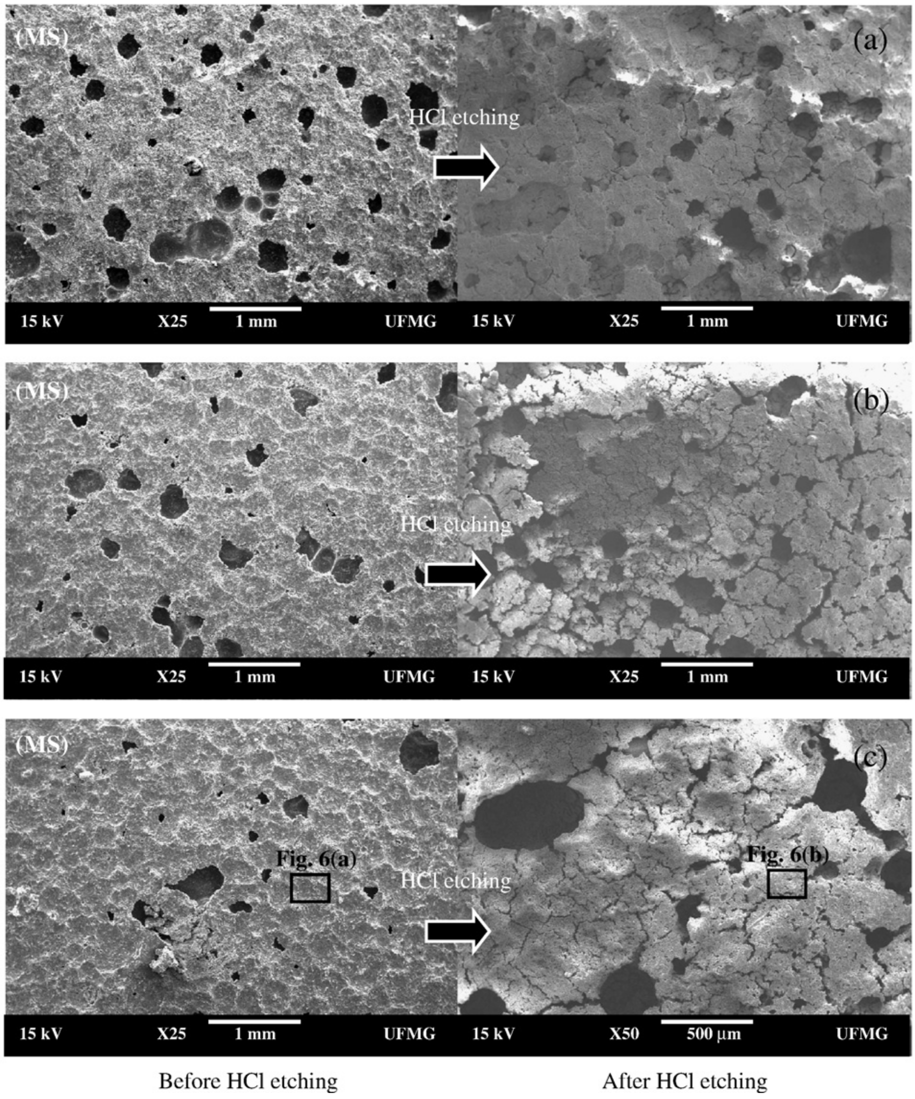

Fig. 5. Images of fractured surface before and after HCl etching. (a) EVA2-5%, (b) EVA2-10%, and (c) EVA2-15% (secondary electron images, magnifications: 25× and 50×).

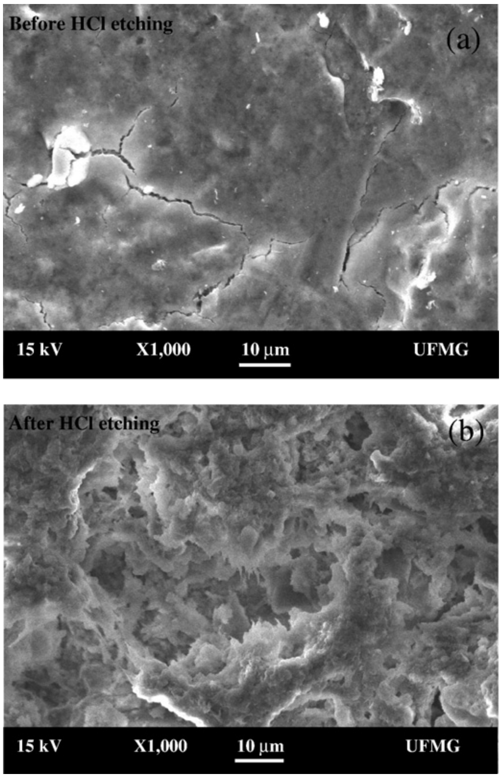

Fig. 6. Detail of non-etched (a) and acid etched (b) surfaces from EVA2-15% (secondary electron image, magnification: 1000×).

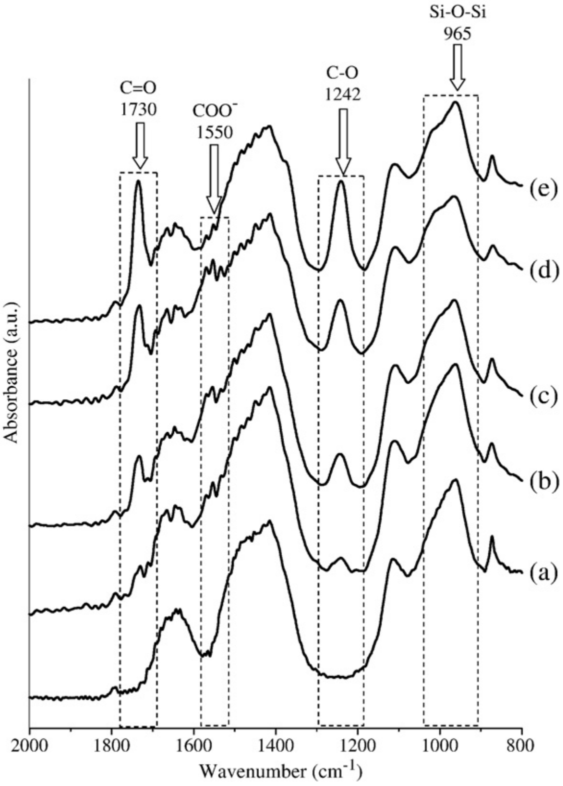

Fig. 7. FTIR spectra for (a) reference paste and (b) EVA2-5%, (c) EVA2-10%, (d) EVA2-15%, and (e) EVA1-15% pastes at the age of 28 days.

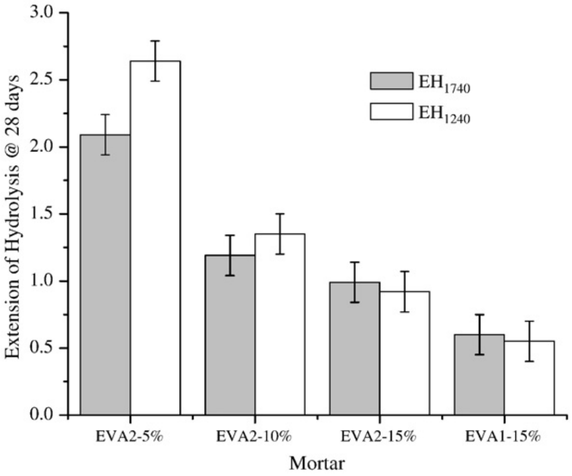

Fig. 8. 'Extension of hydrolysis' evolution results.

coagulation of cement [6], resulting in well-dispersed cement particles, even though the suspension remains flocculated due to polymer chains interactions [20]. So, polymer addition raises the solid–liquid ratio at the interface improving the interfacial bond by pore refinement and grain refinement processes. For EVA modified mortar the more cohesive co-matrix cement–polymer at interface increases the contact area between mortar and porcelain tile increasing the overall effect of secondary bonds. The alkaline hydrolysis of EVA is another important fact that should be also

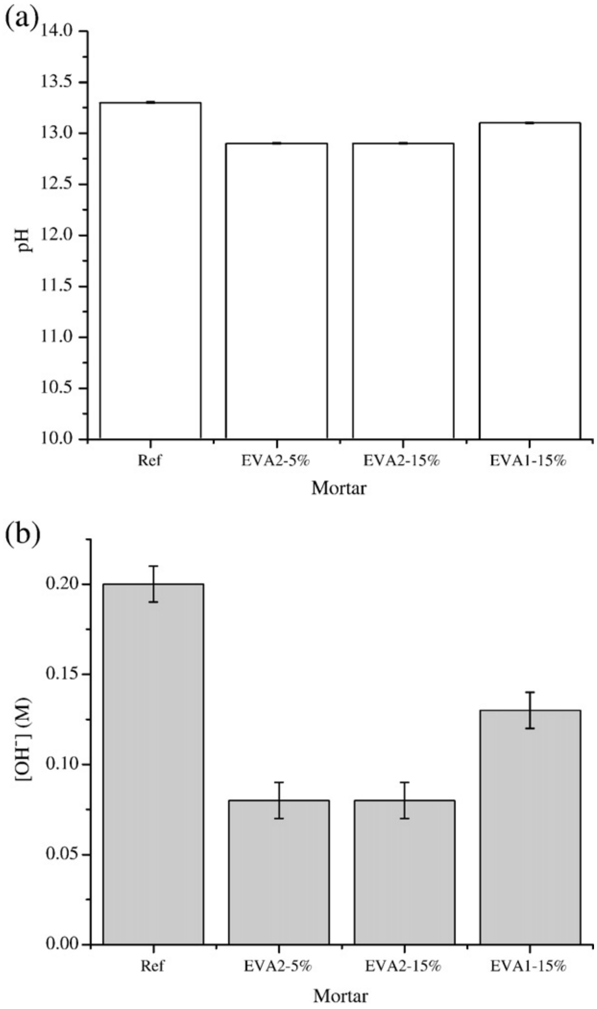

Fig. 9. (a) pH values for reference and modified mortars. (b) Corresponding [OH^-] for reference and modified mortars.

considered for a more accurate understanding of the dynamic formation of interface in PMM complex systems [1,15–17,30,33,34]. Hydroxyl groups are formed associated with the hydrolysis of vinyl acetate sequences in the high pH medium characteristic of cement mortar [16,17,20,35]. Due to saponification, acetate groups from PVAc (poly(vinyl acetate)) are partially or completely replaced by hydroxyls resulting in poly(vinyl alcohol) (PVA) sequences, with pendant –OH groups, with the polyethylene sequences remaining unaltered [17]. Because the attachment of OH groups to the EVA chain, the copolymer is converted to a terpolymer (ethylene-ter-vinyl acetate-ter-vinyl alcohol) increasing the polarity and the hydrophilicity of latex. Hydroxyl side groups from EVA can interact with silanol (Si–OH) species from tile surface through hydrogen bonds. Porcelain tiles are formed by a glassy matrix (75%) based on $(SiO_4)^{4-}$ tetrahedral with silanol groups mostly at surfaces [36]. Besides that, the high pH of cement systems also favors the formation of new Si–OH sites [36].

In order to evaluate the hydrolysis of EVA in the modified mortars, FTIR spectra were performed from reference paste and EVA modified pastes (EVA1-15%, EVA2-5%, EVA2-10%, and EVA2-15%) with 28 days of age (Fig. 7). EVA polymer is characterized by a strong band from carbonyl group (C═O) at $\nu = 1720–1740\ \text{cm}^{-1}$ and a band associated with C–O at 1242 cm^{-1} [16,17,20]. Both are characteristics of PVAc sequences and do not overlap with cement paste peaks. These bands were relatively reduced in the cement paste modified with EVA. This was followed by the appearance of a peak at 1550 cm^{-1} related to the carboxylate group ($–COO^-$), a product of desacetylation reaction [16]. All these events are evidences of EVA hydrolysis with formation of –OH groups in the polymer chain. In these spectra the peaks associated with cement silicates that underwent changes during hydration are also remarkable, the most evident being the shifting of the Si–O asymmetric stretching vibration (in general $\nu_3 \approx 920\ \text{cm}^{-1}$) to higher wavenumber (965 cm^{-1}). This band shift indicates polymerization of the silicate units $(SiO_4)^{4-}$ and it is considered a fingerprint evidence for degree of polymerization with the formation of C–S–H phase [37]. So, based on FTIR spectra, the degree of polymerization of silicates have been almost independent of the EVA content in all investigated samples.

Fig. 8 shows the results obtained for the EH parameter extracted from the curves of Fig. 7. EH_{1740} and EH_{1240} parameters have presented strong linear correlation ($R^2 = 0.99$). As defined, the higher the value calculated for EH, the higher was the global degree of hydrolysis of the EVA (initial hydroxyl content + hydrolysis occurred in cement matrix). Hence, the results have indicated that the higher the polymer amount (measured as p/c) the lower the extension of EVA hydrolysis (EH). Also, to the same amount of polymer to cement (p/c = 15%) EVA1 is less hydrolyzed than EVA2.

The explanation for the differences of EH values for the same polymer (EVA2) at different concentrations (5% and 15%) can be attributed to the alkaline medium of pore solution, as will be discussed in the next paragraphs. The measured pH values and the corresponding OH^- concentrations for reference and modified mortars are presented in Fig. 9. As reported in the literature, the "pore water" chemistry depends on the solubilities of the solid phases

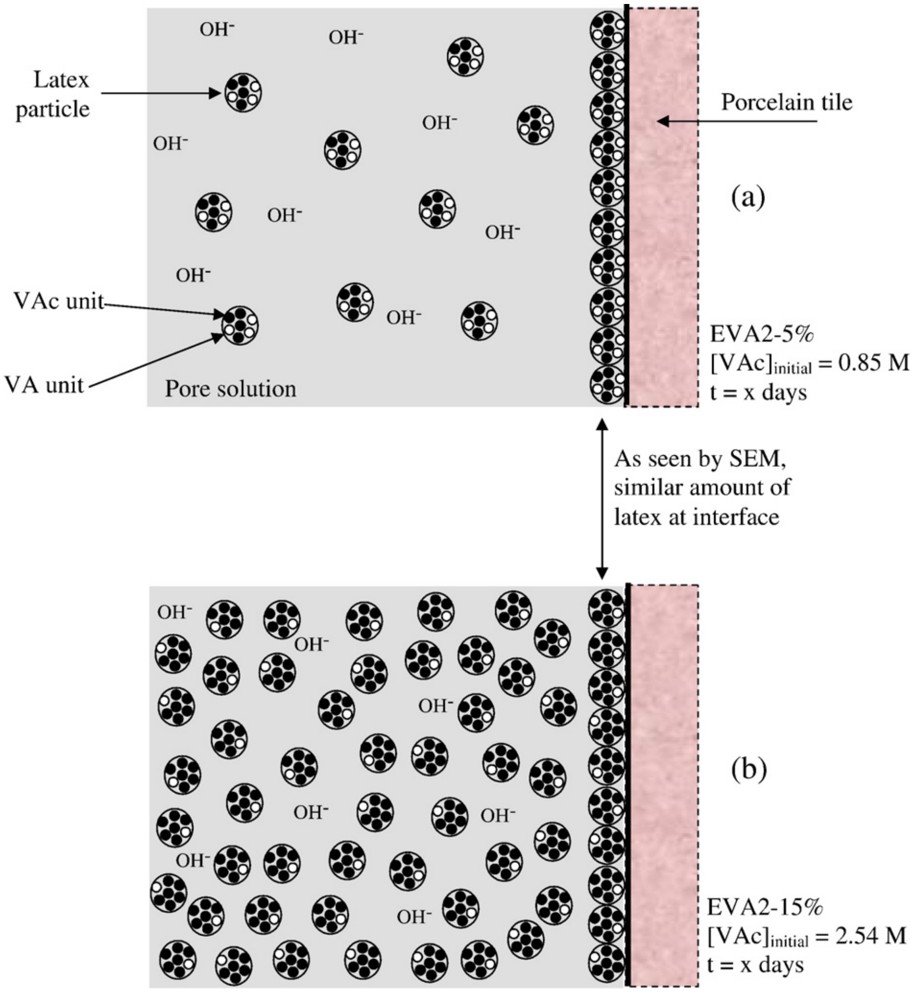

Fig. 10. Schematic representation of EVA hydrolysis effect on latex particles illustrating the measured EH parameters. (a) EVA2-5% and (b) EVA2-15% (VAc, solid circle = ●; VA, open circle = ○).

and in this first stage it is dominated by highly soluble alkali hydroxides (NaOH, KOH) and pH is usually above 13 as detected for reference mortar [38].

In Fig. 9, the reduction of pH observed for modified mortars was also verified by other authors [39,40]. Among the several suggested causes, one is the adsorption of organic compounds onto the surface of cement grains, thereby restricting reaction with water and limiting the initial stage of alkali species solubilization. Also, the introduction of polymer chains, mostly due to PVA surfactant, increases the viscosity of the solution significantly reducing the ions mobility and their dissolution [1,40,41].

The smaller values measured for the EH (extension of hydrolysis) of EVA2-15% compared to EVA2-5% samples can be more clearly understood by analyzing them combined with the pH results. That means, for similar initial pH ~ 12.8 or molar concentration of hydroxyl ($[OH^-] = 0.08$ M), there is a molar concentration of acetate groups three times higher in EVA2-15% (2.54 M) in contrast to EVA2-5% (0.85 M). Even if the kinetics of the acetoxy–hydroxy conversion for the two p/c ratios were assumed to be equivalent (EVA2 polymer is common for both pastes), at the same moment ($t = x$) each latex particle of EVA2-5% will have more vinyl acetate groups transformed to vinyl alcohol units than EVA2-15%, supporting the obtained values for EH (schematic representation in Fig. 10). In this sense, based on these assumptions and endorsed by SEM images of Fig. 5 that show latex film over the entire interface independent of polymer content, it is expected more VA units at the interface tile/modified mortar, for higher values of EH parameter.

As far as EVA1 is concerned, the lower EH value measured is directly associated with the higher ethylene content in the copolymer despite of the higher pH of solution (Fig. 9). In fact, it is well established in literature that as the ethylene content is increased in polymer (EVA) a reduction in the hydrolysis is observed [34,42]. Ethylene copolymerization controls the alkaline hydrolysis of vinyl acetate group due to several factors. First of all, the rate of acetoxy–hydroxy conversion depends on the vinyl acetate content in the EVA copolymers being higher for the copolymer with high vinyl content [17]. Secondly, the alkaline hydrolysis of vinyl acetate is an autocatalytic reaction due to the effect of neighboring [43]. Thus, an acetoxy group having a neighboring hydroxyl group is hydrolyzed a hundred times more easily than an acetoxy group surrounded by two unreacted groups. Therefore, hydroxyl groups are formed preferably in sequence what is expected to be reduced in EVA1 copolymer considering the molar concentration of the copolymers (65% of ethylene) that interrupts the sequence of hydrolysable units. Other important feature is the steric effect. In a first stage, the hydroxyl groups can only react with acetoxy groups on the external part of the latex particle (outer surface). After diffusion, the hydroxyl groups are able to react with inner ester units. In this sense, accessibility from polymer acetate groups to OH^- of alkaline medium base is essential for the reaction [17] and ethylene sequences are highly hydrophobic.

The analysis combining EH parameter and pull-off tests results have clearly endorsed the crucial importance of EVA hydrolysis in the porcelain tile/EVA modified mortar interface formation. As discussed in a previous section, the polymer addition improves the interface formation and favors the development of secondary bonds between tile and mortar. However, the increase of bond strength mortar/tile, verified by the change of the mode of rupture from adhesive at interface to a mixed-mode interfacial-cohesive failure of the mortar, was higher for the pastes with high 'extension of hydrolysis' parameter. It may be associated with the development of hydrogen bonds between silanol groups from tile surface and hydroxyl groups from PVA units from hydrolyzed EVA. As formerly reported for other polymeric systems [29,44], an increase of adhesion between tiles and polymer modified mortar was explained by the formation of a hybrid interface ceramic-polymer based on hydrogen bonds. In Fig. 11, in a SEM image of the interface (after HCl etching procedure) it is showed the polymeric film adhered to the tile surface and the new mechanism of interface formation due EVA hydrolysis is schematically represented.

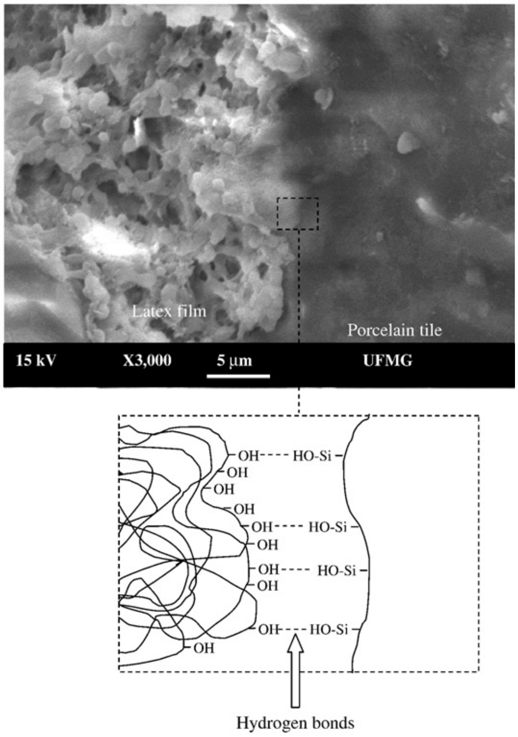

Fig. 11. SEM image of the interface tile/modified mortar (HCl) treated revealing polymer film adhered to tile and showing a schematic representation of hydrogen bonds developed at this interface (secondary electron image, magnification: 3000×).

In order to properly address the complexity of the system under investigation we have summarized in a schematic model as shown in Fig. 12. The mortar/tile interface characteristics associated with tile water absorption and EVA mortar modification as a result of the present study can be observed. Such representation is endorsed by widely reported analogous models in the literature [1,2,4,5,12,13]. In summary, the less favorable behavior of unmodified mortar systems, mostly in systems with low water absorption substrates (e.g. porcelain tiles, rocks, aggregates), is due to the presence of a thick porous transition zone between substrate and dense cement paste/mortar bulk at the interface [6,45] and as a consequence of the formation of a duplex film (CH followed by C–S–H) in contact with substrate surface [7,46–52]. So, despite of the presence of –OH ending groups in hydrate cement paste/mortar products that could even establish hydrogen bonds with tiles, the thick porous transition zone with a CH layer in contact with tiles surface does not favors the development of higher values of bond strength. The first aspect is direct: the higher the porosity, the lower the mechanical resistances. The second aspect is related to CH crystals formed in unmodified mortars. They are unable to withstand stresses due to weak interparticle bonding [53]. Finally, it should be reminded that hydrogen bond, as a chemical bond, is characterized by a bond length that must be accomplished, and that polymer chains mobility contributes to the possibility of development of this bonds even after mortar hardening. On the contrary, in polymer modified mortars, EVA polymer binds directly to the tile and to the cement hydrates through hydrogen bonds.

Hence, it can be stated that polymer-modified-mortar is a rather complex system which has an increasing interest to be properly

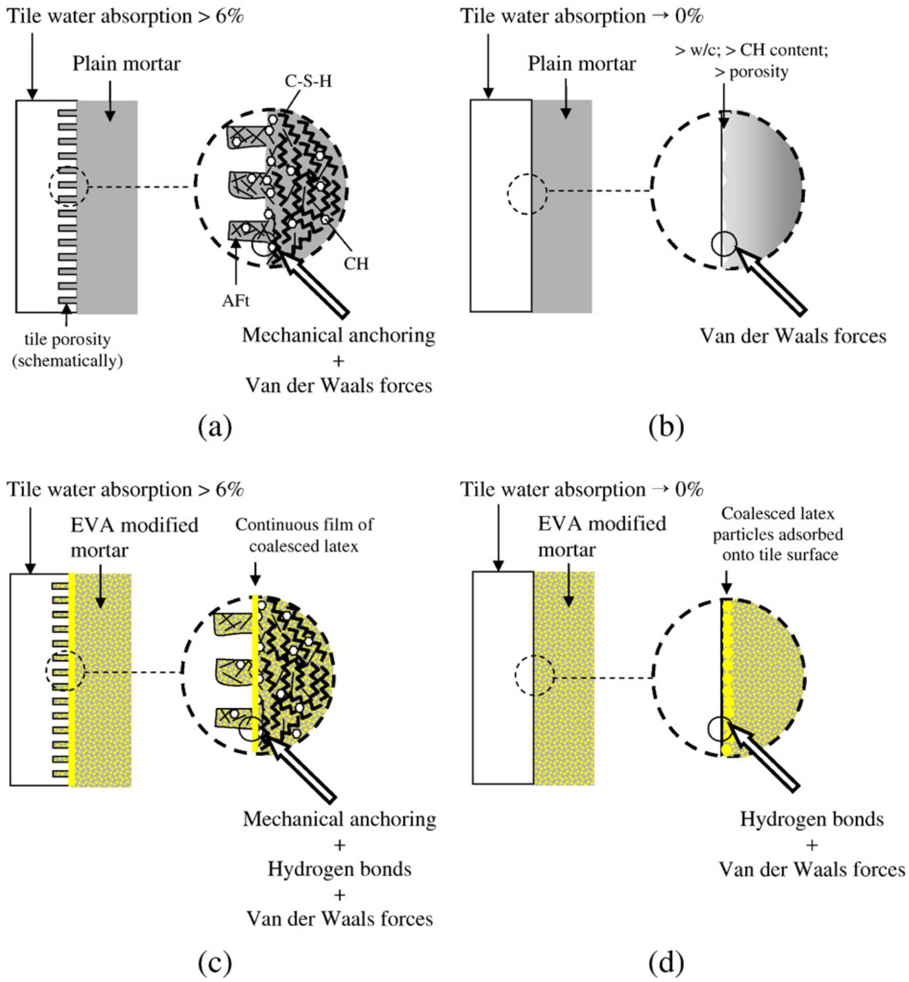

Fig. 12. Scheme of types of interactions developed between tile and mortar depending on water absorption (Abs) of tile and EVA addition. (a) Abs >6%, plain mortar; (b) Abs → 0%, plain mortar; (c) Abs >6%, EVA modified mortar; (d) Abs → 0%, EVA modified mortar (C–S–H: calcium silicate hydrate; CH: $Ca(OH)_2$; AFt: ettrigite).

investigated as far as interface phenomena are concerned where different reactions occur simultaneously and their kinetics will depend on concentration and distribution of all species/phases, medium pH, diffusion mechanisms, surface functional groups just to name a few.

4. Conclusions

The experiments revealed that EVA hydrolysis has a crucial influence on EVA modified mortar/ceramic tile interface formation reflecting on the adhesion resistance. The EVA 'extension of hydrolysis', EH, is dependent on the initial content of copolymers and it can be indirectly assessed using FTIR technique through the EH parameters established in this work. An increased at mortar/tile interfacial resistance is associated with the development of hydrogen bonds between silanol groups from tile surface and poly(vinyl alcohol) sequences from hydrolyzed EVA, besides the increase of secondary van der Waals bonds due to improvement of mortar characteristics at interface generally observed as a consequence of polymers addition.

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References

[1] Y. Ohama, Polymer-based admixtures, Cem. Concr. Res. 20 (2–3) (1998) 189–212.
[2] J.E. Isenburg, J.W. Vanderhoff, Hypothesis for reinforcement of Portland cement by polymer latexes, J. Am. Ceram. Soc. 57 (6) (1974) 242–245.
[3] J.M. Gesit, S.V. Amagna, B.B. Mellor, Improved Portland cement mortars with polyvinyl acetate emulsions, Ind. Eng. Chem. 45 (4) (1953) 759–768.
[4] H. Casarek, O. Cascudo, L.M. Scartezini, Importância dos materiais na aderência dos revestimentos de argamassa, in: Proceedings of IV Simpósio Brasileiro de Tecnologia das Argamassas, Brasília, 2001, pp. 43–67.
[5] E. Sakai, J. Sugita, Composite mechanism of polymer modified cement, Cem. Concr. Res. 25 (1) (1995) 127–135.
[6] J. Kim, R.E. Robertson, Effects of polyvinyl alcohol on aggregate–paste bond strength and the interfacial transition zone, Advn. Cem. Bas. Mat. 8 (2) (1998) 66–76.
[7] L. Struble, Microstructure and fracture at the cement paste–aggregate interface, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 11–20.
[8] A. Bentur, A. Goldman, M.D. Cohen, The contribution of the transition zone to the strength of high quality silica fume concretes, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 97–103.
[9] K.L Scrivener, K.M. Nemati, The percolation of pore space in the cement paste/aggregate interfacial zone of concrete, Cem. Concr. Res. 20 (1) (1996) 35–40.
[10] W. Xueqan, L. Dongxu, W. Xiun, T. Minshu, Modification of the interfacial zone between aggregate and cement paste, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 35–40.
[11] H. Savatano Jr., Zona de transição entre fibras e pasta de cimento Portland: caracterização e inter-relação com as propriedades mecânicas do compósito. São Paulo: Escola Politécnica da Universidade de São Paulo — EPUSP, 1992, 249p. (PhD Thesis).

[12] H. Herold, Fixing of stoneware "porcelanic" tiles by means of ceramic tiles adhesives modified with redispersible polymer powder, in: Proceedings of World Congress on Ceramic Tile Quality, Logui Impresión, Castellón, 2000, pp. P.GII-77–P. GII-88.

[13] A. Jenni, M. Herwegh, R. Zurbriggen, T. Aberle, L. Holzer, Quantitative microstructure analysis of polymer-modified mortars, J. Microsc. 212 (2) (2003) 186–196.

[14] H.F.W. Taylor, Cement Chemistry, Thomas Telford, 1997.

[15] K.M. Atkins, R.N. Edmonds, A.J. Majumdar, The hydration of Portland and aluminous cements with added polymer dispersions, J. Mater. Sci. 26 (9) (1991) 2372–2378.

[16] D.A. Silva, H.R. Roman, P.J.P. Gleize, Evidences of chemical interaction between EVA and hydrating Portland cement, Cem. Concr. Res. 32 (9) (2002) 1383–1390.

[17] C. Fonseca, J.G. Fatou, J.M. Perena, Study of the acetoxy-hydroxide transformation in ethylene-vinyl acetate copolymers, Die Angew Makromol. Chem. 190 (1) (1991) 137–155.

[18] A.L. Morales-Cruz, R. Tremonta, R. Martíneza, R. Romanach, C.R. Cabrera, Atomic force measurements of 16-mercaptohexadecanoic acid and its salt with CH_3, OH, and $CONHCH_3$ functionalized self-assembled monolayers, Appl. Surf. Sci. 241 (3–4) (2005) 371–383.

[19] H.W. Van del Martel, H. Beutelspacher, Atlas of Infrared Spectroscopy of Clay Minerals and their admixtures, Elsevier Scientific Publishing Company, 1976.

[20] A.A.P. Mansur, Mecanismos de aderência na interface argamassa e revestimento cerâmico de fachadas. Belo Horizonte: Escola de Engenharia da Universidade Federal de Minas Gerais — EEUFMG, 2007, 326p (Phd thesis).

[21] M.U.K. Afridi, Y. Ohama, K. Demura, M.Z. Iqbal, Development of polymer films by coalescence of polymer particles in powdered and aqueous polymer-modified mortars, Cem. Concr. Res. 33 (11) (2003) 1715–1721.

[22] M.U.K. Afridi, Y. Ohama, M.Z. Iqbal, K. Demura, Water retention and adhesion of powdered and aqueous polymer-modified mortars, Cem. Concr. Compos. 17 (2) (1995) 113–118.

[23] D.A. Silva, H.R. Roman, A.H. Silva, Efeito dos polímeros MHEC e EVA em algumas propriedades das argamassas colantes, Proceedings of III Simpósio Brasileiro de Tecnologia das Argamassas, Páginas & Letras Editora e Gráfica Ltda., Vitória, 1999, pp. 425–440.

[24] J. Pakusch, H.-J. Denu, B. Reck, L. Egan, Redispersible powders for sealing slurries. Adhes Sealants Ind (2004). Available at: http://www.adhesivesmag.com.

[25] M. Utida, W. Lourenço, U. Peter, Influência da adição de diferentes tipos de polímeros em diferentes dosagens nas argamassas colantes, in: Proceedings of VI Simpósio Brasileiro de Tecnologia de Argamassas, Florianópolis, 2005, pp. 406–413.

[26] A.A.P. Mansur, O.L. Nascimento, H.S. Mansur, Data collection of five years of exterior facade pathologies in Brazil, in: Proceedings of IX World Congress on Ceramic Tile Quality, Logui Impresión, Castellón, 2006, pp. PBB107–PBBI20.

[27] M. Abreu, V. Leitão, J.C. Lucas, Modeling the behavior of ceramic tile covering, Proceedings of VIII World Congress on Ceramic Tile Quality, Logui Impresión, Castellón, 2004, pp. PGII3–PGII17.

[28] J. Schulze, O. Killermann, Long-term performance of redispersible powders in mortars, Cem. Concr. Res. 31 (3) (2001) 357–362.

[29] A.A.P. Mansur, D.B. Santos, H.S. Mansur, A microstructural approach to adherence mechanism of poly(vinyl alcohol) modified cement systems to ceramic tiles, Cem. Concr. Res. 37 (2) (2007) 270–282.

[30] L. Bureau, A. Alliche, P. Pilvin, S. Pascal, Mechanical characterization of a styrene–butadiene modified mortar, Mater. Sci. Eng. A 308 (1–2) (2001) 233–240.

[31] P.K. Metha, P.J.M. Monteiro, Effect of aggregate, cement, and mineral admixtures on the microstructure of the transition zone, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 65–75.

[32] S. Mindess, Bonding in cementitious composites: how important is it? in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 3–10.

[33] R.C. Vekey, A.J. Majumdar, Durability of cement pastes modified by polymer dispersions, Mater. Struct. 8 (4) (1975) 315–321.

[34] J. Rottstegge, M. Arnold, L. Herschke, G. Glasser, M. Wilhelm, H.W. Spiess, W.D. Hergeth, Solid state NMR and LVSEM studies on the hardening of latex modified tile mortar systems, Cem. Concr. Res. 35 (12) (2005) 2233–2243.

[35] C.E.M. Gomes, O.P. Ferreira, M.R. Fernandes, Influence of vinyl acetate-versatic vinylester copolymer on the microstructural characteristics of cement pastes, Mater. Res. 8 (1) (2005) 51–56.

[36] L. Armelao, A. Bassan, R. Bertoncello, G. Biscontin, S. Daolio, A. Glisenti, Silica glass interaction with calcium hydroxide: a surface chemistry approach, J. Cult. Heritage 1 (2000) 375–384.

[37] M.Y.A. Mollah, W. Yu, R.E. Schennach, D.L. Cocke, A Fourier transform infrared spectroscopy of the early hydration of Portland cement and the influence of sodium lignosulfonate, Cem. Concr. Res. 30 (2) (2000) 267–273.

[38] C.C.D. Coumes, S. Courtois, D. Nectoux, S. Leclercq, X. Bourbon, Formulating a low-alkalinity, high-resistance and low-heat concrete for radioactive waste repositories, Cem. Concr. Res. 36 (12) (2006) 2152–2163.

[39] B.E.I. Abdelrazig, D.G. Bonner, D.V. Nowell, J.M. Dransfield, P.J. Egan, The solution chemistry and early hydration of ordinary Portland cement pastes with and without admixtures, Themochim. Acta 340–341 (1999) 417–430.

[40] J.F. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, Cem. Concr. Res. 2 (4) (1972) 415–433.

[41] Z. Su, J.M. Bijen, J.A. Larbi, Influence of polymer modification on the hydration of Portland cement, Cem. Concr. Res. 21 (2–3) (1991) 242–250.

[42] D.A. Silva, P.J.M. Monteiro, Hydration evolution of C3S-EVA composites analysed by soft X-ray microscopy, Cem. Concr. Res. 35 (2) (2005) 351–357.

[43] I. Sakurada, Some fundamental aspects of polymer reactions, Pure Appl. Chem. 16 (2–3) (1968) 263–284.

[44] A.A.P. Mansur, H.S. Mansur, Interface porcelain tile/PVA modified mortar: a novel nanostructure approach, J. Nanosci. Nanotechnol. 9 (2009) 1071–1075.

[45] J. Kim, R.E. Robertson, A.E. Naaman, Structure and properties of poly(vinyl alcohol)-modified mortar and concrete, Cem. Concr. Res. 29 (3) (1999) 407–415.

[46] D. Zampini, S.P. Shah, H.M. Jennings, Early age microstructure of the paste–aggregate interface and its evolution, J. Mater. Res. 13 (7) (1998) 1888–1898.

[47] S. Diamond, The microstructure of cement paste in concrete, Proc. 8th International Congress on the Chemistry of Cement, vol. I, Rio de Janeiro, Brazil, 1986, pp. 122–147.

[48] X. Zhang, G.W. Groves, S.A. Rodger, The microstructure of cement aggregate interfaces, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 89–95.

[49] O.A. Onabolu, P.L. Pratt, The effect of blast furnace slag on the microstructure of the cement paste/steel interface, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 255–261.

[50] I. Odler, A. Zurz, Structure and bond strength of cement–aggregate interfaces, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 21–27.

[51] D.G. Montgomery, A. Samarin, Adhesion between concrete and treated or untreated flat metal surfaces, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 263–270.

[52] T. Sugama, The effect of $Ca(OH)_2$-treated ceramic microspheres on the mechanical properties of high-temperature lightweight cement composites, in: S. Mindess, S.P. Shah (Eds.), Bonding in Cementitious Composites, Materials Research Society, Pittsburgh, 1988, pp. 301–306.

[53] M.U.K. Afridi, Y. Ohama, K. Demura, M.Z. Iqbal, A note on the comparison of crack resistance of $Ca(OH)_2$ crystals of unmodified and polymer-modified mortars in carbonated atmosphere, Cem. Concr. Res. 31 (11) (2001) 1643–1645.