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Evidences of chemical interaction between EVA and hydrating Portland cement

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Abstract

In spite of the widespread use of ethylene/vinyl acetate copolymer (EVA) in mortar and concrete production, there is no agreement among various researchers about the kind of interaction that is developed between cement and polymeric phases. Therefore, the adoption of adequate measures for final product quality achievement is impaired, as well as the adjustment of their properties to the desired performance. The purpose of this research is to fill this lack of knowledge through the microstructural characterization of cement pastes modified with EVA copolymer. Portland cement pastes were prepared with different EVA contents. The water/cement ratio was kept constant. The pastes were submitted to two different curing conditions, and analyzed at 28 days old. Thermal analyses (differential thermal analysis [DTA] and thermogravimetric [TG] analysis), Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) tests were performed, which permitted the evaluation of the EVA effects on the cement hydration. Some evidences of chemical interactions between cementitious and polymeric phases were identified. The results showed that the acetate groups of EVA copolymer undergo alkaline hydrolysis and interact with Ca^{2+} ions of the pastes to form an organic salt (calcium acetate). The calcium hydroxide content is decreased, the ettringite crystals appear to be well formed and many Hadley's grains were observed. A calcium-rich, porous and hexagonal structure phase was detected, probably due to acetic acid attack on calcium hydroxide crystals.

Keywords: Cement paste; EVA copolymer; Microstructure; Thermal analysis; Infrared spectroscopy

1. Introduction

Ethylene/vinyl acetate (EVA) copolymer is added to mortar and concrete during the preparation to improve some properties such as fracture toughness, impermeability and bond strength to various substrates [1]. Water-retention capacity and plasticity in the fresh state are also improved. Water-redispersible powder of EVA can be added to anhydrous cement and aggregates before mixing with water, or can be added in the form of aqueous dispersion.

The kind of interaction developed between cementitious and polymeric phases on the same aqueous solution is not clear, and some controversies exist among researchers. According to some of them [2–7], only physical interactions occur in the system and, in most cases, a polymeric film is formed inside the composite, which is responsible for the improvement of hardened state properties of mortars and concretes. Other authors claim for the occurrence of physical and chemical interactions between polymers and Portland cement [1,8–12]. According to Janotka et al. [12], chemical interaction could result in the formation of complex structures and in changes in the hydrated cement phases morphology, composition and quantity, especially calcium hydroxide.

Since EVA is currently used as a mortar and concrete modifier worldwide, it is important to investigate its action on cement-based materials in order to understand the structure–property relationships for such materials. In Brazil, EVA is used for the production of most dry-set mortars for ceramic tile installation, especially for coating of façades.

Therefore, the purpose of this work is to present some results obtained by the authors in an extensive research developed with EVA-modified cement pastes. To investigate the possibility of a chemical interaction between EVA and cement, the morphology of hydrated cement phases was analysed, the content of calcium hydroxide was determined and the infrared spectra of EVA and cement pastes were compared. Techniques for microstructural characterization

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such as infrared spectroscopy, differential thermal analysis (DTA), thermogravimetric (TG) analysis and scanning electron microscopy (SEM) were employed.

2. Materials, experimental design and methods

The materials employed for paste preparation were ordinary Portland cement with up to 5% of limestone filler (CPI-S 32 type according to Brazilian standard NBR 5732/91), deionized water and water-redispersible EVA powder. Characteristics of the materials used are presented in Tables 1 and 2. Figs. 1 and 2 show the infrared spectra of cement and EVA in KBr pellets, respectively.

The following procedure was employed for mixing of pastes: (i) dry mixing of EVA and cement in a low-speed mechanical mixer for 120 s; (ii) dry mixture flowing over deionized water; (iii) paste mixing in a low-speed mechanical mixer for 120 s; (iv) paste resting for 15 min; (v) remix for 15 s; (vi) casting in hermetic polyethylene cylindrical flasks of 30 mm diameter and 50 mm high. These were then sealed and rotated on rollers in the horizontal position (approximately 20 rpm) up to initial setting for bleeding prevention. The temperature and relative humidity in the laboratory were approximately 23 °C and 80%, respectively.

The actual EVA contents in the mixtures were 10% and 20% by cement weight. These contents were corrected due to the presence of inorganic compounds in the copolymer powder, measured by the ash content (Table 2). Consequently, EVA copolymer/cement ratios of 10% and 20% were obtained by adding, respectively, 10.8% and 21.6% of EVA. The water/cement ratio was kept constant at 0.4, in weight basis.

The effect of different curing methods was also studied. Specimens submitted to *dry cure* were maintained at 75% relative humidity (RH) from demoulding (24 h after casting), up to the age of 28 days. Those ones submitted to *mixed cure* were maintained inside the moulds, sealed and immersed in water during the first 7 days. They were then demoulded and kept at 75% RH until 28 days old. For the prevention of carbonation and maintenance of relative humidity, all specimens were stored during the curing period in a CO_2-free, airtight vessel containing a supersaturated NaCl solution. Carbon dioxide was withdrawn from the atmospheric air before entering the vessel by passing it through a $Ba(OH)_2$ saturated solution.

Table 2
Physical characteristics of EVA copolymer

Ash content (30 min at 1000 °C)	7.63%
Apparent density of the powder[a]	529 g/l
Particle size (laser granulometry in ethanol)	11% above 250 μm
Minimum film-forming temperature[b]	Approx. 4 °C

[a] Characteristic determined by mercury intrusion porosimetry.
[b] Characteristic informed by the copolymer producer.

EVA-modified cement pastes were submitted to thermal analysis in a Netzsch STA 409EP equipment, which permits performing DTA and TG analysis simultaneously. The pastes were manually ground with an agate mortar and pestle inside a flexible polyethylene chamber filled with N_2 gas. Particles with diameter lower than 65 μm were analysed. The experimental conditions were (a) continuous heating from 25 to 1100 °C, heating rate: 10 °C/min; (b) N_2 gas dynamic atmosphere (40 cm^3 min^{-1}); (c) alumina, top-opened crucible; (d) reference material: α-Al_2O_3 (corundum); e) sample mass: 30 mg approximately. DTA and TG curves were obtained.

Statistical analysis of the DTA/TG results was carried out by analysis of variance (ANOVA) in order to estimate the effect of some factors on the pastes microstructure. The commercial software Statistica for Windows version 5.0 was used. The content of EVA (percent of the weight of cement) and the curing method (dry or mixed) were considered as controllable factors (independent variables). The dependent variables were the contents of calcium hydroxide and carbonate phases, as well as their dehydration/decomposition temperature. Duplicate tests on a single set of castings were performed for each treatment.

All the weight loss data are expressed as a function of the ignited weight of the sample, as suggested by Taylor [13].

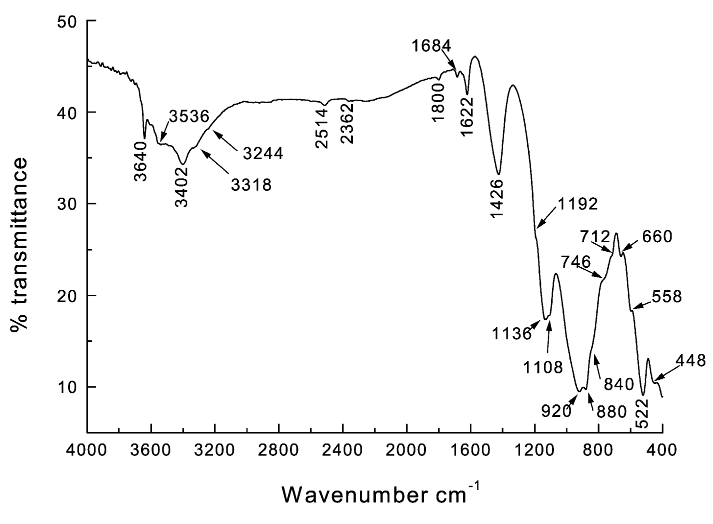
Table 1
Characteristics of Portland cement

Chemical analysis (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	MnO	TiO_2	P_2O_5	L.O.I.	Free lime
18.73	4.44	2.62	60.69	4.87	2.96	0.23	1.00	0.06	0.17	0.22	3.34	1.68

Physical characteristics

Setting time (min)		Water for 255±10 mm flow table (%)	Blaine surface area m^2/kg	ϕ<45 μm (%)	Compressive strength (MPa) w/c ratio = 0.48, 1:3 (cement:sand in weight)			
Initial	Final				1 day	3 days	7 days	28 days
160	235	26.3	323.6	93.00	13.2	27.8	33.8	44.2



Bands identification	
(cm^{-1})	Group
3640	OH
3402	S-O
1622	S-O
1426	CO_3^{2-}
1136	S-O
920	Si-O
880	Si-O; Al-O; CO_3^{2-}
746	Al-O
712	CO_3^{2-}
660	S-O
558	Si-O
522	Si-O; Al-O
448	Si-O; Al-O

Fig. 1. Fourier-transform infrared spectrum of Portland cement in KBr pellet.

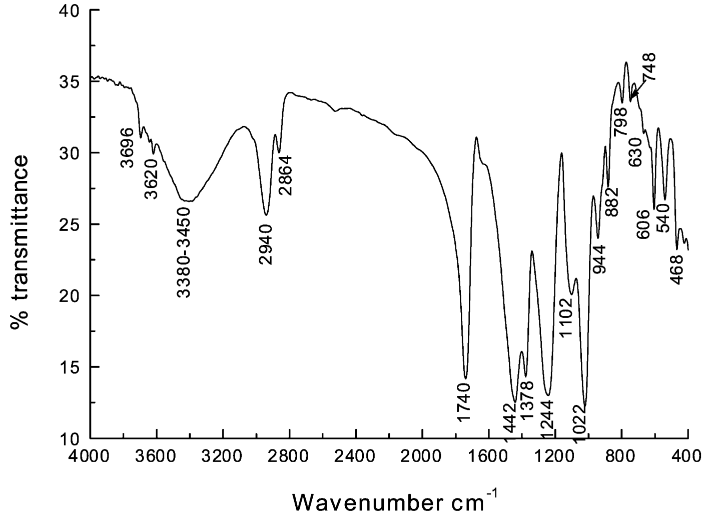
The calcium hydroxide content was determined from the following equation:

$$CH(\%) = WL_{CH}(\%) \times \frac{MW_{CH}}{MW_H}, \qquad (1)$$

where CH(%) is the content of $Ca(OH)_2$ (in weight basis), WL_{CH}(%) is the weight loss occurred during the dehydration of calcium hydroxide (in weight basis), MW_{CH} is the molar weight of calcium hydroxide and MW_H is the molar weight of water. Since the exact stoichiometry of decomposition reactions of the carbonate phases is not known, the results are expressed in function of the weight of CO_2 gas released during the decomposition, and not as carbonate phases content.

A Perkin-Elmer 16PC Fourier-transform infrared spectrometer (FT-IR) was used. Mixed cured, 28-day-old pastes were manually ground with the mortar and pestle set inside the N_2 gas chamber, and particles with diameter lower than 38 μm were tested in KBr pellets. The spectra were traced in the range 4000–400 cm^{-1} (wave number), and the band intensities were expressed in transmittance (%T).

SEM was performed in a Philips XL-30 microscope equipped with an energy-dispersive X-ray analyser (EDAX). For these analyses, prismatic specimens of cement paste were moulded. After 40 h they were demoulded. The specimens were kept from the casting until 21 days old in a CO_2-free recipient at 75% RH and 23 °C. The specimens were then broken and dried, and the cross-sectional surface



Bands identification	
(cm^{-1})	Group
3696	OH
3620	CH_2
3380-3450	C=O
2940 e 2864	CH_2, CH_3
1740	C=O
1442	CH_2, CH_3, CO_3^{2-}
1378	C-CH_3
1244	C-O
1102	C-O, OH
1022	C-O, CH_3
944	C-C in ester group*
882	CO_3^{2-}
748	CH_2, CO_3^{2-}
630	OCO
606	C=O; ester group
540	C=O

* ester group: $(CH_3COO)^-$

Fig. 2. Fourier-transform infrared spectrum of EVA copolymer (redispersible powder) in KBr pellet.

was analysed. To obtain a conductive surface for analysis, a thin gold layer was deposited over it.

3. Results

The DTA and TG curves obtained in all of the tests are typical of hydrated cement pastes containing carbonate phases. Three major endothermic reactions occurred during the heating of the samples: (a) release of the evaporable and part of the adsorbed water at 110 °C approximately; (b) $Ca(OH)_2$ dehydration, between 420 and 500 °C; (c) decomposition of the carbonate phases at 550–850 °C.

As shown in Fig. 3, EVA copolymer strongly influences the DTA/TG curves, causing (a) enlargement of the exothermic shoulder at 200–400 °C, (b) decreasing of the endothermic peak intensity and weight loss on the dehydration of calcium hydroxide, (c) sharp changes in the curves at temperatures higher than 500 °C (in most cases, an endothermic peak at 550 °C and an exothermic shoulder at 630–660 °C were detected), (d) widening of the decomposition temperature range of carbonate phases (from 680–760 to 580–850 °C) and increasing of the peak temperature (from about 730 to 790 °C), and (e) increasing of the weight loss in the latter temperature range. Cement pastes with 10% EVA showed a slight weight gain at 480–570 °C, immediately after the calcium hydroxide dehydration. When more copolymer is present (20%), a flat segment in the TG curve could be observed in the same temperature range, indicating that if some weight gain occurs, a weight loss also occurs with the same intensity.

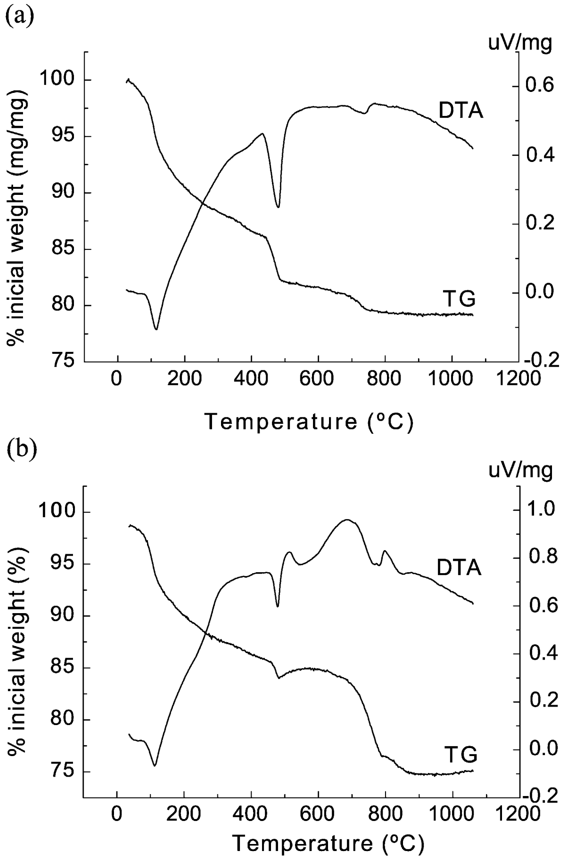


Fig. 3. DTA/TG curves of pure (a) and 10% EVA-modified (b), mixed-cured pastes.

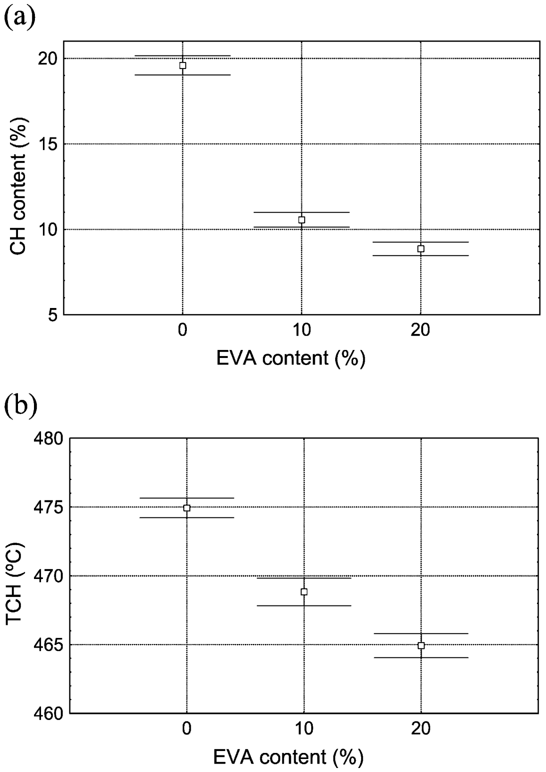


Fig. 4. Effect of EVA content on the calcium hydroxide content (CH) and its dehydration temperature (TCH).

EVA strongly reduces the calcium hydroxide (CH) content and dehydration temperature, as can be seen in Fig. 4 and Tables 3 and 4 (ANOVA results). The curing method does not influence these variables at a statistical significance

Table 3
Analysis of variances for $Ca(OH)_2$ content data (CH)

Factor	Sums of squares	*df*	Mean squares	*F* test	*P* value
Manner effects					
A: EVA content	1156.413	2	578.2066	144.6391	.0000
B: Curing method	24.5541	1	24.5541	6.1422	.0164
Interactions					
AB	5.5837	2	2.7918	0.6984	.5018
Residual	215.869	54	3.9976		
Total	1402.4198	59			

Table 4
Analysis of variances for $Ca(OH)_2$ dehydration temperature data (TCH)

Factor	Sums of squares	*df*	Mean squares	*F* test	*P* value
Manner effects					
A: EVA content	799.0212	2	399.5106	24.3351	.0000
B: Curing method	53.4633	1	53.4633	3.2562	.0767
Interactions					
AB	7.3437	2	3.67187	0.2236	.8003
Residual	886.6153	54	16.4188		
Total	1746.4435	59			

Table 5
Analysis of variances for weight loss due to carbonate phases decomposition data

Factor	Sums of squares	*df*	Mean squares	*F* test	*P* value
Manner effects					
A: EVA content	779.8308	2	389.9154	237.8236	.0000
B: Curing method	0.14990	1	0.14990	0.09143	.7635
Interactions					
AB	0.88506	2	0.269916	0.2699	.7645
Residual	88.5338	54	1.6395		
Total	869.3996	59			

of 95%, but it was possible to observe a tendency of mixed-cured pastes to show higher $Ca(OH)_2$ content that dehydrates at slightly higher temperatures compared to dry-cured pastes.

Fig. 5 shows that EVA copolymer sharply increases the quantity of carbonate phases in the pastes, measured by DTA/TG.

There is a strong negative correlation ($r = -.80$) between the calcium hydroxide content data and the weight loss due to decomposition of carbonate phases. It means that the increase in the quantity of carbonate phases is related to a decrease of CH content in the pastes. The curing method has no statistically significant effect on the carbonate phase content (Table 5).

Regardless of the presence of EVA in the pastes, the following bands could be observed on the FT-IR spectra: calcium hydroxide bands (3642 cm^{-1}), combined and adsorbed water of C-S-H, AFm and AFt phases (3440–3446 cm^{-1}), molecular water (3440–3446 and 1640–1654 cm^{-}1), carbonate phases (1424–1436, 874–880 and 704–712 cm^{-1}), sulphate phases (1116–1118 cm^{-1}), anhydrous calcium silicates (920, 526–536 and 458–464 cm^{-1}) and hydrated calcium silicates (970–986 cm^{-1}). As can be seen in Fig. 6, EVA causes some modifications in the spectra profile. Besides some bands attributed to ethyl and acetate groups of EVA, a band at 1558–1568 cm^{-1} was detected. This band does not appear in the spectra of pure materials and pure hydrated paste.

SEM showed that pure paste has reasonable maturity with dense deposits of calcium hydroxide encapsulating C-S-H dense structures, although it also presents some regions where the intergranular space is relatively large and the hydrating cement grains boundaries are clear. In these regions, C-S-H Types I and II, many thin ettringite crystals (Fig. 5a) and Hadley's grains, as described by Hadley et al. [14], could be seen.

EVA-modified paste microstructure is more homogeneous than that of pure pastes, but they appear to be less hydrated, since the intergranular space is larger than in the pure paste. A great number of Hadley's grains with large ettringite rods inside were detected (Fig. 7b). There are no dense deposits of C-S-H or calcium hydroxide. It could be clearly noted that the quantity of this latter phase is sharply lower. However, a calcium-rich, porous phase with hexagonal structure, similar to calcium hydroxide, was observed

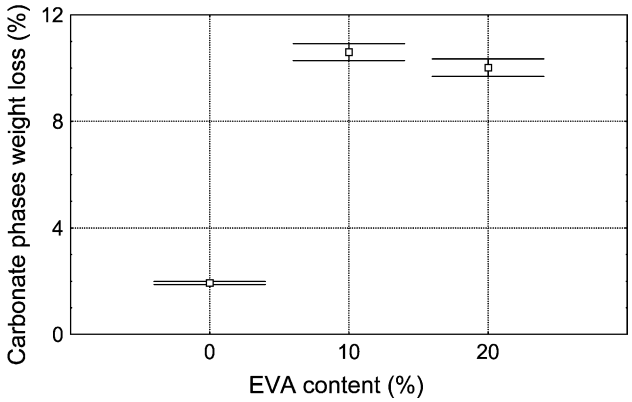


Fig. 5. Effect of EVA content on the weight loss due to carbonate phases' decomposition.

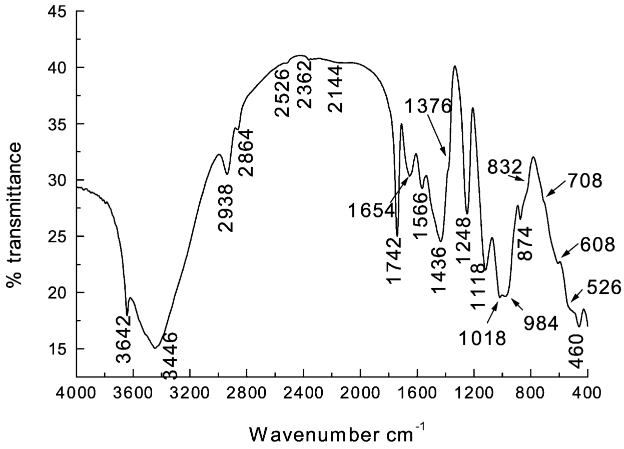


Fig. 6. Fourier-transform infrared spectrum of 20% EVA-modified cement paste, 28 days old.

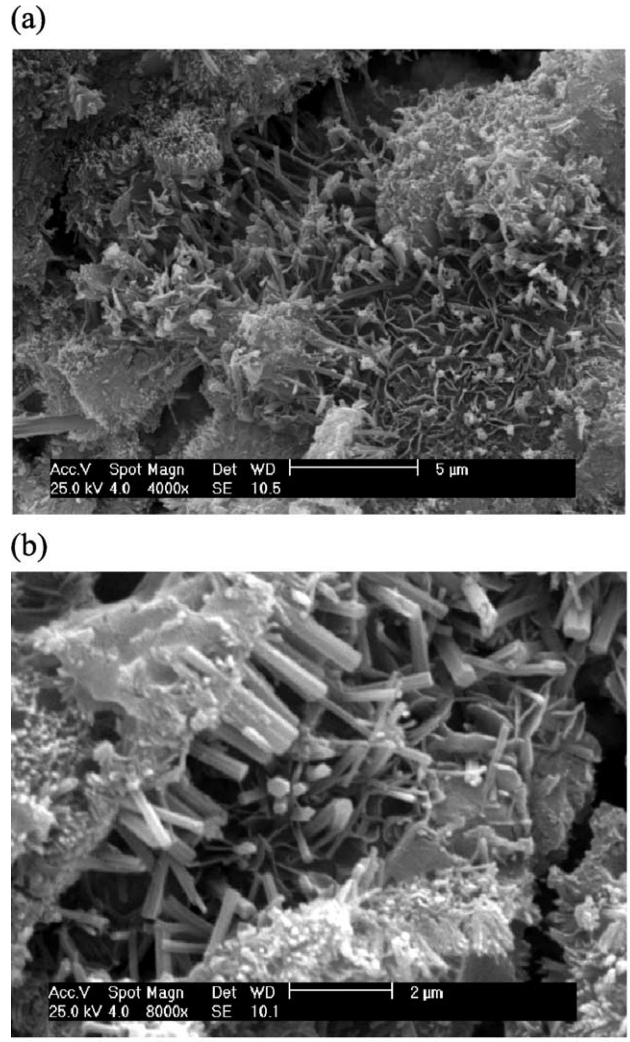


Fig. 7. Ettringite crystals in pure paste (a) and inside Hadley grains of EVA-modified pastes (b).

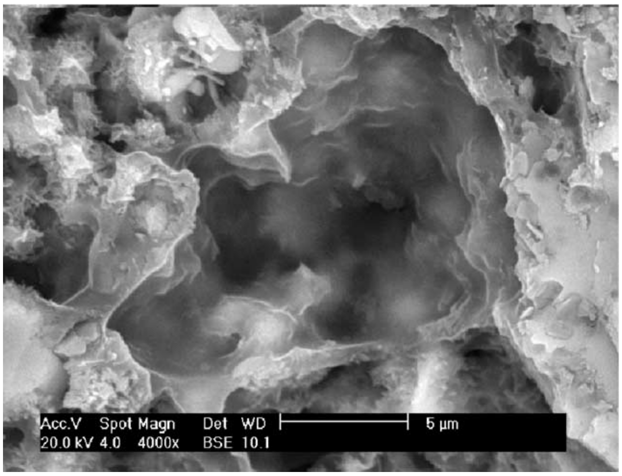


Fig. 9. Polymeric film in fractured surface of EVA-modified cement paste.

(Fig. 8). A polymeric film partially covering the hydrated phases was also observed (Fig. 9).

4. Discussion

EVA copolymer contains a vinyl acetate group that suffers hydrolysis when dispersed in an alkaline medium, producing polyvinyl alcohol [15]. This reaction is called saponification. When dispersed in a Ca(OH)$_2$ saturated solution, as in the case of pore water of cement pastes, the acetate anion (CH$_3$COO)$^-$ released in the alkaline hydrolysis combines with Ca^{2+} ions released in the dissolution of anhydrous cement grains. The product of this interaction is calcium acetate—Ca(CH$_3$COO)2×H$_2$O. The infrared bands at 1558–1568 cm^{-1} indicate the presence of carboxylate anion (–COO$^-$) in the EVA-modified pastes [16],

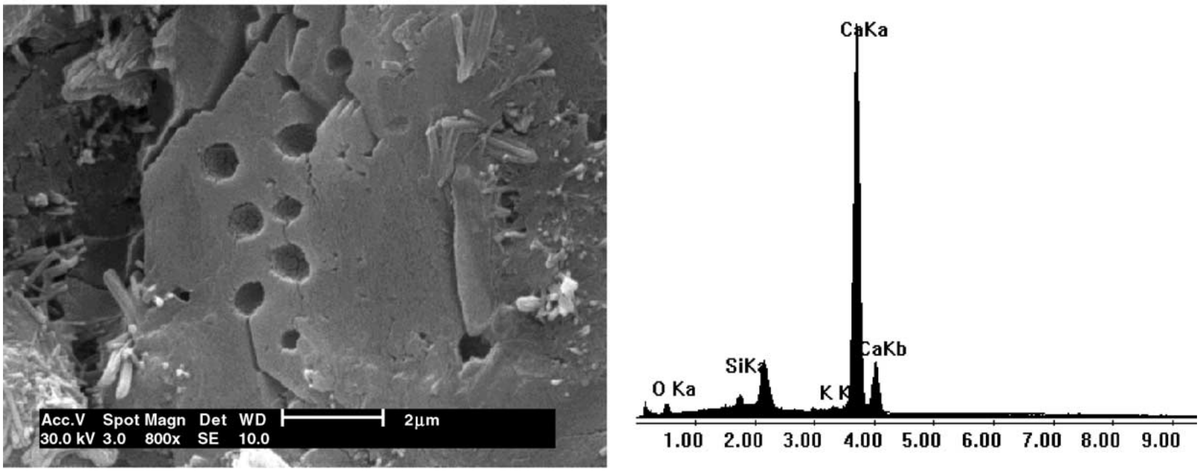


Fig. 8. Aspect of rich calcium phase in EVA-modified pastes, and EDAX spectrum.

confirming that alkaline hydrolysis of acetate groups has occurred. However, the band at 1740–1742 cm^{-1} (due to CO bond) indicates that the hydrolysis is not complete, i.e., some acetate groups rest bonded to the EVA main chain.

The exothermic region in DTA curves of EVA-modified pastes at 200–400 °C may be due to the decomposition of the calcium acetate [17] that results on the formation of calcium carbonate, according to the following reactions [18]:

$$\underset{\text{calcium acetate}}{Ca(CH_3COO)_2} \xrightarrow{380-400\ ^{\circ}C} \underset{\text{acetone}}{CH_3COCH_3} + \underset{\text{calcium carbonate}}{CaCO_3}$$

and $CaCO_3 \rightarrow CaO + CO_2$

According to Kasselouri et al. [17], the thermal decomposition of calcium carbonate formed in this way occurs at a temperature as low as 550 °C, probably due to an instability of the phase. Therefore, the enlargement of the decomposition temperature range of the carbonate phases in EVA-modified pastes can be due to this fact. In the hydrated pastes the formation of calcium acetate can occur also by acetic acid attack (CH_3COOH) on calcium hydroxide particles, resulting in the structures shown in Fig. 8. According to Sasaoka et al. [18], $CaCO_3$ and CaO particles expand due to acetic acid vapour attack. The micrographs seem to indicate that this mechanism also occurs when $Ca(OH)_2$ particles are exposed to acetic acid.

Taylor and Turner [19], on the other hand, attribute the exothermic region at 200–400 °C to the gradual formation of carbonate phases from the interaction between organic phases and hydroxyls released on calcium hydroxide and C-S-H dehydration, according to the following reaction:

$$RCH_2OH + OH^- \rightarrow RCO_2^- + 2H_2$$

where the first term is an alcohol, the second one is the hydroxyl and the third one is the carboxylate ion. According to Taylor and Turner, it is possible that some interaction occurs between the carboxylate ions so produced and inorganic phases, forming carbonate ions. In the case of EVA, the polyvinyl alcohol used as a protective colloid and that one formed in the saponification reaction can interact with the hydroxyls released from cement hydrated phases on heating. The product of this interaction is a carbonate phase. The weight gain occurred in EVA-modified pastes immediately after the calcium hydroxide decomposition can be due to this kind of interaction.

DTA, TG and infrared spectroscopy results allow the authors to conclude that at least one of the following phenomena occurs in EVA-modified cement pastes:

(a) Interaction of Ca^{2+} ions with acetate anions $(CH_3COO)^-$ in aqueous solution at room temperature, forming calcium acetate, which decomposes on heating producing calcium carbonate;

(b) Interaction of hydroxyls (OH^-)—released from hydrated cement phases during heating—with polyvinyl alcohol, which exists in the paste as a protective colloid of EVA particles and is formed in the saponification reaction. The products of this interaction are carbonate phases.

In both cases, the reduction of weight loss in the decomposition of calcium hydroxide can be explained in two ways: (a) since Ca^{2+} ions are consumed and drawn from the aqueous solution to form calcium acetate, there is a decrease of calcium hydroxide content; and (b) the interaction between OH^- and alcohol on sample heating decreases the weight loss in the dehydration of calcium hydroxide, since the release to the atmosphere is not permitted. It is also possible that some carbonation of calcium hydroxide dissolved in the aqueous phase has occurred due to the presence of CO_2 in the air entrapped in the paste during the mixing process. Besides, according to Janotka et al. [12], polymers with film-forming capacity can improve the carbonation of calcium hydroxide in the pastes, since the film surface contains innumerous air bubbles that carry CO_2 gas.

The presence of well-crystallized rods of ettringite in EVA-modified cement pastes is as indication of its slow formation process, probably due to the capture of sulfate ions ($SO_4{}^{2-}$) in solution due to the consumption of Ca^{2+} ions by acetate groups of EVA, retarding the nucleation and growth of ettringite crystals [11].

The presence of innumerous Hadley's grains in EVA-modified pastes is an indication that the copolymer indeed retards the whole hydration process. According to Taylor [20], this kind of structure appears when the precipitation process of the hydrated phases is slower than the dissolution of the anhydrous phases. Probably, EVA retards the precipitation of hydrated phases due to the consumption of Ca^{2+} ions from the aqueous phase and to the adsorption on hydrated and anhydrous cement phases.

5. Conclusions

From the microstructural tests performed with pure and EVA-modified cement pastes it was possible to conclude that:

(a) There are evidences of chemical interaction of acid groups released by alkaline hydrolysis of EVA with Ca^{2+} ions in the pore water of the cement pastes. The products of this interaction are calcium acetate and polyvinyl alcohol. Calcium acetate is an organic salt with high hygroscopicity, and polyvinyl alcohol is water soluble. These two factors can impair the performance of EVA-modified mortars and concretes when saturated by water.

(b) As shown by infrared analysis, the alkaline hydrolysis is not complete, and EVA copolymer changes into a terpolymer formed by ethylene, vinyl acetate and polyvinyl alcohol.

(c) EVA retards the whole cement hydration reactions and leads to the formation of Hadley's grains and big rods of ettringite. The quantity of calcium hydroxide in cement pastes is decreased also because EVA consumes Ca^{2+} ions from the solution.

(d) EVA-modified cement pastes showed expressive formation of polymeric film deposited on the surface of anhydrous and hydrated cement phases, and also partially sealing pore walls.

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