CHARACTERIZATION OF COPOLYMERS POLY(ETHYLENE-CO-VINYL ACETATE) AND EVALUATION OF THEIR EFFECTS IN THE MODIFIED MORTARS PROPERTIES

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ABSTRACT

Poly(ethylene-co-vinyl acetate), EVA, is a water-redispersible polymer used as cement modifier. Latex modified Portland cement mortars based on EVA are the standard product in the market for ceramic tile installation. However, several EVA latexes are available with different features, including amount of each copolymer, type of protector colloid, and nature of anti-blocking agent. In this sense, the object of the present work was to characterize two EVA redispersible powders with different amounts of vinyl acetate groups in their composition and evaluate the effect of the use of these two EVAs in some properties of mortars. X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and mechanical evaluations were conducted in order to characterize the two selected EVA. Also, we have prepared mortars with additives (modified mortar) and reference mortar (without polymer) using Portland cement CPII-F32 and quartzose sand. The additives were incorporated in amounts of 5%, 10%, and 15% in relation to cement weight. Consistency, water retention, air entrainment, and flexural strength of mortars were evaluated. In order to evaluate the effect of EVAs on adhesion properties pull-off tests were conducted. The results of XRD, FTIR, and mechanical tests allow us to characterize and differentiate both EVA products. The global features of polymers are a consequence of the polymer composition and type and kind of surfactant and anti-caking agent. Also some properties of the EVA films in mortars may be predicted. Mortar tests evaluation showed that the surfactant used in the process to produce the powder polymer greatly affects mortar properties at fresh state. Water retention was also a consequence of latex particles presence. Flexural strength values measured were a consequence of EVA film mechanical properties. Based on these results, in the selection of the EVA for mortar modification, the evaluation of its composition/properties is crucial to the final properties of the mortar.

1. INTRODUCTION

Poly(ethylene-co-vinyl acetate), EVA, is a water-redispersible polymer used as cement modifier. Latex modified Portland cement mortars based on EVA are the standard product in the market for ceramic tile installation. However, several EVA latexes are available with different features, including amount of each copolymer, type of protector colloid, and nature of anti-blocking agent. In this sense, the object of the present work was to characterize two EVA redispersible powders with different amounts of vinyl acetate groups in their composition and evaluate the effect of the use of these two EVAs in some properties of mortars.

2. EXPERIMENTAL PROCEDURE

The characteristics of the two commercial redispersible polymer powder selected are presented in Table 1.

X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and mechanical evaluations were carried on in order to characterize the two selected EVA. XRD assays were conducted in PW1710, Philips, that uses KαCu radiation with λ=1.5406 Å, in the range of 2θ from 3° to 90°. FTIR spectroscopy with diffuse-reflectance accessory (Perkin-Elmer, Paragon 1000) was used. Samples were placed in a sampling cup and 32 scans were acquired at 2 cm^{-1} resolution with the subtraction of KBr background (4000 to 400 cm^{-1}). XRD and FTIR analyses were conducted in EVA powder samples, as supplied by manufacturers. Tensile properties were performed according to ASTM D638 in a EMIC DL3000 machine, at (23±2)ºC and 50% relative humidity, at a crosshead speed of 50 mm/min. Six dumbbells specimens were obtained per batch through films cast from EVA latex after redispersion with water. In order to reduce the effect of protective colloid and anti-blocking agents, tensile strength were also measured through films from both EVAs after extraction and dissolution in dichloromethane.

EVA		EVA1	EVA2
Glass transition temperature – Tg (°C)		-12	16
% Mass of Acetate		62%	87%
% Mass of Ethylene		38%	13%
Minimum Film Formation Temperature (MFFT) of redispersion (°C)		NF[b]	4
Protective Colloid		Poly(vinyl alcohol) - PVA	PVA
Particle Size	**Before redispersion**	90 µm (average)	Maximum of 4% > 400 µm
	After redispersion	-	0,5-8 µm
% Solids		99±1 (99,7)	99±1 (99,4)
% Ash		10±2 (10)	11±2 (10,1)
Manufacturer		Manufacturer 1	Manufacturer 2

Table 1. Characteristics of EVAs redispersible polymer powder.

In order to evaluate the effect of these EVA in the properties of the mortars modified with these polymers we have prepared mortars with additives (modified mortar) and reference mortar (without polymer) using Portland cement CPII-F32 (according to Brazilian Standard NBR 11578/91) and quartzose sand. Mortars were mixed in the 1:1.7 ratio (cement: sand), in weight, and 0.60 water to cement ratio. The additives were incorporated in amounts of 5%, 10%, and 15% ratio to cement weight (polymer to cement ratio = p/c). Consistency, water retention, air content, flexural strength and pull-off tests were conducted.

The mortars were mixed in a low speed mechanical mixer according the following procedure: (a) mixing of de dry materials (cement, sand and EVA powder) for 2 minutes; (b) pouring the dry mixture on the water for 0.5 minute and mixing for 1 minute; (c) interruption of the mechanical mixing , when the mixture was manually stirred with a spatula for 1 minute; (d) mechanical mixing for 1 minute; (e) mortar rest for 15 minutes, covered by a humid cloth to avoid the evaporation of water; and (f) mechanical mixing for 15 seconds.

After mixing, the fresh mortars were tested for consistence, water retention and air entrainment. Consistency was measured using the flow table apparatus following Brazilian Standard NBR 13276/2002. Water retention (WR) was evaluated in accordance with NBR 13277/1995 in which the WA percentage is calculated from the water contents of the mortar sample before and after filter paper suction. The air content (AC) was calculated from the densities of mortar and mortar components, obtained by measuring the weight of mortar that filled a PVC vessel of having a volume of 400 ml (NBR 13278/1995). The individual densities of cement, polymer and sand were determined by displacement in kerosene (cement and polymer) or water (sand).

Flexural strengths have been measured according to NBR 14992/03 with bars 300 mm x 25 mm x 25 mm. The test specimens were demoulded after 48 hours and then placed in a humidity chamber at (23±2)°C and > 90% relative humidity for the next 26 days when the three point bend test were carried out. For bond strength test, a single layered mortar, 6 mm thick, was applied on the back side of the porcelain ceramic tile, followed by the application of a 0.03 kgf/cm^2 load for 45 seconds to promote spreading of mortar over tile surface. The samples were stored at humidity chamber conditions for 28 days before the evaluation of bond strength between mortars and tiles determined with the pull-out method adapting the recommendations of NBR 14084/98. Eight squared sections were sawn in the mortar layer for each mortar and steel plates were glued to the mortar with epoxy adhesive for the loading application for bond strength measurement.

3. RESULTS AND DISCUSSION

3.1. EVA CHARACTERIZATION

Figure 1 shows the typical XRD curves obtained from both EVA under evaluation. The XRD curves have presented the characteristic pattern of amorphous materials with some crystalline peaks associated with inorganic materials (calcium carbonate and quartz for EVA1 and kaolinite for EVA2). These inorganic parts, known as anti-caking or blocking agents, are additives added to redispersible powders formulations in order to prevent the adhesion between polymer particles during manufacturing, transporting, and storage.

The amorphous feature of these polymers was expected considering the amount of vinyl acetate (VAc) in the EVA polymers. Poly(ethylene) is a semi-crystalline polymer and the introduction of VA groups reduces its degree of crystallinity due the distortion of unit cell due the bigger size of the acetoxy lateral group. The higher the VA side groups content the lesser is the degree of crystallinity of the copolymer, and it becomes completely amorphous when the VA content exceeds 50 wt%. As expected, in the amorphous EVA, the well defined peaks are substituted by one or two broader halos centred near the major peaks.

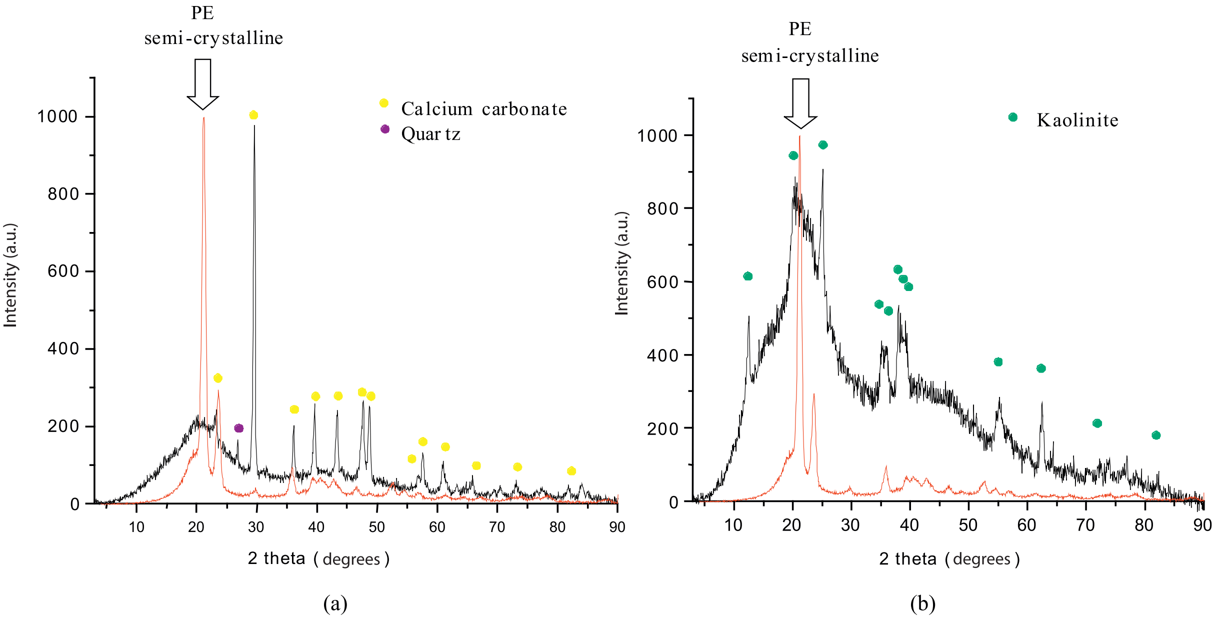


Figure 1. XRD curves from (a) EVA1 and (b) EVA2.

FTIR spectra have presented, as expected, specific peaks related to PE and PVAc (Figure 2 and Table 2). Also, vibrations associated with the inorganic fraction (quartz, calcite, and kaolinite), were verified. Infrared spectroscopy is used to determine the vinyl acetate incorporation into EVA copolymers using the ratio between the characteristic band of acetoxy group and ethylene sequences. Among the several different absorption ratios proposed in literature, the intensities ratio I_{610}/ I_{2680} (C=O / CH_2) was chosen to evaluate the amount of acetate in the copolymer. Based on the spectra, this ratio was calculated as (2.8±0.1) and (3.3±0.0) for samples EVA1 and EVA2, respectively. These results are in accordance with the data of Table 1 which indicates a higher acetate amount for sample EVA2.

Stress versus Elongation curves for EVA films are shown in Figure 3. From the curves, it can be seen that EVA1 specimens have presented lower tensile strength and elongation at break compared to EVA2 samples. The mechanical properties from latex films are a consequence of anti-caking agents, surfactants, and EVA resin, being very difficult identify the influence of each one of the components in the measured values. For the films obtained from EVA after extraction and solubilization in dichloromethane (DCM), it was observed a decrease in the tensile strength and an increase in the elongation at break for both polymers as compared to that of the properties of latex films.

3.2. MORTAR CHARACTERIZATION

The results of consistency tests done on reference mortar and modified mortars with p/c of 5%, 10% and 15% of latex are shown in Figure 4 for the two types of EVA under evaluation.

EVA1 has presented an increase of consistency (higher workability) for p/c ratio of 5% followed by a decrease for higher amounts of polymer reaching similar value to the obtained for reference mortar for p/c equal to 15%. On the other hand, the addition of EVA2 reduced the consistency of the mortar as the content of EVA was increased. Generally, latex modified mortar provides an improved workability over ordinary cement mortar, which was not verified for the polymers under evaluation. This increase in workability for mortars with latex addition is mainly due to the "ball bearing" action of polymer particles, the entrained air and the dispersing effects of surfactants.

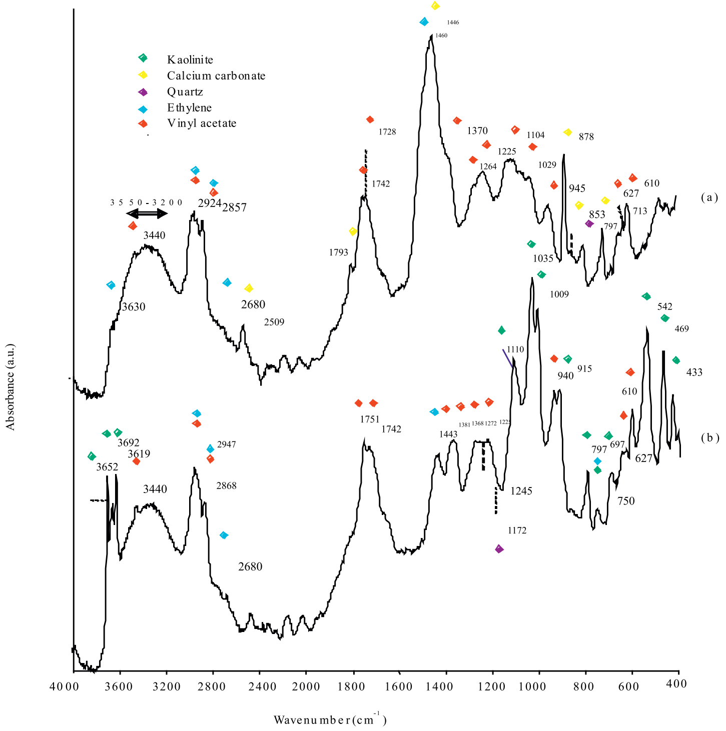
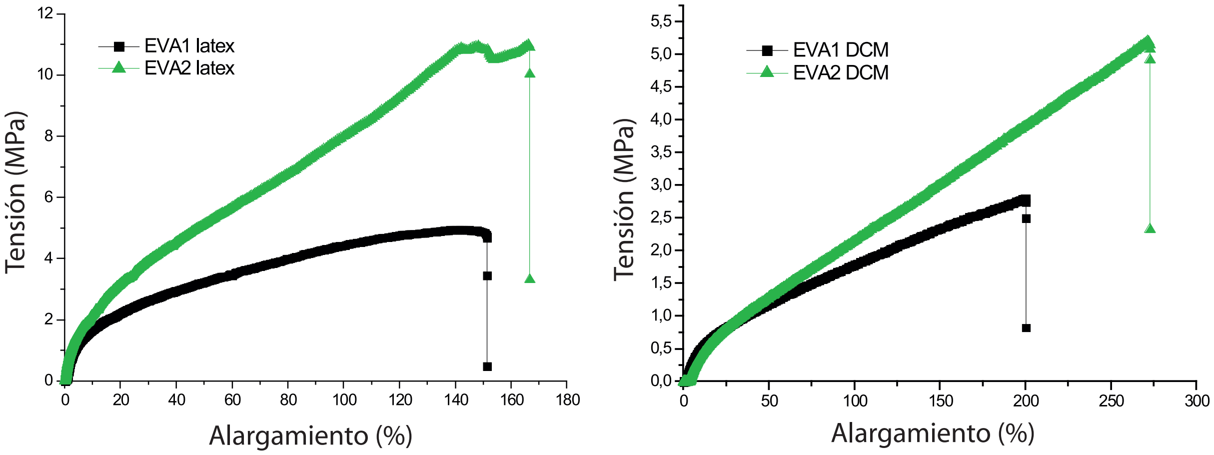


Figure 2. FTIR spectra obtained from (a) EVA1 and (b) EVA2.

Wavenumber (cm^{-1})	Functional Group	Wavenumber (cm^{-1})	Functional Group
3630-3620	CH_2 (ethylene)	1275-1200	C-O
3460-3350	C=O	1105-1100	C-O
3550-3200	OH	1030-1020	C-O, CH_3
2900-2850	C-H	950-940	C-C
2680	CH_2 (ethylene)	750-720	CH_2 (ethylene)
1742 (split)	C=O	635-625	O-C-O
1730-1725	C=O	610-600	C=O
1470-1440	CH_2 (ethylene), CH_3	540-530	C=O
1370-1380	CH_3	-	-

Table 2. Absorption bands of the EVA copolymers.

In the literature, it was observed that for modified mortars with EVA there was a slight increase in consistencies or the consistencies were kept practically constant. This can be explained by the fact that the measured consistency is the expression of the overall effect of the water to cement ratio, nature of the surfactant used for spray drying and redispersion, amount and molecular weight of this surface active agent. In several cases, the improved workability for modified mortars is a consequence of anionic surfactants that promote deflocculation of cement grains, releasing the entrapped water in the flocculated structure of cement paste. On the other hand, stabilizers that result in the increase of the viscosity of cement paste, as verified for PVA depending on the molecular weight and amount of PVA in the EVA powder, could reduce the consistency of mortar.



(a) (b)

Figure 3. Stress x Elongation curves for (a) EVA latex films and (b) EVA after solubilization in dichloromethane.

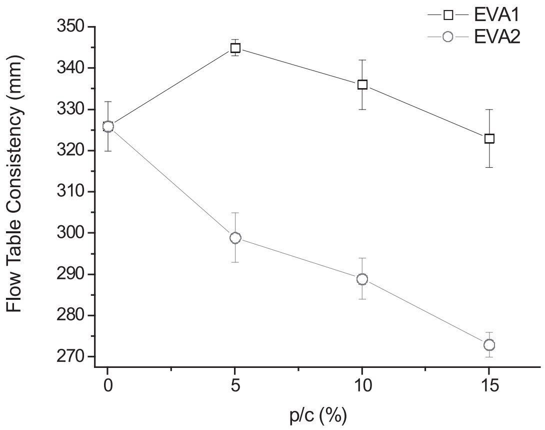


Figure 4. Flow table consistency values for the EVA copolymers under evaluation (n=2; error bar = standard deviation).

According to Table 1, both EVAs selected for this study were manufactured with PVA for latex particle stabilization. The differences observed in the values of consistency for the mortars modified with the two polymers could be related to variable quantity of PVA in both polymers. In literature, some authors have reported that latexes used in mortar modification are generally commercially manufactured with presence of up to 5% surfactants. Others, however, have indicated the presence of 15 wt% of PVA in EVA2 powder. In this sense, different amount of PVA could be expected for EVA1 and EVA2, the former presenting high amount of PVA as stabilizer. It should be noted that during mortar preparation and manipulation, the higher quantity of PVA in the EVA2 polymer was evidenced.

Based on that, it is believed that for EVA1 modified mortar with p/c = 5%, the "ball bearing" effect is more effective than the effect of the liquid phase viscosity. However, for higher amounts of polymer (p/c= 10% and 15%) the PVA viscosity effect is determinant in the measured consistency value. For EVA2, in all concentrations, the viscosity defines the consistency of the system.

Figure 5 illustrates the relationship between polymer to cement ratio and water retention of polymer modified mortar in fresh state. Addition of both polymers has increased the water retention of mortars compared to the reference one. According to literature, latex modified mortars have improved water retention over ordinary cement mortar. The reasons for this can be explained in terms of the viscosity of the liquid phase, the hydrophilic colloidal properties of the polymer latexes and the inhibited water evaporation due to the filling and sealing effects of impermeable polymer films formed.

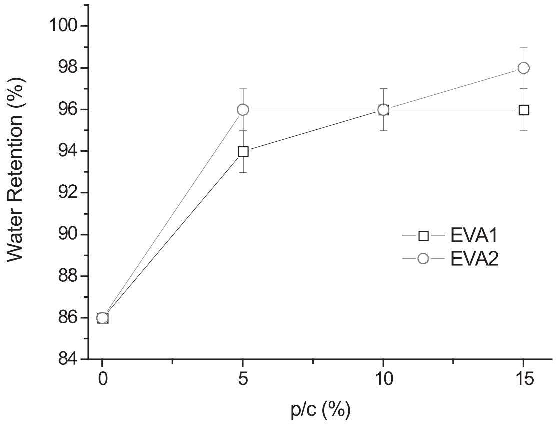


Figure 5. Water retention results for EVA modified mortars (n=2; error bar = standard deviation).

The air contents of the different mortars are shown in Figure 6. As expected, according to literature, a large quantity of air is entrained when compared to ordinary cement mortar because of the action of the surfactants that enhanced the stability of the air voids. It is remarkable the difference between the air content of mortar modified with EVA1 and EVA2. The obtained values are in agreement with the previous considerations about the higher content of PVA stabilizer in EVA2 compared to EVA1.

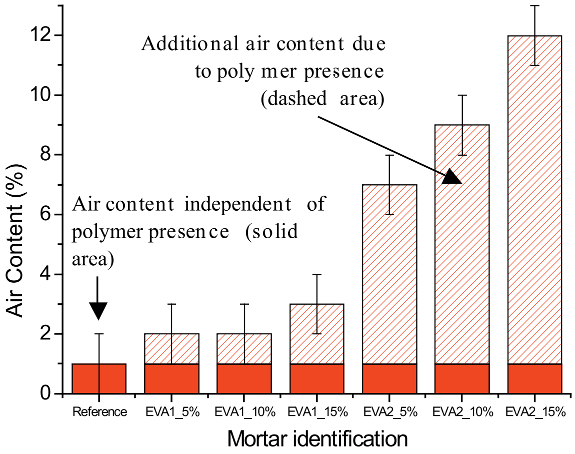


Figure 6. Air contents of mortars without (reference) and with latex.

The influence of the p/c ratio and the type of EVA polymer on the flexural strength of the modified mortar is shown in Figure 7. In EVA1 modified mortars (Figure 7a) there was a continuous decrease of the flexural strength with increasing polymer to cement ratio at constant water to cement ratio. On the other hand, it was noted in Figure 7b that the p/c ratio did not seem to influence the flexural strength of EVA2 modified mortar. It should be observed that the reduced resistance of EVA2 mortar with p/c = 5% is believed to be associated with the defects density at the surfaces of the specimens verified only at these samples (Figure 8).

Based on literature, the effect of polymer addition in flexural strength is influenced by various factors that tend to interact with each other. The main factors are the nature of polymer latex, polymer to cement ratio, water to cement ratio, air content, curing methods, among others. OHAMA (1998), SCHULZE (1999), and AFRIDI et al. (1994) reported that the flexural strength is increased by polymer resin modification with an emulsion or redispersible powder. The polymer is concentrated in the pore system of the hardened mortar and acts as reinforcement. This is attributed to the fact that the strength in tension of polymer material is in the order of 7-10 MPa while cement itself has tension strength only in the order of 1 MPa. For EVA modified mortars some authors have described a slightly increase of flexural strength for lower polymer concentration. For higher polymer content the strengths were kept at the same level or reduced. In general, this loss in mechanical properties is related to mortar air content, non-continuous film formation, retardation of hydration reactions and the mechanism of composite formation.

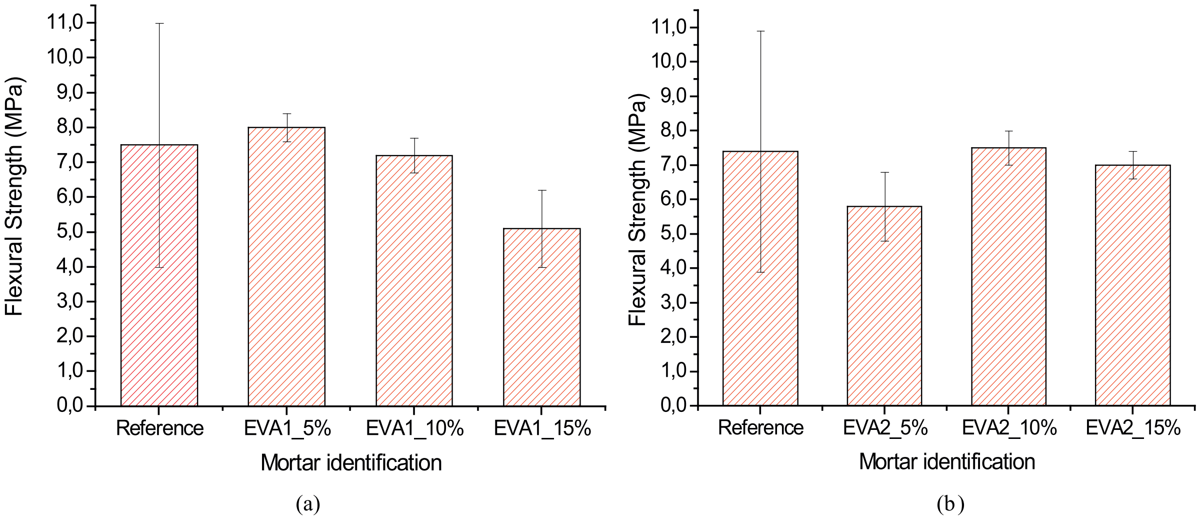


Figure 7. Flexural strength for modified mortars with (a) EVA1 and (b) EVA2.

The flexural strength results obtained in this work may be explained considering the volume of polymer in the hardened mortar and the strength of the polymer latexes EVA1 and EVA2 (Figure 9). In the determination of the volumetric fraction of each mortar component it was considered that 70% of cement was hydrated, that there was no water loss from mortar or drying shrinkage. The percentage volumetric fraction of each component was calculated following the methodology proposed by NEVILLE (1982).

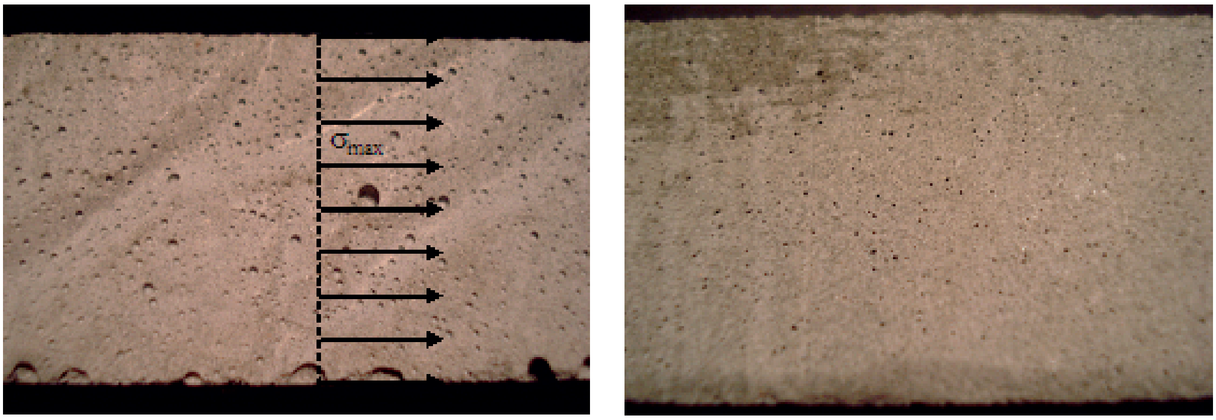


Figure 8. Surface image from EVA2_p/c = 5% (a) and typical image for all the other samples surface specimens (b).

Based on the graph of Figure 9, raising the polymer level, the concentration of the polymer per volume is increased and the overall resistance of the hybrid matrix will be a consequence of the contribution of each phase, organic and inorganic. The resistance of the reference mortar is about 7 MPa and this value has changed (EVA1) or unaltered (EVA2) when polymer was added (Figure 7). The explanation for the tendency observed for each latex can be evaluated through EVA films tension strength previous determined in Figure 3. EVA1 and EVA2 strengths are about 4 MPa and 8 MPa, respectively. In this sense, increasing the polymer to cement ratio raises the polymer contribution to the final resistance. As EVA1 has presented lower strength than inorganic matrix, an increase on its content leads to a lower resistance while for EVA2, due to its similar strength to reference mortar, same resistance level is expected, as observed.

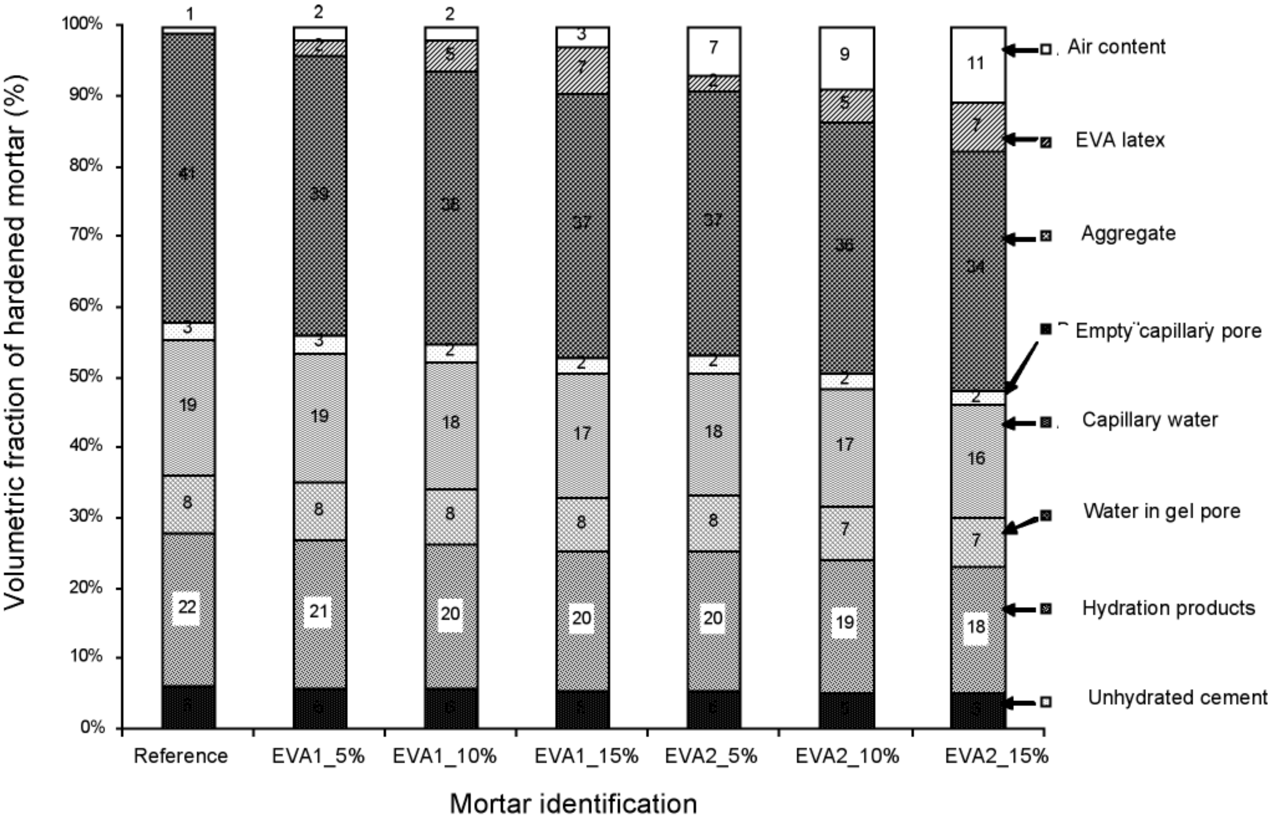


Figure 9. Percentage fraction of hardened mortar occupied for each one of the components considering air content.

4. CONCLUSIONS

The results of XRD, FTIR, and mechanical tests allow us to characterize and differentiate both EVA products. The global features of polymers are a consequence of the polymer composition and type and kind of surfactant and anti-caking agent. Also some properties of the EVA films in mortars may be predicted. Mortar tests evaluation showed that the surfactant used in the process to obtain the powder polymer greatly affects mortar properties at fresh state. Water retention was also a consequence of latex particles presence. Flexural strength values measured were an outcome of EVA film mechanical properties.

5. ACKNOWLEDGMENTS

The authors acknowledge the financial support of CNPq. Also, they thank to Precon Industrial S.A. for kindly donating polymer samples.

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