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Pore size distribution of hydrated cement pastes modified with polymers

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Abstract

Mercury intrusion porosimetry (MIP) tests were performed on pure and polymer-modified cement pastes in order to evaluate the influence of hydroxyethyl cellulose (HEC polymer) and vinyl acetate/ethylene copolymer (EVA) on the pore size distribution. Cement pastes containing 0%, 10%, and 20% of EVA and 0%, 0.5%, and 1.0% of HEC of the weight of cement were prepared and the water/cement ratio was kept constant (0.4). The effects of two curing methods (*dry cure:* 27 days at 23°C and 75% relative humidity (RH); *mixed cure:* 7 days at 23°C under sealed conditions and 20 days at 23°C and 75% RH) were also evaluated. Analysis of variances (ANOVA) showed that the most important factors affecting pore size distribution are the curing method and EVA content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cement paste; Polymer; Pore size distribution; Mercury porosimetry

1. Introduction

Polymers are employed as mortar and concrete modifiers due to the improvement of some properties such as fracture toughness, impermeability, durability, and bond strength to various substrates [1]. Water retention capacity and rheology are also improved. Basically, four polymeric compounds are used for these purposes: latexes or polymeric dispersions, redispersible powders, water-soluble polymers, and liquid polymers [2]. Some examples of polymer-modified cement-based materials currently used on construction sites are adhesive mortars for ceramic tile installation (dry-set mortars), structural repair mortars, overlays for bridge and parking decks, and impermeable mortars.

Research dealing with polymer addition in mortars for ceramic tile installation started in the 1960s in Europe and the USA. Methylcellulose was the most studied water-soluble polymer. The effects of other cellulosic water-soluble polymers on mortar properties have also been investigated, and they have been used for adhesive mortar production [3].

Nowadays in Brazil, most adhesive mortars are modified with water-soluble polymers and water-redispersible powders. Hydroxyethyl cellulose (HEC) and vinyl acetate/ethylene copolymer (EVA) are the most employed. HEC is a water-soluble polymer added in powder form to dry materials (cement and aggregates). After dissolution in water, it forms a gel and has major effect on fresh mortar properties, such as water retention capacity, rheology, and adhesiveness. EVA is a water-redispersible powder, and is also added to anhydrous cement and aggregates before mixing with water. EVA markedly influences hardened mortars behavior [4].

One of the most important characteristics of adhesive mortars is the pore structure since it affects the hardened mortars' behavior. Some mortars properties can be estimated from pore size distribution and total porosity. According to Ohama et al. [5], the total pore volume of the polymer-modified mortars, determined by mercury porosimetry, tends to decrease with an increase in polymer/cement ratio and decrease in water/cement ratio. However, the isolated effect of polymer/cement ratio was not studied, since in these experiments the water/cement ratio is changed to produce mortars with the same consistency.

The purpose of this study is to evaluate the effects of EVA and HEC on the pore structure of adhesive mortars by mercury intrusion porosimetry (MIP). Portland cement

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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	LOI	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)	$\phi < 45$ μm (%)	Compressive strength (MPa) water/cement 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

pastes were modified with different contents of both polymers. The water/cement ratio was kept constant in order to evaluate the actual effect of polymers. The threshold diameter, total pore volume, and pore size concentration over four distinct diameter ranges were evaluated and the paste behavior was then estimated.

2. Materials, experimental design, and methods

Materials employed for preparation of the pastes were ordinary Portland cement with up to 5% of limestone filler (type CPI-S 32 according to Brazilian standard NBR 5732/91), deionized water, water-redispersible EVA powder and water-soluble HEC powder. Tables 1 and 2 present the materials characteristics.

The following procedure was employed for paste mixing: (i) dry mixing of polymers and cement, in a low-speed mechanical mixer for 120 s, (ii) dry mixture flowing over deionized water, (iii) paste mixing in 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 × 50 mm ($d \times h$). They were then sealed and rotated on rollers in horizontal position (approximately 20 rpm) up to initial setting for bleeding prevention. The temperature and relative humidity (RH) in the laboratory were approximately 23°C and 80%, respectively.

Table 3 summarizes the experimental design adopted. The actual polymer contents in the mixtures were 10% and 20% of EVA and 0.5% and 1.0% of HEC of cement weight. These contents were corrected due to the presence of inorganic compounds in the polymer powders, measured by the ash content (Table 3). Consequently, EVA polymer/cement ratios of 10% and 20% were obtained by adding, respectively, 10.8% and 21.6% (of the weight of cement). For HEC actual contents of 0.5% and 1.0%, 0.51%, and 1.03% were added.

The water/cement ratio was kept constant at 0.4, in weight basis. The effect of different curing methods was also studied. Half of the specimens were submitted to *dry cure* (75% RH after demoulding, which was done 24 h after casting) until the age of 28 days. *Mixed cure* was applied to the other half of the specimens, which 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 carbonation prevention and maintenance of RH at 75%, all specimens were stored during the curing period in a CO_2-free, air-tight 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.

Since it can affect the pore size distribution, the degree of cement hydration was estimated by the determination of nonevaporable water contents in a Netzsch STA 409EP thermal analyzer. Thermogravimetric curves were determined using 30 mg pulverized samples ($\phi < 65$ μm) at a heating hate of 10°C/min, in N_2 flowing at 40 cm^3/min. Nonevaporable water contents (related to the ignited weight of cement) were considered as the weight losses between 170°C and 1000°C, as recommended by Taylor [6]. The contributions from other volatiles, as CO_2 from carbonate phases and acetic acid from EVA, were discounted.

3. MIP experimental procedure

At 28 days old, the specimens were cut with a diamond saw and four 1.0 ± 0.2 mm thick slices were taken from different regions. Ethyl alcohol was used to cool the saw.

Table 2
Physical characteristics of EVA and HEC polymers

EVA	
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]	approximately 4°C
HEC	
Ash content (30 min at 1000°C)	2.47%
Apparent density[a]	579 g/l
Particle size (laser granulometry in ethanol)	6% over 250 μm
Molecular weight[b]	1,900,000
Polymerization degree[b]	7,600
Viscosity (2% aqueous solution)[b]	100,000 mPa s

[a] Characteristics determined by mercury intrusion porosimetry.
[b] Characteristics informed by the polymer producer.

Table 3
Variables involved in the experiment

Designation	Independent variable (factor)	Levels
A	EVA content (percent of cement weight)	0, 10, and 20
B	HEC content (percent of cement weight)	0, 0.5, and 1
C	curing method	dry (− 1) and mixed (+ 1)
D	pore size ranges	1: $\phi < 10$ nm 2: 10 nm $< \phi <$ 50 nm 3: 50 nm $< \phi <$ 1 μm 4: $\phi >$ 1 μm

The slices were then immersed on ethyl alcohol and submitted to 20 min in ultrasonic cleaning equipment, manually fragmented, and stored in alcohol for at least 6 days for hydration interruption and solvent replacement drying.

Before the test, the pieces were removed from the alcohol and vacuum-oven-dried at 40°C for 25 h. This procedure is a variation of the method recommended by Feldman and Beaudoin [7] for specimen preparation to MIP, since temperature as high as 100°C, as suggested by the authors, can degrade the polymers.

For pore size distribution of polymer-modified pastes, a Micromeritics Autopore III 9420 porosimeter was employed, which is able to apply a pressure of 414 MPa. The assumptions were 485 dyn/cm mercury surface tension and 13.5413 g/cm^3 mercury density. Equilibration time in both low and high pressure was 60 s. Sample weight was approximately 1.0 g. Since there are no references for EVA- or HEC-modified pastes, the advancing/receding contact angle was assumed to be 130°, as recommended by Taylor [8] for ordinary cement pastes.

For the analysis of the results, the intruded mercury values (intruded mercury volume by sample unit mass, in milliliters per gram) were arranged within four distinct pressure ranges corresponding to different pore size ranges. Pressure and pore size values are related by the Washburn equation (Eq. (1)) [9], where d is the diameter equivalent to the mercury filled pores, γ is the mercury surface tension, θ is the contact angle between mercury and pore walls, and p is the pressure applied.

$$d = \frac{-4\cos\vartheta}{p} \tag{1}$$

Due to some technical problems during the last pressure step application, the maximum pressure considered for results analysis was 375.7 MPa, which is related to 3.9 nm pore diameter.

The selected pore size ranges permits a good approach to paste properties based on intruded mercury volumes. According to Jennings [10], Taylor [8], and Mehta and Monteiro [11], these pore size ranges can be correlated to paste properties as shown in Table 4.

Statistical analysis was carried out by ANOVA (analysis of variances) in order to estimate the effect of some factors on the pore structure of the pastes. The commercial software *Statgraphics Plus for Windows* was used. In the first analysis, the contents of EVA and HEC (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 threshold diameter and the total intruded mercury volume. In the second analysis, the pressure applied by the porosimeter (related to pore diameter by the Washburn equation) was also considered as a controllable factor, and the intruded mercury volume by sample weight unit (in milliliter per gram) arranged in four pore diameter ranges was the dependent variable. Duplicate intrusion tests on a single set of castings were performed for each treatment. However, some treatments were tested more than twice in order to take maximum advantage of the prepared samples. Actually, 4 and 20 additional tests were performed, totalizing 40 and 164 tests on the first and second analysis, respectively.

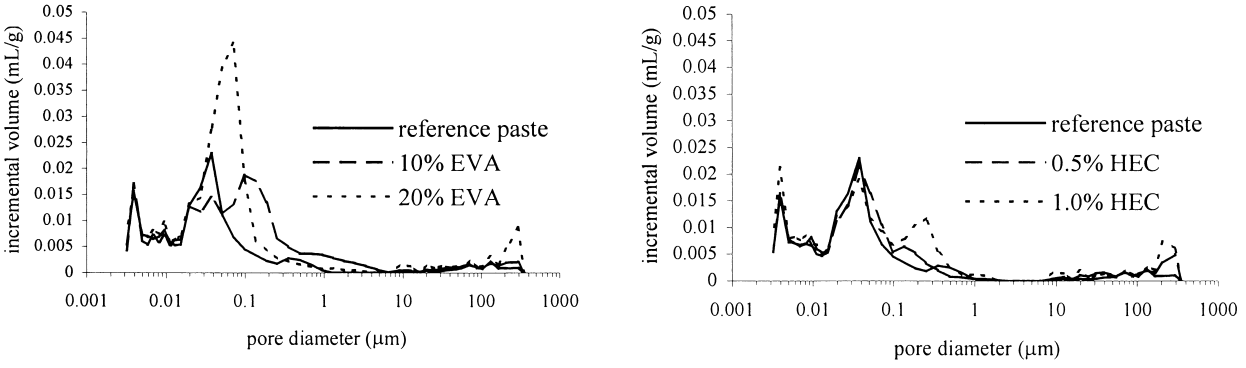
4. Results and discussion

Fig. 1 shows the characteristic curves of intruded mercury volume in function of pore diameter (incremental volume) for mixed-cured pastes. It is possible to observe that pore size distribution curves of pure (reference) pastes and HEC- and EVA-modified pastes typically exhibit at least two peaks. The first one lies approximately at the 3.9-nm diameter, while the second and sharpest one corresponds to a diameter around 40–75 nm. For dry-cured pastes (results not shown), the profile is quite the same, but the diameter values for the second peak are higher, as expected.

For HEC-modified pastes, a third peak appears in the diameter range of 100–500 nm, corresponding to large capillaries according to Table 4. The higher the HEC content, the sharper is the peak. This behavior is probably related to the water retention capacity of the polymer, since the water/cement ratio (0.4) assures higher quantity of water

Table 4
Classification of pore size in hydrated cement paste and properties affected

Designation	Pore diameter	Level code	Properties affected
Hydrated phases ("gel") porosity	< 10 nm	1	shrinkage and creep
Medium capillaries	10–50 nm	2	strength, permeability, creep, and shrinkage at high RH
Large capillaries	50 nm–1 μm	3	strength and permeability
Large capillaries and entrained air	>1 μm	4	strength



(a) (b)

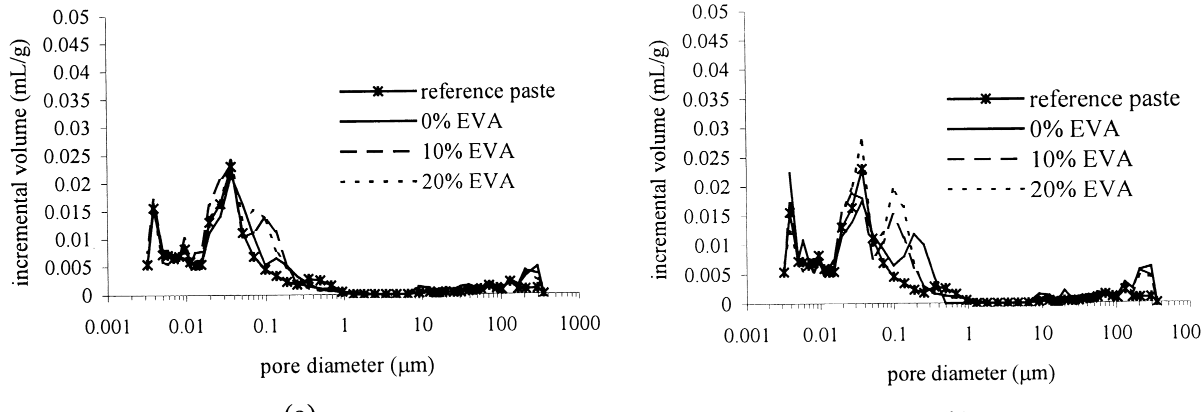
Fig. 1. Typical pore size distribution of (a) EVA- and (b) HEC-modified, mixed-cured pastes.

than is necessary to completely hydrate the cement grains [10]. The excess of water remains in capillary pores and is lost in drying procedures. A fourth, less sharp peak, could be observed on some modified pastes probably due to entrained air (pore width larger than 100 μm).

The maximum concentration of pores in the reference paste lies in the range 16–100 nm, and changes to 50–300 nm for 10% EVA pastes (Fig. 1). For 20% EVA addition, the profile is much different, indicating that a great volume of mercury has intruded on the pore size ranging from 16 to 160 nm. This behavior can be attributed to the material characteristic itself and to the test method, which is capable of applying high pressures on the sample. The EVA used in this research has a film-forming ability on drying out. Indeed, micrographs obtained by the authors show the presence of polymeric film that partially seals the pores and is responsible for the water tightness of EVA-modified pastes [12]. The higher the polymer content, the higher the pressure necessary to intrude the mercury into partially sealed pores, causing a great mercury intrusion at once. Besides, the polymeric films probably endure great volume contraction under compression, increasing the apparent porosity when the sample is subjected to the MIP test. These phenomena can explain part of the porosity modification observed. They must be taken into account when analyzing pore size distribution measured by MIP.

Figs. 2 and 3 show the effect of adding both polymers in the same paste. EVA addition in HEC-modified pastes increases the intruded mercury volume in the pore size range between 50 and 250 nm, enlarging the third peak. On the other hand, higher HEC contents in EVA-modified pastes decrease the pore size concentration in these ranges (large capillaries) relative to pastes with the same amount of EVA and without HEC. This effect is opposite to that observed for HEC addition on pure pastes, probably due to a physical interaction between both polymers in the same aqueous solution.

It was possible to obtain information about the threshold diameter, which is the maximum pore diameter at which the continuous mercury intrusion begins [13]. According to Cook and Hover [14], it may provide a good indication of cement paste permeability and diffusion characteristics. The threshold diameter can be obtained from the incremental curves of intruded volume, where there is a rapid increase in dV/dD [7], or from the inflection point of accumulated curves, which signals the formation of the sample-spanning



(a) (b)

Fig. 2. Effect of EVA addition on pore size distribution of (a) 0.5% and (b) 1.0% HEC-modified, mixed-cured pastes.

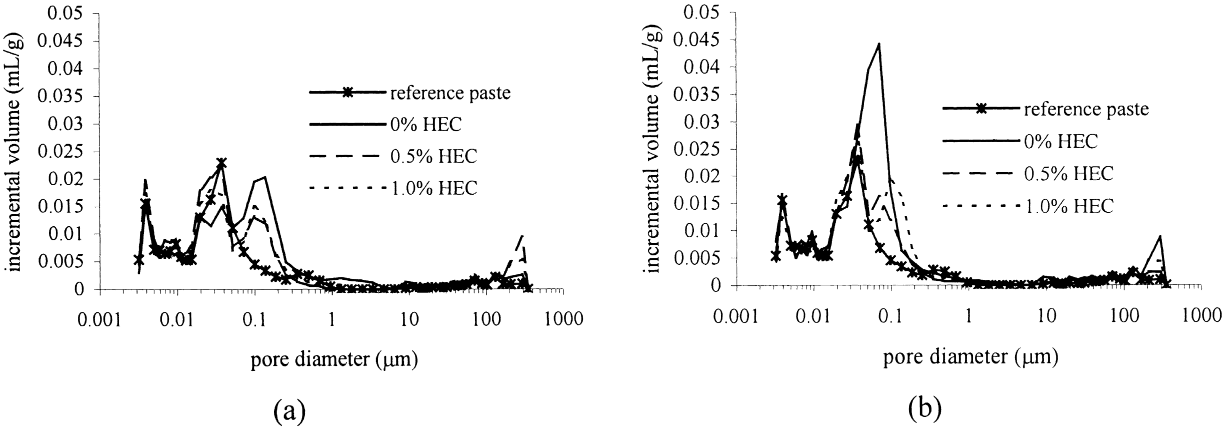


Fig. 3. Effect of HEC addition on pore size distribution of (a) 10% and (b) 20% EVA-modified, mixed-cured pastes.

cluster [15]. In this experiment, the threshold diameter is the smallest diameter with differential intrusion volume ≥ 0.0004 ml/g, which corresponds to zero intrusion when rounded up to three decimal places.

Table 5 shows the results of the ANOVA for threshold diameter and total intruded mercury volume data. EVA and HEC contents, and the interaction between them, are significant factors. Fig. 4 graphically shows their effects. HEC has major effect on the reduction of the threshold diameter of EVA-modified pastes (Fig. 4a), and pastes with 0.5% HEC, regardless the EVA content, show the minimum values. The threshold diameter of EVA-modified pastes determined by MIP is related to the formation of the polymeric film in the pores, besides other factors inherent to cement based materials, like the degree of cement hydration. As shown in Fig. 4a, the effect of EVA depends on the HEC content, but in a general manner it increases the threshold diameter. The higher threshold diameter of 10% EVA compared to 20% EVA-modified pastes (dry- and mixed-cured) might be related to the lower strength of its film, which probably shows faster disruption by the high-pressure mercury intrusion.

The effect of HEC on total pore volume (Fig. 4b) depends on the EVA content. For non-EVA-modified pastes, HEC increases the total pore volume, and the opposite effect is observed for EVA-modified pastes. The higher the EVA content, the higher the HEC effect. Another interpretation is that, in presence of 1% or 0.5% HEC, EVA addition up to 20% does not significantly affect the pore size distribution of the paste. These results permit the authors to conclude that, since HEC is added on a small volume and its main effect is to convert water into a gel, it actually modifies the effect of EVA when the paste is still fresh.

Table 6 presents the results of the ANOVA for intruded mercury volume data. Fig. 5 graphically presents all two-factor interactions. As can be seen, all factors significantly affect total intruded mercury volume. This effect can be direct, as in the case of pressure (Factor D: Pores) and EVA content (Factor A), or it can appear as an interaction (AB, AD, BD, and CD are significant interactions). Pressure exerts the major effect, since it is associated to test procedures.

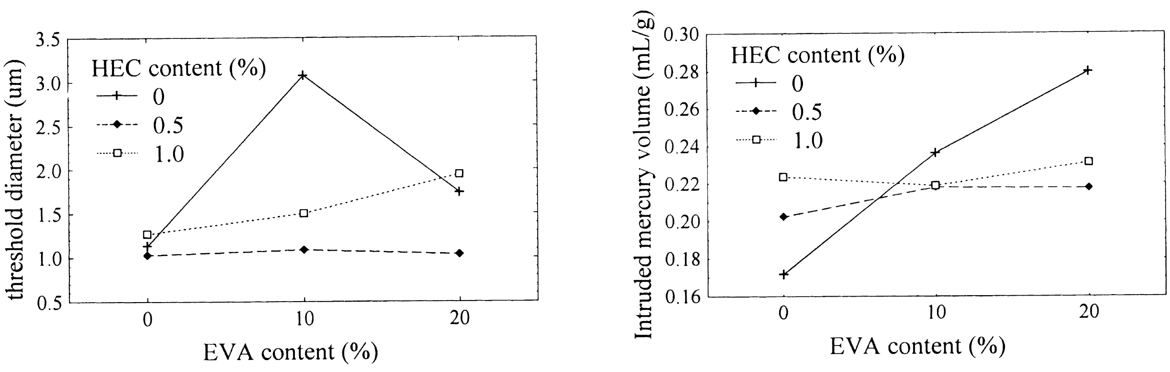
The interaction between pressure (or pore size distribution) and curing method (CD interaction) is the next major effect. The analysis of the influence of curing type on pore

Table 5
ANOVA for threshold diameter (TD) and total intruded mercury volume (TV) data

Factor	Sums of squares TD	Sums of squares TV	*df*	Mean squares TD	Mean squares TV	*F* test[a] TD	*F* test[a] TV	*P* value TD	*P* value TV
Manner effects									
A: EVA content	3.63353	0.011437	2	1.816763	0.005718	**4.507**	**29.517**	**.0209**	**.0000**
B: HEC content	5.73246	0.001955	2	2.866230	0.000978	**7.111**	**5.046**	**.0034**	**.0141**
C: Curing method	1.00827	0.000571	1	1.008265	0.000571	2.501	2.948	.1258	.0979
Interactions									
AB	5.73474	0.013041	4	1.433684	0.003260	**3.557**	**16.828**	**.0192**	**.0000**
AC	1.97391	0.000163	2	0.986953	0.000082	2.440	0.422	.1061	.6602
BC	4.17796	0.000406	2	2.088980	0.000203	**5.182**	1.049	**.0127**	.3646
Residual	10.48007	0.005037	26	0.403079	0.000194				
Total	24.48686	0.030010	39						

Items with factors statistically significant appear in bold.

[a] All *F* tests were carried out using the error term, which was achieved using the three-factor interaction.



(a) (b)

Fig. 4. Effect of EVA and HEC contents on (a) threshold diameter and (b) total mercury volume.

size distribution shows that mixed cure results are greater on pore concentration below 50 nm, which corresponds to hydrated phases and medium capillary pores (Fig. 5a). On the other hand, dry-cured specimens have greater concentration of pores larger than 50 nm, which mainly affect paste strength and permeability. These results show that the seven initial days of sealed cure cause pore structure refinement, and are in accordance with the known behavior of cement-based materials. The addition of EVA and/or HEC (interaction AC and BC on Table 6) to the paste does not significantly change the effect of curing (Fig. 5d and e).

EVA does affect the porosity in a statistically significant way, increasing the porosity in large capillary pores and air entrained pores. This increase can be as great as 40% for 20% EVA content. This effect is much more important on Ranges 2 and 3 (10–1000 nm) as shown in Fig. 5b. According to Mehta and Monteiro [11], these ranges directly affect some properties of cement-based materials such as shrinkage, creep, strength, and permeability. Since EVA increases the pore concentration in these ranges, one can suppose that it is responsible for greater shrinkage, creep deformations, and permeability, besides lower strength values at a given age. However, according to Chandra and Ohama [16], the permeability of EVA-modified pastes is lower than pure pastes. Permeability tests performed by the authors also show the same result. This contradiction might be related to the MIP test method itself, which applies high pressures capable of damaging the thin polymeric film, which seals the pores. Therefore, for EVA-modified pastes the correlation between permeability and MIP results may not be correct.

Table 6
ANOVA for intruded mercury volume data

Factor	Sums of squares	*df*	Mean squares	*F* test[a]	*P* value
Manner effects					
A: EVA content	0.00284515	2	0.00142257	**17.17**	**.0000**
B: HEC content	0.000498575	2	0.000249287	3.01	.0527
C: Curing method	0.000062651	1	0.000062651	0.76	.3861
D: Pore size range	0.0799254	3	0.0266418	**321.61**	**.0000**
Interactions					
AB	0.00336459	4	0.000841147	**10.15**	**.0000**
AC	0.0000442104	2	0.0000221052	0.27	.7662
AD	0.00495294	6	0.000825489	**9.97**	**.0000**
BC	0.0000453231	2	0.0000226615	0.27	.7611
BD	0.00345554	6	0.000575923	**6.95**	**.0000**
CD	0.017665	3	0.00588834	**71.08**	**.0000**
Residual	0.0109347	132	0.0000828385		
Total	0.12598	163			

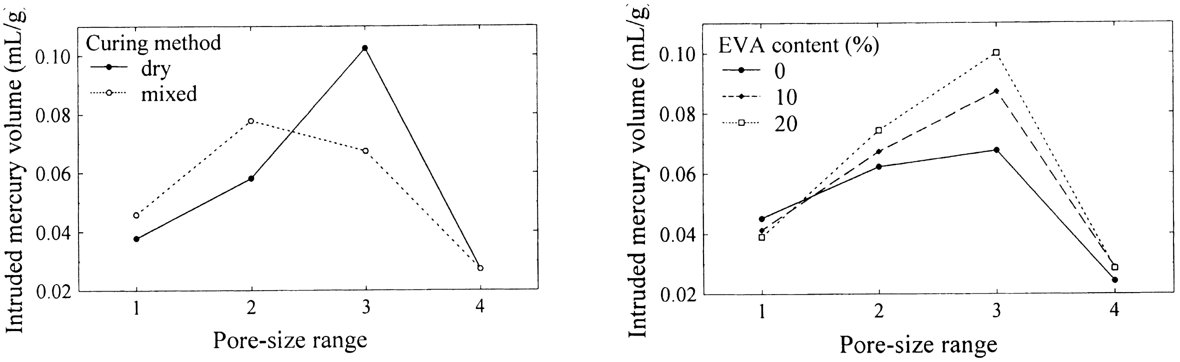
Items with factors statistically significant appear in bold.

[a] All *F* tests were carried out using the error term, which was achieved using the three- and four-factor interaction.

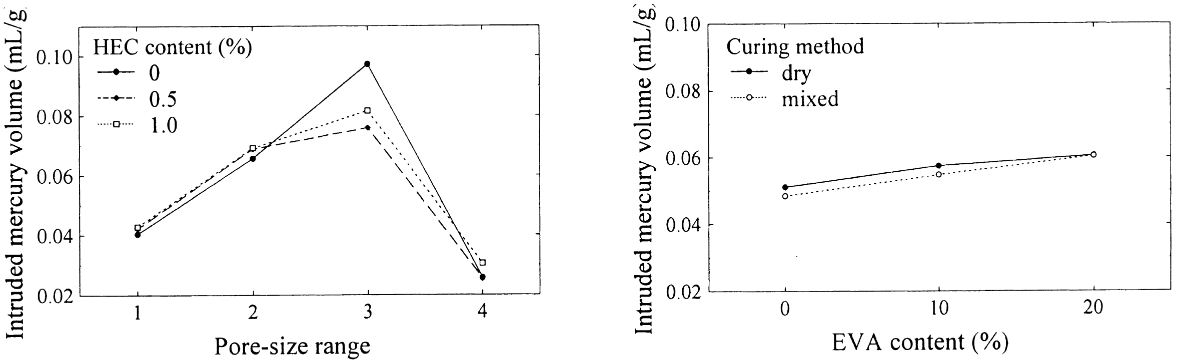
Fig. 5b also shows a slight reduction of hydrated phases porosity ($\phi < 10$ nm) of EVA-modified pastes, which might be due to the presence of polymeric film that seals pores or it might be related to a morphological change on phases microstructure due to an interaction between cement and polymer. Researchers have pointed out the formation of hydrated phases from this kind of interaction [16,17], which might be responsible for a lower porosity in this diameter range. According to Chandra and Flodin [18], the interaction between polymers and $Ca(OH)_2$ can result in large aggregate formation, and this fact might reduce porosity. A lower degree of cement hydration in the presence of EVA could also cause such reduction.

The effect of adding HEC is a small decrease in pores volume mainly on the same range 3 affected in the opposite way by EVA (Fig. 5c). However, for pastes without EVA the effect of adding HEC is to increase the porosity, as already seen in Fig. 4b. This apparent contradiction is a consequence of the interaction between HEC and EVA.

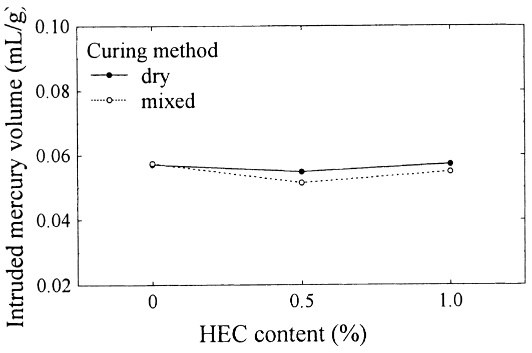
It must also be considered that, as observed by the authors on SEM micrographs, the polymer partially covers the pore walls, probably changing the mercury contact angle. However, such a change only affects the peak diameters of incremental curves, but not the relative peak positions nor the pore volume estimation. It can be concluded that the interpretation of MIP data based on simple changes of peak positions must be carried on carefully.



(a) *Pressure (pores) x curing method.* (b) *Pressure (pores) x EVA content.*



(c) *Pressure (pores) x HEC content.* (d) *EVA content x curing method.*



(e) *HEC content x curing method.*

Fig. 5. Graphic showing the effects of two-factor interactions on the intruded mercury volume.

Table 7 shows the nonevaporable water contents estimated by thermogravimetric analysis (TG). Unfilled cells are due to the experimental design. It can be seen that, regardless the HEC content, EVA reduces the degree of hydration of dry-cured pastes. Its slighter effect on mixed-cured pastes is related to the curing method itself, which maintains more water available for cement hydration for 7 days. While EVA's major effect is to decrease the cement hydration of pastes submitted to dry cure, HEC increases the nonevaporable water for both curing methods, but its effect is weaker than EVA effect.

Table 7
Nonevaporable water contents (%) obtained from TG[a]

HEC content (%)	0	0	0	0.5	0.5	0.5	1.0	1.0	1.0
EVA content (%)	0	10	20	0	10	20	0	10	20
Dry-cured pastes	12.11		6.12		11.26		11.75		8.54
Mixed-cured pastes		8.25		12.03	10.85	10.13		10.83	

[a] Average of two samples.

From these results, it is possible to conclude that the higher volume of capillary pores in only-HEC-modified pastes cannot be attributed to a lower degree of cement hydration. On the other hand, the higher capillary pore volume observed on EVA-modified pastes might in part be due to the lower cement hydration. Its stronger effect under dry cure conditions might be related to a retardation of hydration reactions and to a quick release of water when the paste is demoulded.

5. Conclusions

From the MIP tests performed with EVA and/or HEC-modified cement pastes it was possible to conclude that:

1. Pore size distribution curves of pure and polymer-modified pastes show at least two peaks corresponding to micropores and capillaries that lie around 3.9 and 40–75 nm, respectively. High contents of HEC change this profile, and the curve shows two more peaks. This is probably due to the lower degree of cement hydration, to the transformation of water into a gel and, for larger pores, to the air entrainment effect. EVA strongly increases the main peak, especially at 20% content.

2. As expected, pore size distributions of polymer-modified pastes are greatly governed by the curing method. Seven initial days of sealed cure were able to sharply reduce pore size concentration in the range of 50 nm to 1 μm.

3. The effect of EVA and HEC on porosity depends on the interaction of polymers. On plain pastes, EVA increases the porosity up to 40%. When in the presence of HEC, the addition of EVA causes smaller changes on porosity. Since the effect of HEC is mainly to transform the mixing water into a gel, it modifies the effect of EVA on porosity, and the polymers interact when the paste is still fresh.

4. Compared to reference paste, EVA increases the threshold diameter of hydrated cement pastes. Nevertheless, the data published on permeability of EVA-modified mortars show that it causes a reduction in permeability. This apparent contradiction can be due to the disruption of the polymeric film during the mercury intrusion under high pressure.

5. The higher capillary pore volume of HEC-modified pastes measured by MIP is not related to the degree of cement hydration. However, for EVA-modified pastes, the higher capillary and total pore volume of the pastes might be due to a lower hydration degree.

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