

EFFECTS OF POLYMERS USED FOR DRY-SET MORTAR PRODUCTION ON PERMEABILITY AND PORE-SIZE DISTRIBUTION OF CEMENT PASTES

D.A. Silva^(*); H.R. Roman^(*); Alarcon, O.E.^(**)

^(*)Building Research Centre, Federal University of Santa Catarina, Brazil

^(**)Materials Laboratory (LabMat), Federal University of Santa Catarina, Brazil

ABSTRACT

HEC and EVA polymers are currently used in Brazil for the production of dry-set mortars, which are used for the installation of ceramic tiles. In spite of the widespread application in construction sites, the knowledge of physical interactions between the polymers, cement and aggregates is poor. Since the system is not known at all, it is hard to improve its performance. The purpose of this paper is to fill some of this lack of knowledge, presenting the results obtained in porosimetry and permeability characterization tests on HEC and/or EVA modified pastes. Mercury intrusion porosimetry and N₂-gas permeability tests were performed. Pastes containing 0, 10 and 20% of EVA, and 0, 0.5 and 1.0% of HEC were prepared, quantities relative to the weight of cement. The water/cement ratio was kept constant at 0.4. The pastes were subjected to dry and mixed curing, and tested 28 days old. The results of the analysis of variances have shown that EVA content and the curing method are the most important factors to affect the porosity of cement pastes. On the other hand, HEC content strongly reduces cement paste permeability, without sharp changes in the porosity. No correlations were found between the results of mercury intrusion porosimetry and permeability tests, probably due to the rupture of EVA film when subjected to high pressures, and to the microcracking of the pastes modified with HEC when subjected to strong drying procedures.

1. INTRODUCTION

Most dry-set mortars for ceramic tile installation have HEC and EVA polymers as additives, since they improve some mortar properties in the fresh and hardened states. After dissolution in water, HEC forms a gel and has a major effect on fresh mortar properties, such as water retention capacity, rheology and adhesion. EVA is a water-redispersible powder, and is also added to anhydrous cement and aggregates before mixing with water. EVA markedly influences hardened mortar behavior (SILVA et al., 2000).

One of the most important characteristics of adhesive mortars is pore structure since it affects hardened mortar behaviour. Some mortar properties can be estimated from pore-size distribution and total porosity. According to OHAMA et al. (1991), 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.

Permeability tests can give good information about the durability of cement-based materials and is closely related to the pore characteristics of such materials. The addition of polymers to cement based materials can significantly alter their permeability properties.

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) and permeability. Portland cement 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. The permeability of the pastes to N₂-gas was also estimated.

2. MATERIALS AND EXPERIMENTAL DESIGN

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), de-ionized water, water-redispersible EVA powder (vinyl acetate/ethylene copolymer) and water-soluble HEC powder (hydroxy-ethyl cellulose). Tables 1 and 2 present the materials characteristics.

Chemical Analysis (%)												
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O 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				

Table 1. Characteristics of Portland Cement.

Vinyl acetate/ethylene copolymer (EVA)	
Ash content (30 min. at 1000°C)	7.63 %
Apparent density of the powder (*)	529 g/l
Particle size (laser granulometry in ethanol)	11% above 250µm
Minimum film forming temperature (**)	Approx. 4°C
Hydroxy-ethyl cellulose (HEC)	
Ash content (30 min. at 1000°C)	2.47 %
Apparent density (*)	579 g/l
Particle size (laser granulometry in ethanol)	6% over 250µm
Molecular weight (**)	1,900,000
Polymerization degree (**)	7,600
Viscosity (2% aqueous sol.) (**)	100,000 mPa.s

(*) characteristics determined by mercury intrusion porosimetry

(**) characteristics informed by the polymer producer

Table 2. Physical Characteristics of EVA and HEC Polymers.

The following procedure was employed for paste mixing: i) dry mixing of polymers and cement, in a low speed mechanical mixer for 120 seconds; ii) dry-mixture flowing over de-ionized water; iii) paste mixing in low speed mechanical mixer for 120 seconds; iv) paste resting for 15 minutes; v) remix for 15 seconds; vi) casting in hermetic polyethylene cylindrical flasks of 30mm (d) by 50mm (h) for porosimetry tests and 37mm (d) by 60mm (h) for permeability tests. They were then sealed and rotated on rollers in horizontal position (approximately 20 r.p.m.) up to initial setting for bleeding prevention. The temperature and relative humidity in the laboratory were approximately 23°C and 80%, respectively.

Tables 3 and 4 summarize the experimental design adopted for porosimetry and permeability tests, respectively. 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% e 1.03% were added.

Designation	Independent variable (Factor)	Levels
A	EVA content (% of cement weight)	0, 10 and 20
B	HEC content (% of cement weight)	0, 0.5 and 1
C	Curing method	Dry (-1) and Mixed (+1)
D	Pore size ranges	1: $\phi < 10\text{nm}$ 2: $10\text{nm} < \phi < 50\text{nm}$ 3: $50\text{nm} < \phi < 1\mu\text{m}$ 4: $\phi > 1\mu\text{m}$

Table 3. Variables Involved in MIP Experiment.

Designation	Independent variable (Factor)	Levels
A	EVA content (% of cement weight)	0, 10 and 20
B	HEC content (% of cement weight)	0, 0.5 and 1
C	Curing method	Dry (-1) and Mixed (+1)

Table 4. Variables Involved in Permeability Experiment.

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 subjected to dry-cure (75% R.H. after demoulding, which was done 24 hours 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% R.H. until 28-days old. For carbonation prevention and maintenance of relative humidity at 75%, all specimens were stored during the curing period in a CO₂-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 and permeability, the degree of cement hydration was estimated by the determination of non-evaporable water contents in a Netzsch STA 409EP thermal analyzer. Thermogravimetric curves were determined using 30-mg pulverized samples ($\phi < 65 \mu\text{m}$) at a heating rate of 10°C.min⁻¹, in N₂-flowing at 40 cm³.min⁻¹. Non-evaporable 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 (1984). The contributions from other volatiles, as CO₂ 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. The slices were then immersed on ethyl alcohol and subjected to 20 minutes 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 hours. This procedure is a variation of the method recommended by FELDMAN and BEAUDOIN (1991) for specimen preparation to mercury intrusion porosimetry, since temperature as high as 100°C, 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 dynes/cm mercury surface tension and 13.5413 g/cm³ mercury density. Equilibration time in both low and high pressure was 60 seconds. Sample weight was approximately 1.0g. 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 (1990) for ordinary cement pastes.

For the analysis of the results, the intruded mercury values (intruded mercury volume by sample unit mass - ml/g) 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] (COOK and HOVER, 1993), 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.

$$d = \frac{-4 \cos \theta}{p} \quad [\text{Eq. 1}]$$

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 3.9nm pore diameter.

The selected pore-size ranges permits a good approach to paste properties based on intruded mercury volumes. According to JENNINGS (1988), TAYLOR (1990) and MEHTA and MONTEIRO (1994), these pore-size ranges can be correlated to paste properties as shown in Table 5.

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 (% 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 (ml/g) 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, totalling 40 and 164 tests on the first and second analysis, respectively.

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 R.H.
Large capillaries	50 nm - 1 μ m	3	Strength and permeability
Large capillaries and entrained air	> 1 μ m	4	Strength

Table 5. Classification of Pore-Size in Hydrated Cement Paste and Properties Affected.

4. N₂-GAS PERMEABILITY TESTS

At 28-days old, each specimen was imbedded in epoxi resin and cut to remove the top and bottom regions. The cut surfaces were polished, and the specimens were immersed on ethyl alcohol and subjected to 20 minutes in ultrasonic cleaning equipment.

For drying purposes, the specimens were subjected to continuous vacuum at -750 mmHg for 90 minutes, and maintained inside a desiccator with silica-gel until the test.

An apparatus was especially developed for permeability tests. It consisted in a pressured N_2 -gas bottle connected to a device where the specimen is adjusted to obtain a hermetic system. The gas passed through the specimen and was directed within a gauged pipette filled with water, allowing to determine the flow of N_2 -gas that crossed over the specimen.

For each treatment, at least two samples drawn from different specimens, moulded from the same mixture, were tested. The samples were subjected to three or four different N_2 -gas pressure levels. Duplicate tests were performed for each pressure level. Graphs $k \times 1/P_m$ were drawn, where k represents the permeability and P_m is the average N_2 pressure. Permeability value (k) could be obtained for different P_m . In this research, an average pressure of 1,5 atm was considered for the determination of k .

ANOVA (Analysis of Variances) was also applied to estimate the effect of EVA and HEC contents (% of the weight of cement) and the curing method (dry or mixed) on the permeability of the pastes.

5. RESULTS AND DISCUSSION

Figure 1 shows the characteristic curves of intruded mercury volume in function of pore diameter (incremental volume) for mixed-cured paste. For dry-cured pastes, the profile is quite the same. It is possible to observe that the maximum concentration of pores in the reference paste lies in the range 16-100nm, and changes to 50 - 300 nm for 10% EVA pastes (Figure 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. 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.

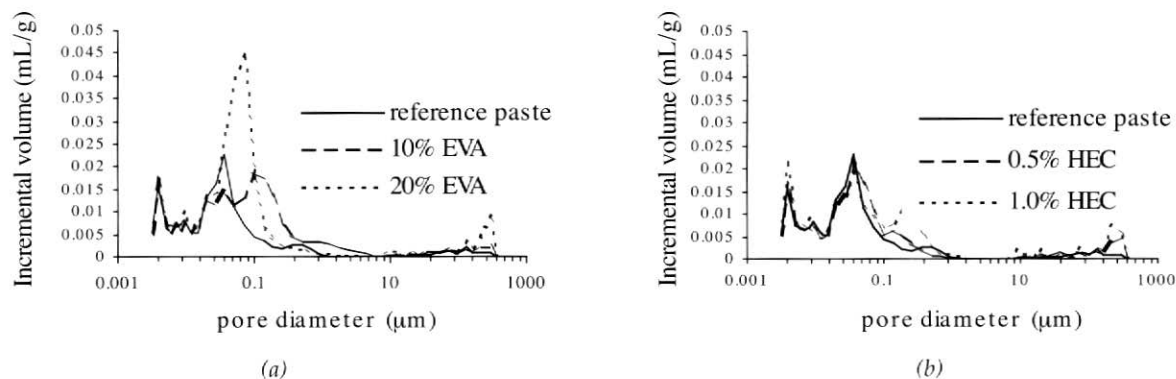


Figure 1. Typical pore size distribution of (a) EVA- and (b) HEC-modified, mixed-cured pastes.

It was possible to obtain information about the threshold diameter, which is the maximum pore diameter at which the continuous mercury intrusion begins (Massazza, 1998). According to Cook and Hover (1999), 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 (FELDMAN and BEAUDOIN, 1991), or from the inflection point of accumulated curves, which signals the formation of the sample-spanning cluster (SAHIMI, 1995). 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 6 shows the results of the analysis of variances for threshold diameter and total intruded mercury volume data. EVA and HEC contents, and the interaction between them, are significant factors. Figure 2 graphically shows their effects. HEC has major effect on the reduction of the threshold diameter of EVA-modified pastes (Figure 2a), and pastes with 0.5% HEC show the minimum values, regardless the EVA content. 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 Figure 2a, 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.

Factor	Sums of Squares		Df	Mean Squares		F Test*		p-value	
	TD	TV		TD	TV	TD	TV	TD	TV
Manner effects									
A: EVA content	3.63353	0.011437	2	1.816763	0.005718	4.507	29.517	0.0209	0.0000
B: HEC content	5.73246	0.001955	2	2.866230	0.000978	7.111	5.046	0.0034	0.0141
C: Curing method	1.00827	0.000571	1	1.008265	0.000571	2.501	2.948	0.1258	0.0979
Interactions									
AB	5.73474	0.013041	4	1.433684	0.003260	3.557	16.828	0.0192	0.0000
AC	1.97391	0.000163	2	0.986953	0.000082	2.440	0.422	0.1061	0.6602
BC	4.17796	0.000406	2	2.088980	0.000203	5.182	1.049	0.0127	0.3646
RESIDUAL	10.48007	0.005037	26	0.403079	0.000194				
TOTAL	24.48686	0.030010	39						

* all F tests were carried out using the error term, which was achieved using the 3-factors interaction

Table 6. Analysis of Variances for Threshold Diameter (TD) and Total Intruded Mercury Volume (TV) Data.

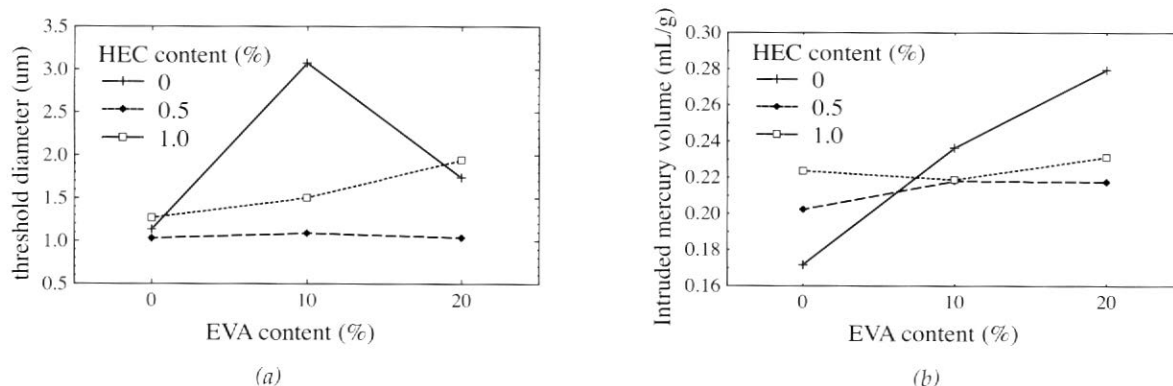


Figure 2. Effect of EVA and HEC contents on threshold diameter (a) and total mercury volume (b).

The effect of HEC on total pore volume (Figure 2b) 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.

Table 7 presents the results of the analysis of variance for intruded mercury volume data. Fig. 3 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.

Factor	Sums of Squares	df	Mean Squares	F Test*	p-value
Manner effects					
A: EVA content	0.00284515	2	0.00142257	17.17	0.0000
B: HEC content	0.000498575	2	0.000249287	3.01	0.0527
C: Curing method	0.000062651	1	0.000062651	0.76	0.3861
D: Pore-size range	0.0799254	3	0.0266418	321.61	0.0000
Interactions					
AB	0.00336459	4	0.000841147	10.15	0.0000
AC	0.0000442104	2	0.0000221052	0.27	0.7662
AD	0.00495294	6	0.000825489	9.97	0.0000
BC	0.0000453231	2	0.0000226615	0.27	0.7611
BD	0.00345554	6	0.000575923	6.95	0.0000
CD	0.017665	3	0.00588834	71.08	0.0000
RESIDUAL	0.0109347	132	0.0000828385		
TOTAL	0.12598	163			

* all F tests were carried out using the error term, which was achieved using the 3 and 4-factors interaction

Table 7. Analysis of Variances for Intruded Mercury Volume Data.

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-size distribution shows that mixed cure results are greater on pore concentration below 50 nm, which corresponds to hydrated phases and medium capillary pores (Figure 3a). On the other hand, dry-cured specimens have greater concentration of pores larger than 50nm, 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 7) to the paste does not significantly change the effect of curing.

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 (10nm to 1000nm) as shown in Fig. 3b. 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 (figure 3c). However, for pastes without EVA the effect of adding HEC is to increase the porosity, as already seen in Figure 2b. This apparent contradiction is a consequence of the interaction between HEC and EVA

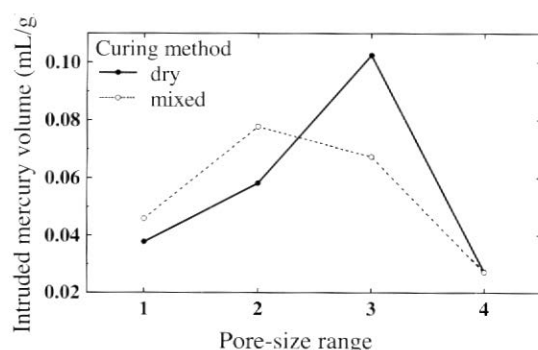
Table 8 shows the non-evaporable water contents estimated by thermogravimetric analysis (TG). Unfilled cells are due to the experimental design. It can be seen that, regardless the HEC content, EVA reduces the degree of hydration of dry-cured pastes. Its slighter effect on mixed cured pastes is related to the curing method itself, which maintains more water available for cement hydration for seven days. While EVA major effect is to decrease the cement hydration of pastes subjected to dry cure, HEC increases the non-evaporable water for both curing methods, but its effect is weaker than EVA effect.

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	

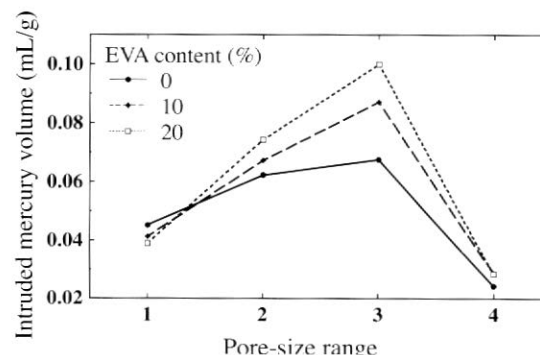
*average of two samples.

Table 8. Non-evaporable water contents (%) obtained from TG*.

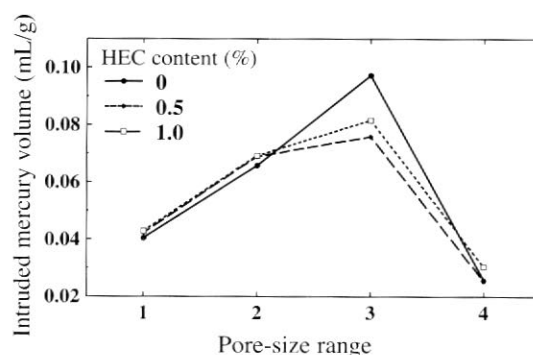
From these results, it is possible to conclude that the higher volume of capillary pores in only-HEC modified pastes cannot be attributed to a lower degree of cement hydration. On the other hand, the higher capillary pore volume observed on EVA-modified pastes might in part be due to the lower cement hydration. Its more strong 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.



(a) Pressure (pores) x curing method.



(b) Pressure (pores) x EVA content.



(c) Pressure (pores) x HEC content.

Figure 3. Graphic showing the effects of two-factor interactions on the intruded mercury volume.

Table 9 presents the ANOVA results of permeability tests. Figure 6 shows the graph of three-factor interaction. Two-factor interaction graphs are shown in Figures 7 and 8. The most important factors are HEC content (factor B) and the curing method (factor C), and also the interaction between factors B and C. EVA content (factor A) affects only slightly the permeability of cement pastes to N_2 -gas.

Factor	Sums of Squares	df	Mean Squares	F Test	p-value
Manner effects					
A: EVA content	0.39371	2	0.196855	1.7060	0.2097
B: HEC content	3.889822	2	1.944911	16.8547	0.0001
C: curing method	1.886428	1	1.886428	16.3479	0.0008
Interactions					
AB	0.951876	4	0.237969	2.0623	0.1284
AC	0.231062	2	0.115531	1.0012	0.3870
BC	1.714154	2	0.857077	7.4275	0.0044
ABC	0.68724	4	0.171810	1.4889	0.2472
Residual	2.077074	18	0.115393		
Total	11.831366	35			

Table 9. ANOVA results of paste permeability to 1,5 atm N_2 -gas.

The k values varied in a wide range depending on the polymer type and content, and on the curing method (from $4,67 \times 10^{-19}$ to $2,67 \times 10^{-16} \text{ m}^2$).

HEC strongly decreases the permeability of the pastes, especially those ones subjected to dry cure. The effect of EVA is statistically poor, but there is a tendency to a lower permeability with EVA addition (Figure 4).

The curing method has great influence on paste permeability, as expected. Regardless any other factor, dry-cured pastes present higher permeability to N_2 -gas under pressure, as shown in Figures 5 and 6. The effect of HEC content can clearly be seen in Figure 5, especially for dry-cured pastes, whose permeability reduction is as great as 85%. These results permit the authors to conclude that HEC addition has similar effect on permeability as the application of mixed-cure on cement pastes. Both factors, acting simultaneously, assure minimum permeability.

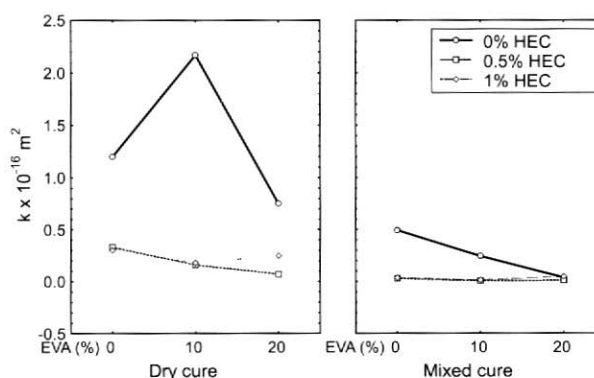


Figure 4. Three-factor graph showing the effect of HEC and EVA contents and curing type on the N_2 -gas permeability of cement pastes.

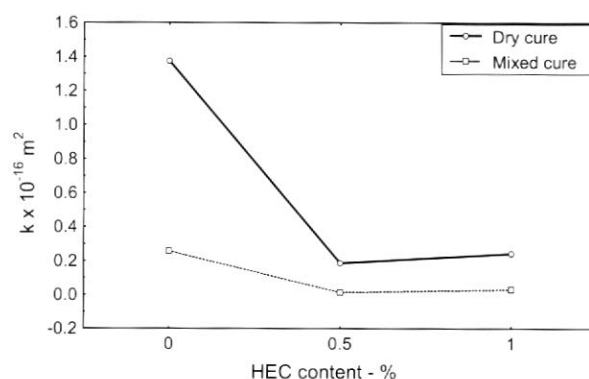


Figure 5. Two-factor graph showing the effect of HEC content and curing type on the N_2 -gas permeability of cement pastes.

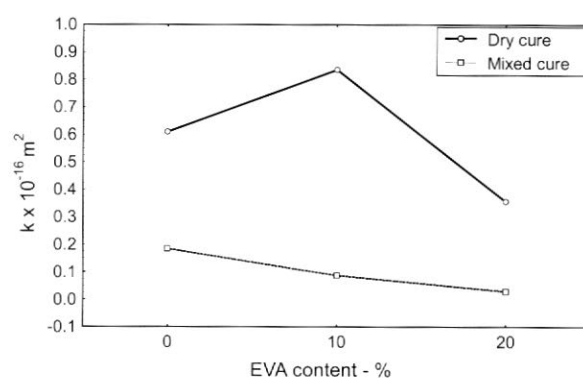


Figure 6. Two-factor graph showing the effect of EVA content and curing type on the N_2 -gas permeability of cement pastes.

6. CORRELATION BETWEEN THE RESULTS OF POROSITY AND PERMEABILITY TESTS

The results of porosity and permeability tests were compared, since the transport of fluids inside materials is intimately related to its pore structure. A correlation study was performed considering the following characteristics of the pore structure:

- Total intruded mercury volume
- Pore volume with diameter larger than 40 nm, corresponding to the mean free path of a N_2 molecule
- VPore volume with diameter between 10 nm and 1 μm (corresponding to the capillary pores, according to Table 5)
- Threshold diameter

Table 10 shows the correlation coefficient found in each case. Correlations are weak ($r < 0.70$), that is, it is not possible to establish a model correlating the characteristics determined by MIP and the property of N_2 -gas permeability.

Pore structure characteristics	Correlation coefficient (r)
Total intruded mercury volume	0.045692
Volume of pores with $\phi > 40$ nm	0.369024
Volume capillary pores	0.186309
Threshold diameter	0.101396

Table 10. Correlation coefficients between pore structure characteristics and N_2 -gas permeability results of cement pastes.

Although no strong correlation exists, some tendencies could be noted. For only-EVA modified, mixed-cured pastes, higher EVA contents result in an increase of threshold diameter, capillary pore concentration and total pore volume. On the other hand, the permeability is reduced. For dry-cured pastes, the permeability is reduced only for 20% EVA modified pastes. There is a great increase of permeability for 10% EVA modified pastes, as shown in Figure 4a.

This behavior might be related to the film forming capacity of EVA. The film covers the cement hydrated phases and pore walls. One can conclude that the film restricts fluid transportation within cement pastes, but it is not capable to resist to the high pressure applied during MIP. According to SU (1995), polymer particles fill the pores of the paste, contributing to a lower permeability. However, the high permeability of 10% EVA-modified, dry-cured pastes indicates that this EVA content is not sufficient to fill and to seal satisfactorily the capillary pores resulting from the combination of both factors. For higher EVA content, the effect of porosity on permeability is balanced by the presence of polymer particles and by pores sealing.

Mixed-cured pastes have lower capillary and total porosities, and an EVA content as low as 10% is capable to decrease the permeability. As can be seen in Figure 4b, higher EVA contents further reduce the permeability.

Only-HEC modified pastes show higher capillary and total pore volumes, regardless the curing type. However, a strong reduction of the permeability was noted for 0.5% HEC pastes. Higher HEC contents sharply change the threshold diameter and do not affect the paste permeability.

This behavior may be due to the drying process itself and to the dimensions of the samples subjected to the MIP test. Microcracking can be caused by both factors due to drying shrinkage. Indeed, only-HEC modified pastes showed intense microcracking when observed by SEM. Since the pastes were subjected to severe drying procedures (water replacement by ethyl alcohol, simultaneous low pressure and 40°C temperature for 25 hours), one can expect great drying shrinkage and microcracking. The microcracks are considered by the method as pores. On the other hand, the dimensions of the samples subjected to permeability tests, as well as their previous storage, probably did not result in strong cracking. This might be the cause of the inverse relation between total and capillary pore volumes and the results of permeability of only-HEC modified pastes.

Besides, according to OHAMA (1984), cellulose derivative polymers (such as HEC) form thin and impervious films within cement based materials. Although the existence of such film was not confirmed on SEM analysis by the authors, HEC indeed forms extremely thin and weak film after water removal from a pure aqueous solution. Therefore, the inverse relation between porosity and permeability results of only-HEC modified pastes might be due to the presence of thin films partially sealing the pores and to the ready rupture of such film during mercury intrusion. According to NAKAMURA,

cited by OHAMA (1984), water permeability of cement-based materials is also reduced in the presence of cellulose ethers, since they suffer expansion when absorb water, sealing the pores. However, as has been demonstrated, there is an increase of imperviousness of the pastes to gases, and it can be an indication that the impermeability of these systems is due to a factor different from polymer expansion.

In the presence of EVA, HEC causes reduction of capillary pores and total porosity and permeability of cement pastes. The threshold diameter is also reduced. The effect of HEC on the reduction of permeability is more expressive for dry-cured than mixed-cured pastes, and for 10%-EVA modified pastes. The addition of EVA to HEC-modified pastes increases the total and capillary porosities, but has no effect on the permeability property.

7. CONCLUSIONS

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

1. No strong correlation was found between gas-permeability and MIP results for polymer-modified cement pastes.
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 50nm to 1 μ m. As would be expected, the application of mixed cure causes a sharp reduction of gas permeation.
3. EVA increases the capillary pores and threshold diameter of cement pastes, but the effect on gas-permeability is not statistically significant. However, the overall effect of EVA addition is to reduce permeability. This contradiction might be related to the presence of polymeric film within the pastes, that suffers rupture and allow high-pressure mercury to enter the pores, but do not permit the percolation of gases at low pressures.
4. The addition of HEC to pure pastes results in higher capillary and total porosities. On the other hand, HEC strongly decreases the 1.5atm, N₂-gas permeability of the cement pastes. This lack of correlation might be due to the MIP samples microcracking on drying procedures, which does not occur in the large samples subjected to permeability tests.
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.
6. For cement pastes modified with film-former polymers, it is not possible to correlate the gas-permeability property to pore structure characteristics obtained by MIP, since the high pressure applied on the sample by the latter can cause the rupture of the polymeric film that seals the pores. The establishment of numeric models based on pore structure characteristics determined by a technique less aggressive than MIP could provide better estimation of the permeability of polymer / cement composite materials.

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