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Cement and Concrete Research 35 (2005) 2047–2050

Cement and Concrete Research

Communication

ESEM analysis of polymeric film in EVA-modified cement paste

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Received 22 December 2003; accepted 8 October 2004

Abstract

Portland cement pastes modified by 20% weight (polymer/cement ratio) of poly(ethylene-co-vinyl acetate) (EVA) were prepared, cured, and immersed in water for 11 days. The effects of water saturation and drying on the EVA polymeric film formed in cement pastes were observed using environmental scanning electron microscopy (ESEM). This technique allowed the imaging of the EVA film even in saturated samples. The decrease of the relative humidity inside the ESEM chamber did not cause any visual modification of the polymeric film during its drying.

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Keywords: Cement paste; Polymers; SEM; Drying; Water saturation

1. Introduction

Recent research has demonstrated that improved adherence of EVA-modified mortars and concretes is mainly due to the formation of a polymeric film at the interface with other materials [1,2]. Because EVA is able to form film even under the high alkalinity of concrete pore solutions, this film has been also associated to the higher flexibility of mortars and concretes containing EVA. Besides the ability to form film, EVA chemically reacts with hydrating cement and eventually forms composite products [3,4].

Researchers [2,5,6] have reported, however, that EVA-modified mortars and concretes are sensitive to water, i.e., they show a decreased mechanical strength when they are under high humidity or fully saturated with water. Current hypotheses on this mechanism are as follows:

a) The polymeric film existing in cement-based materials absorbs water due to two factors: (a) the presence of polar groups (vinyl acetate groups) in the EVA structure [7]; and (b) the presence of a water-soluble protective colloid [poly(vinyl alcohol)—VA] that partially or completely shields the EVA particles, even in the dry film. Water absorption causes the swelling of the PVA protective membrane throughout the film, leading to its plasticization and resulting in lower mechanical strengths [8]. Because the PVA membrane around each particle of EVA expands, it is reasonable to assume that the EVA polymeric film also expands.
b) The chemical interaction of EVA with hydrating cement includes the saponification (alkaline hydrolysis) of the acetate groups of the copolymer [3] and the expected bond of such anions with metal cations, which are provided by the dissolution of cementitious phases, mainly calcium silicates and aluminates. Such chemical interaction might produce water-sensitive composite phases, such as calcium acetate or other organometallic phases [4,9].
c) Silva et al. [10] have shown that EVA increases the pore size concentration of cement pastes in the range 10–50 nm. According to Mehta and Monteiro [11] and Jennings [12], pores and capillaries in this size range would be moderately or greatly affected by the surface tension of the aqueous phase, meaning that the saturation of such pores would cause the mechanical strengths to drop to some extent.

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doi:10.1016/j.cemconres.2004.10.037

Table 1
Characteristics of redispersible EVA copolymer[a]

Ash content (30 min at 1000 °C)	13.0%
Apparent density of the powder (DIN 53189)	472 g/l
Particle size	75 μm>ϕ>37 μm
Protective colloid	Poly(vinyl alcohol)
Minimum film forming temperature	Approx. 4 °C
pH of EVA dispersion in DI-water, 25 wt.%[b]	9.1

[a] Characteristics informed by the copolymer producer.

[b] Characteristic determined by pH meter.

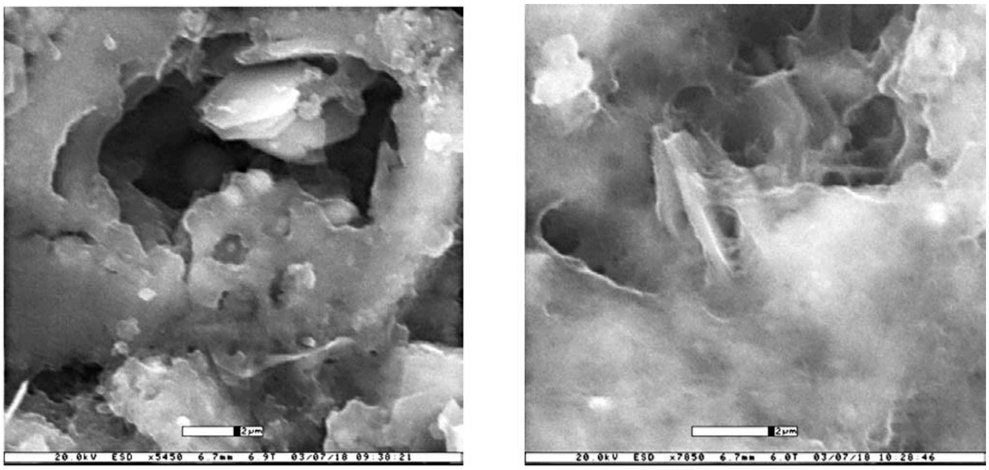
The abovementioned phenomena can occur simultaneously. Different experimental techniques would be necessary to prove each one. The main purpose of this communication is to present the results of an investigation of the EVA polymeric film formed in cement-based materials imaged through environmental scanning electron microscopy (ESEM). The technique has proven to be an important tool to investigate the aspect of the film in samples subjected to a relative humidity as high as 100%.

2. Materials and methods

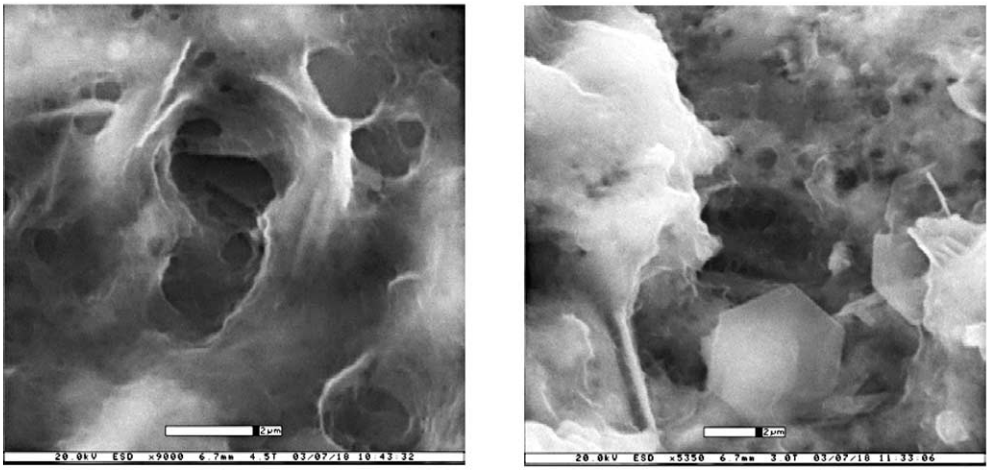
An EVA-modified paste was mixed with ASTM type I/II portland cement, a commercial redispersible-powdered EVA copolymer and de-ionized water. The proportion of the materials was 1:0.2:0.4 (cement:EVA:water) in weight basis. Characteristics of the EVA are presented in Table 1. The inorganic part (ash content) of the copolymer contains magnesite (37% wt of the inorganic compounds), dolomite (13%), calcite (14%), talc (16%) and kaolinite (20%), identified and semi-quantified by XRD analysis.

The paste was manually mixed and moulded, and kept in a moist room for 7 days. The specimens were then demoulded and stored at 64% RH and 24 °C for 7 days. They were then crushed and immersed in tap water. After 11 days, small fragments of the specimens were collected from the water for the analysis.

Electroscan E3 environmental scanning electron microscope (ESEM) equipped with a Peltier cooling stage and an environmental secondary detector was used to investigate



(a) 90% RH. **(b)** 80% RH.



(c) 60% RH. **(d)** 40% RH.

Fig. 1. EVA film in different locations of an EVA-modified cement paste kept under water for 11 days and analyzed under different relative humidities.

the polymeric film in the hardened cement pastes The temperature was set to 7 °C and the pressure inside the chamber was varied from 7 to 3 torr in order to have the relative humidity varying from 90% to 40%, respectively. The samples were not coated for this analysis.

For the analysis, the fragments of the cement paste were taken from the container where they were kept immersed in water and analyzed right away. In the beginning of the analysis, the fragments were wet and the chamber was kept under 90% RH. The analysis continued under consecutive, decreased relative humidity until 40%.

3. Results

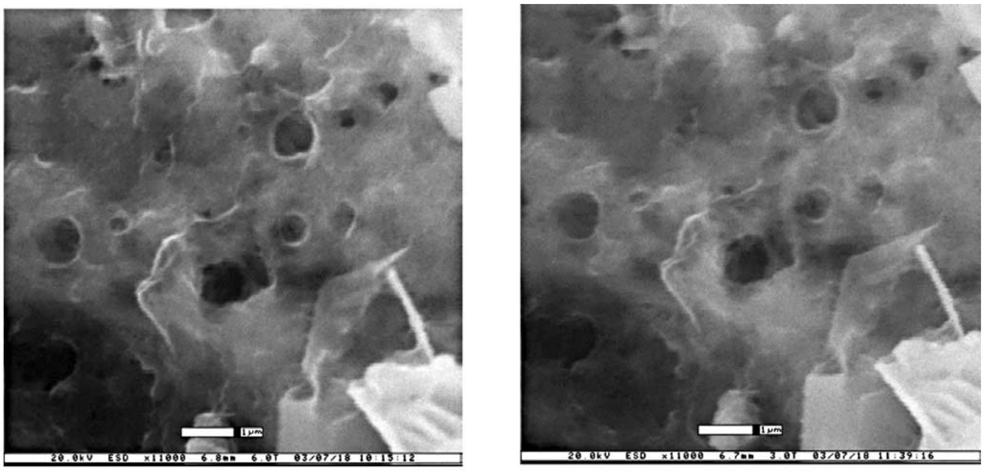
The polymeric phase was detected in many locations of the sample, regardless of the relative humidity of the chamber. Fig. 1 shows some images at 90%, 80%, 60% and 40% RH, where the EVA film can be seen.

Because of the long storage of the paste under water (11 days) and the continuous cement hydration under such conditions, a large amount of calcium hydroxide crystals grew in the sample. Fig. 1d shows a very well-formed, thin hexagonal $Ca(OH)_2$ crystal.

During the analysis, images were taken in some locations under 80% RH and later on under 40% RH in order to detect volumetric changes in the polymeric phase due to drying. Fig. 2 shows two different locations of the sample analyzed under 80% and 40% RH. It can be observed that no important volumetric change was detected.

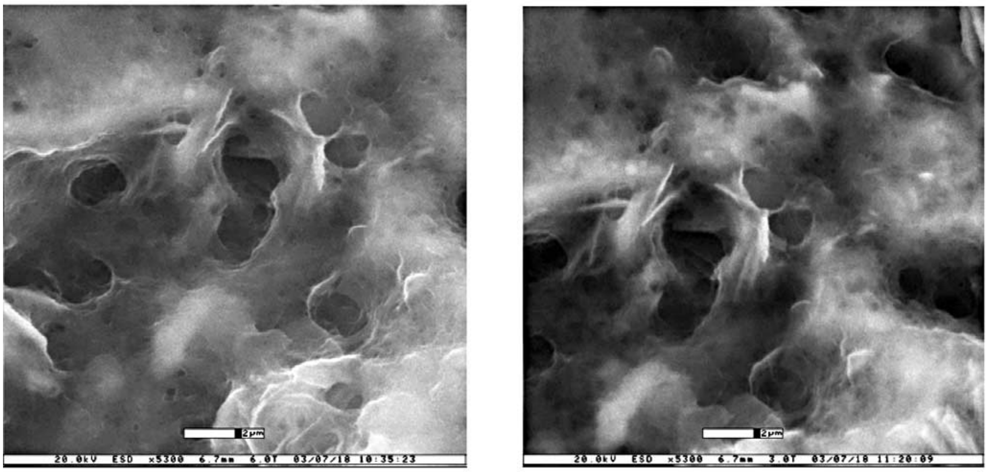
4. Conclusion

As shown in the above images, the polymeric film formed in EVA-modified cement pastes does not disaggregate when the hardened paste is immersed in water for a period of up to 11 days; however, even though the film was



(a) Location A at 80% RH.

(b) Location A at 40% RH.



(c) Location B at 80% RH.

(d) Location B at 40% RH.

Fig. 2. Aspect of the EVA film formed in cement pastes under (a,c) 80% and (b,d) 40% RH, in two locations of the sample.

not destroyed, structural changes may have occurred during the immersion period.

The observation of the sample during a controlled decrease of the relative humidity—from 80% to 40%—in the ESEM chamber has shown that the film does not suffer important volume or morphological change during drying. It is possible that the elapsed time from 80% to 40% RH (less than two hours) was not long enough to produce any detectable contraction of the EVA film. Again, some structural changes may have occurred that is not detectable by ESEM.

Acknowledgments

The authors acknowledge the financial support of CAPES (Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior–Ministério da Educação–Brasil) and are grateful to Dr. Gordon Vrdoljak of the Electron Microscope Laboratory (EML–College of Letters and Sciences, UC Berkeley). The research at EML is supported by the National Science Foundation and the Federal Highway Administration (grant CMS-981275).

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