

Polymer-cement and polymer-alite interactions in hardening of cement-polymer composites

1. Introduction

Polymer redispersible powders are a group of modern organic cementitious materials modifiers. They are widely used especially in dry pre-mix mortars, like ceramic tiles adhesives, plasters, repairing mortars, sealing compounds etc. Redispersible polymer powders acts as a binder. After the powder granules came into contact with water they start to redisperse, releasing small particles of a diameter about 1µm. During film forming process polymer particles form a thin polymer films on the surfaces of mineral phases. If the amount of polymer is high enough the films form a continuous polymeric net which binds the material. This polymeric microstructure interpenetrates the mineral one forming a mineral – polymer composite (1). Ethylene – vinyl acetate (EVA) copolymer is the most commonly used as a raw material for redispersible powder manufacturing. It has better resistance for alkaline hydrolysis comparing to vinyl acetate homopolymer what is especially important in such alkaline environment like hydrating cement paste. What is important both from basic as well technological point of view are interactions within the system and how polymer presence influence cement hydration and also on the other hand how cement paste environment influence polymeric films. It was observed that EVA undergoes alkaline hydrolysis, what was stated on the basis of IR observations as well as direct pore solution analysis (2, 3). Presence of chemical interactions within the EVA – cement system were shown to be present and influence the cement hydration (2, 3). Less attention was put on the influence of cement paste environment on the properties of polymeric films present within the cement – polymer composite. In present paper some new data on the properties of polymeric films in cement polymer composites are presented.

2. Experimental

For liquid phase analysis cement type I according to ASTM C-150 was used (denoted as cement 1). For FTIR experiments, CEM I 42.5R cement according to PN-EN 197-1 standard was used (denoted as cement 2). The characteristic of cements are presented in Tables 1-2.

Alite used in experiments was obtained by sintering of stoichiometric mix of silicon and calcium oxides with the addition of 1.5% of MgO and 0.8% of Al₂O₃ by mass. Oxides were homogenized, palletized and sintered three times in 1500°C. Than it was ground to specific surface of 3400 cm²/g according to Blain. XRD analysis based on patterns published by de la Torre et. al. (4) revealed that alite used was mainly monoclinic of the M₃ modification, according to Taylor (5). Powders used in experiments were two commercial EVA powders and one PVAc powder used as a reference. Basic characteristic of powders used are presented in Table 3.

Liquid phase of hydrating pastes was obtained using extraction method with the use of hydraulic press and special hermetic pressure extraction device. Construction of the apparatus was described by Barneyback et al. (6). Liquid phase was extracted from

Table 1

PROPERTIES OF CEMENT 1 (CEMENT TYPE I ACCORDING TO ASTM C-150)

chemical composition, %							LOI	specific surface area according to Blaine
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _e		
20.6	5.2	2.3	65.3	1.2	3.3	0.6		
phase composition, % (Bogue)								
C ₃ S		C ₂ S		C ₃ A		C ₄ AF	%	cm ² /g
61		13		10		7	1.75	3670

Table 2

PROPERTIES OF CEMENT 2 (CEM I 42.5R)

chemical composition, %								water demand	specific surface area according to Blaine	compressive strength	
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _{eq}	Cl ⁻			2 days	28 days
19.1	5.7	2.9	62.7	1.6	3.3	0.82	0.1				
phase composition, % (Bogue)											
C ₃ S		C ₂ S		C ₃ A		C ₄ AF		%	cm ² /g	MPa	MPa
58.3		11.1		10.2		8.8		28.6	3370	31.9	58.2

Table 3

BASIC PROPERTIES OF POLYMER POWDERS USED IN EXPERIMENTS

denotation	polymer base	anticaking agent	MFFT, °C*	T _g , °C*	ash content, %
EVA1	ethylene – vinyl acetate copolymer (EVA)	kaolinite	0	-9	17.2**
EVA2	ethylene – vinyl acetate copolymer (EVA)	amorphous silica	0	14	10 % ± 2 %*
PVAc	vinylacetate homopolymer (PVAc)	amorphous silica	18	23	4.7**

* manufacturer data, ** 30 min at 1000°C

pastures of water/cement ratio equals 0.4, after 1, 3, 7 and 21 days of hydration at 20°C in tightly sealed polypropylene jars. This cement pastures samples were mixed in vacuum mixing device in order to avoid air entrainment during mixing. Two pastures were investigated: control one and pasture modified with 10% of EVA1 powder. Clear pore solutions obtained, were diluted and analyzed. K⁺ and Na⁺ ions concentrations were determined using Varian SpectrAA 20 emission spectrophotometer. Hydroxyl group concentration was determined with titration. Diluted solutions were titrated with 0.06M HCl versus phenolphthalein as an indicator. Acetate ions concentration was measured with ion chromatography. General purpose ion exchange column were used (Dionex IonPac AS4A) together with borate eluent.

Samples for IR spectra determination were prepared without the use of organic solvents. Pastures of w/c ratio = 0.5, cured at 25°C were dried using p-drying method described by Powers (7). Than they were mixed with KBr and pressed into pellets. Infrared spectra were measured with transmission technique in the range 400 cm⁻¹ – 4000cm⁻¹ with 4cm⁻¹ resolution using Fourier infrared spectrophotometer Bio-Rad FTS 60VM. Each spectra was the result of 256 individual scans.

2. Results

In Figure 1 changes in ions concentration in liquid phase in time is presented. It can be seen that the presence of EVA 1 causes substantial changes in ions concentration. First the acetate ions are present in liquid phase of EVA modified pastures. The amount of acetate ions present within the liquid phase is really high, and is increasing with time. It reaches about 0.9 M after 21 days of curing. Hydroxyl ions concentration is reduced from almost 0.7 down to below 0.2 after 21 days of curing in the presence of EVA. Potassium and sodium ions concentration are also seriously changed in the presence of EVA 1 powder. In general it can be say, that the concentration of alkali metal ions is increased. Potassium

concentration increases stronger than sodium concentration does. As a result of changes in all the ions concentration the ionic strength is increasing in the presence of EVA powder.

Figure 2 presents FTIR spectra of cement pastures modified with EVA 1 powder. It can be noticed, that new band at about 1580 cm⁻¹ can be observed in pastures containing EVA1. This band is characteristic for acetate salts. It confirms the observations made during liquid phase analysis that free acetate ions are present within the system. But what is even more important from the point of view of present paper is that bands characteristic for EVA copolymer (1744 cm⁻¹ from C=O bonds and 1250 cm⁻¹ from C-O bonds) are altered when EVA copolymer is a part of cement - polymer matrix. Half - width of bands is decreased and bands are sharpened. In Figure 2 detailed view of bands at 1744 cm⁻¹ are presented. It can be seen that while for neat EVA 1 powder half-width is 46 cm⁻¹ for 10% and 20 % EVA modified pastures it is reduced to 25 cm⁻¹ and 24 cm⁻¹ respectively. In order to reduce the possibility of interferences between EVA and hydrated cement pasture mixture of hydrated pasture and unreacted EVA 1 powder was also examined. In this case half - width was 42 cm⁻¹.

Figure 3 presents analogous spectra for alite pastures modified and unmodified with EVA 1 powder. Similar observations were made. When EVA 1 powder is a part of cement - polymer composite, the half - widths of bands characteristic for EVA copolymer decrease and bands become sharper. Band at 1580 characteristic for free acetates is also present in case of EVA - alite pastures.

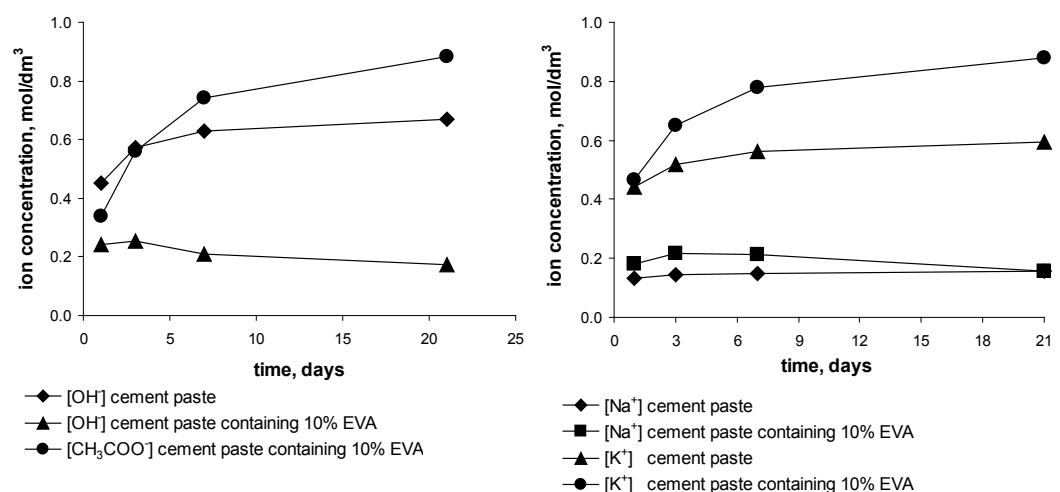


Fig. 1. Concentration of ions in liquid phase of cement paste (on the left) and cement paste modified with 10% of EVA 1 redispersible powder

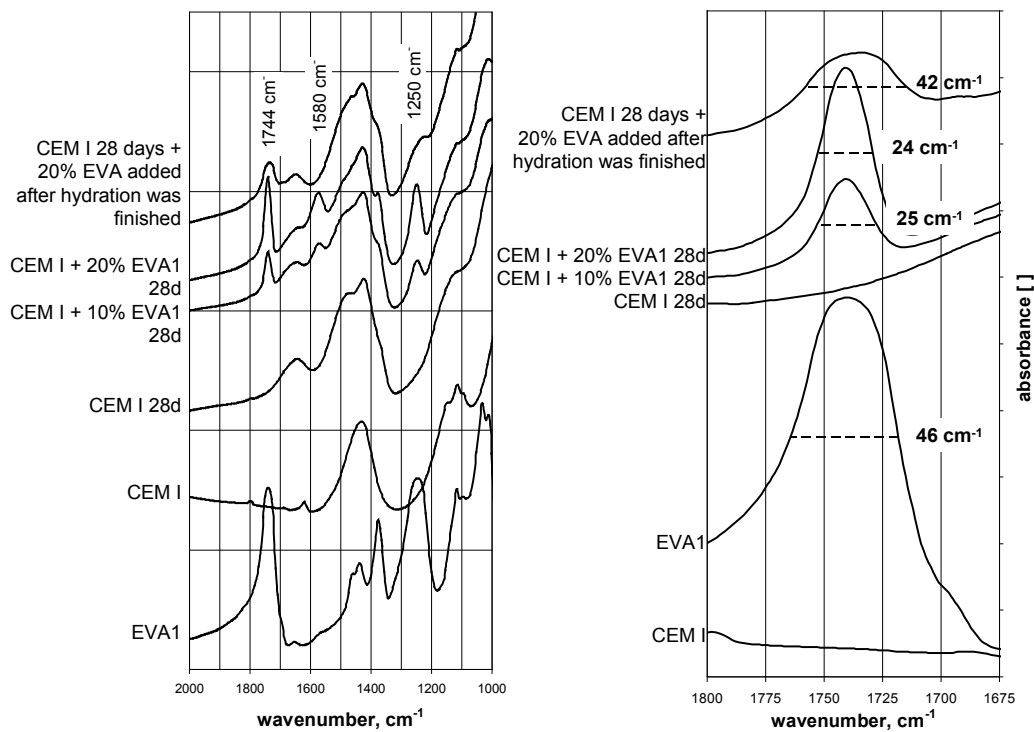


Fig. 2. FTIR spectra of cement pastes modified and unmodified with EVA 1 powder, pure EVA 1 powder, unhydrated cement and spectra of mixture of unmodified paste mixed with 20% of EVA 1 powder after hydration was finished; On the left spectra in the range 1000 – 2000 cm^{-1} , on the right detailed view of C=O band at 1744cm^{-1} with half-width of bands

cases band at 1580 cm^{-1} is present and EVA bands half width is reduced comparing to pure EVA powders. Spectra of alite paste modified with PVAc powder is different comparing to EVA ones. It can be observed, that bands characteristic for EVA copolymer disappeared almost completely and band characteristic for free acetates is very strong. It indicates, that the hydrolysis of copolymer is almost complete and far more pronounced comparing to EVA modified samples. Comparing neat powders it can be observed, that half – width of the band at 1744 cm^{-1} is increasing in an order EVA1 < EVA 2 < PVAc ($46, 60$ and 75 cm^{-1} respectively).

3. Discussion

Results shown in present paper allow to draw some conclusions on the interactions within EVA – cement and EVA – alite composite. First, results of direct measurement of ions concentration are presented. They reveal some serious changes in liquid phase composition. Most important is that there is very high acetate concentration caused by alkaline hydrolysis of EVA copolymer. pH is also significantly lowered. It changes the equilibrium between solid and liquid phases. Increased ionic strength of pore solution indicates that the solubility of solid phases is increased. It can be caused by pH reduction. It is known that cementitious phases are less stable in environment of lowered pH. It is important point from durability point of view. This is the reason why PVAc powders cannot be used for

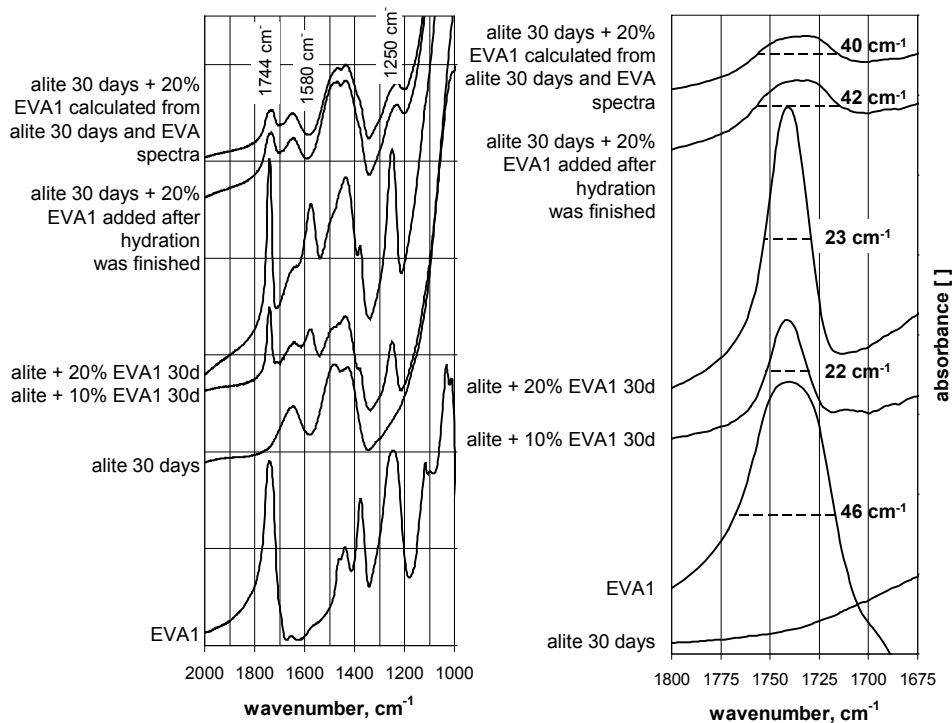


Fig. 3. FTIR spectra of alite pastes modified and unmodified with EVA 1 powder, pure EVA 1 powder, spectra of mixture of unmodified paste mixed with 20% of EVA 1 powder after hydration was finished and spectra calculated as 0.8 spectra alite 30 days + 0.2 spectra EVA 1. On the left spectra in the range 1000 – 2000 cm^{-1} , on the right detailed view of C=O band at 1744cm^{-1} with half-width of bands

In Figure 4 FTIR spectra of alite pastes modified with 10% of EVA 1 EVA 2 and PVAc powders respectively are presented. Pastes modified with EVA 1 and EVA 2 exhibit similar spectra. In both

modification of cementitious materials. As it can be seen from IR spectra PVAc hydrolysis is almost complete so it can be suspected that the concentration of acetate ions and depletion of pH would

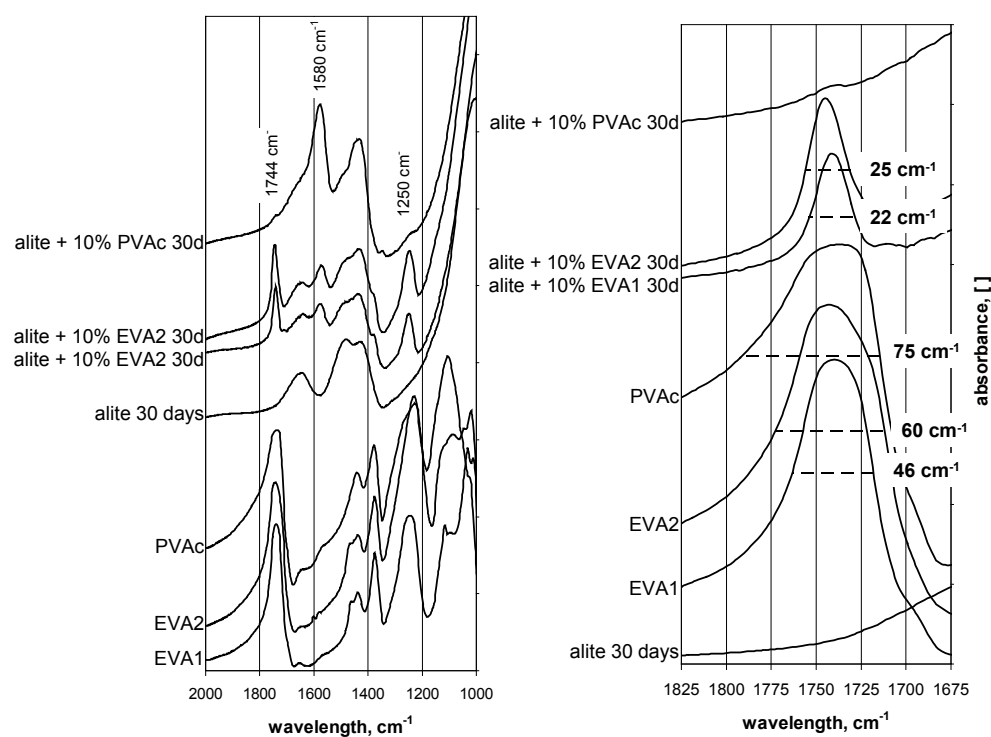


Fig. 4. FTIR spectra of polymer powders used in the investigations and alite pastes modified it 10% of each of the polymers; on the left spectra within the range 1000 – 2000 cm^{-1} , on the right detailed view of bands at 1744cm^{-1}

be even more pronounced comparing to EVA. It is worth to notice, that cement paste is a kind of buffer, and presence of an excess of calcium hydroxide avoids pH drops. It means that to lower pH within the system it is not enough to introduce protons, but it is necessary to form another buffer system which will maintain pH on changed level. Acetic acid together with its salt, calcium acetate can form such a buffer. Acetic acid – calcium acetate buffer seems to be responsible for pH lowering within the EVA modified cement pastes.

Except the fact that alkaline hydrolysis of polymer influence the hydration of cement (2, 3), alite (8), and tricalcium aluminate (8, 9) it also alters the structure and properties of polymer itself. As it is shown in Figs. 2, 3 and 4 in details the band characteristic for EVA associated with C=O bond in acetic group at 1744cm^{-1} is changing during the hydration and maturing of the polymer – cement composite. The half-widths of bands are lowered after 30 days of hydration comparing to raw EVA powder. The same phenomena can be observed for C-O band at 1250cm^{-1} (although it is not presented in details). It suggests that the structure of the copolymer tends to be more organized, and that the degree of crystallinity is increasing (10). The same phenomena is observed in case of alite pastes as it can be seen in Figs. 3 and 4. It was also confirmed not only for EVA 1 powder but also for another EVA powder with different ethylene/vinyl acetate ratio (it was examined using thermogravimetric analysis, also the T_g is different for EVA 2 comparing to EVA 1 – 14°C and -9°C respectively). Moreover, the detailed analysis of IR spectra published by Silva et. al. (2) brings to similar conclusions.

The phenomenon of structure increasing order was described in polymer literature. For EVA copolymers which were not subjected

to hydrolysis the amorphous fraction content is increasing with the increase in acetate groups content (11). The hydrolysis process leads to replacement of acetate groups by hydroxyl ones and transformation of copolymer into terpolymer. The process is diffusive in its nature and leads to formation of acetate groups concentration gradient across the thickness of polymer film (12). Hirata et al. (13, 14) showed, that with the increase of vinyl alcohol monomeric units content within the terpolymer the degree of crystallinity increasing. Detailed investigations (15) showed that crystallinity of terpolymer depends linearly on the acetate groups content. It applies for both polymers hydrolysed in solution and then used for films preparations as well as films subjected to hydrolysis (15). Similar observations are reported by Fan et al. (16). What is especially important from the point of view of

polymer modified cementitious composites properties is that partial hydrolysis of EVA films and changes in their structures improve some properties of film like mechanical strength (16, 17) and also permeability towards water and gases is decreased (11, 12, 13).

4. Conclusions

Observations made on the hydrolysis of EVA copolymer and its influence on both cement hydration and properties of mineral matrix, as well as properties of polymeric films enforce to perceive EVA modified cement pastes and mortars as composites in which polymeric phase acts as an active component which not only influence the hydration of cement but also undergoes changes caused by the hydrating cement paste environment. The interactions are mutual and influence the properties of final material.

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