Intrinsic modification of repair mortars made with EVA and CaO, impacts at early ages

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Abstract. Many studies have been realised on polymer-modified mortars (PMMs). Among the polymers used, ethylene vinyl acetate (EVA) has revealed evident interaction between calcium ions and its acetate groups. Most of the studies have shown a positive impact of EVA on mortar performance, which is enhanced by the combination of the EVA with calcium oxide CaO. However, there is still a lack of understanding of the nature of these interactions and no clear link has been established between these interactions and the properties of the cementitious materials at early ages. This article aims to tackle this topic by focusing on the evolution of EVA particles in a pore solution and the properties of a cement modified with EVA and CaO, especially the rheological behaviour. As results, it is observed that the zeta potential of the pore solution decreases when EVA is added. Furthermore, the hydrodynamic radius of this polymer tends to increase over time in the pore solution. On the other hand, the EVA tends to delay the setting time while the CaO accelerates it. For the rheological state, EVA tends to govern the plastic viscosity of the cement paste while CaO governs the yield stress and these parameters are not affected by the mixing time during the first 100 min. Their combination enhances these rheological parameters.

1 Introduction

Organic polymers have been used as admixtures in mortars for more than five decades. They are often used to enhance the performance, for instance in the field of repair and maintenance. In fact, the elastomeric properties of the commonly used polymers (e.g. styrene butadiene (SBR) or styrene acrylate (SA)) increase the adhesive strength of the mortars, which leads to a better bond between the mortar and the substrate. Even though many studies testify about the improvement of repair mortars modified with polymers, early failure on repaired works remain. These failures currently appear as cracks in the repair mortar and/or its peeling off the substrate. Premature cracking of the repair mortar layer is often attributed to its shrinkage that occurs during cement hydration and its hardening.

A study was conducted at the University of Cape Town on this topic for two years. In this study, repair mortars were modified with a combination of two additives;

- ethylene vinyl acetate (EVA) as organic admixture, which is known for its elastomeric properties, and
- calcium oxide (CaO) as a mineral expansive addition, which is less commonly used than EVA.

The aim of this study was to control and even avoid shrinkage in mortars to prevent cracking. The results of this study show a positive effect of combination of EVA and CaO on mortar performance. Indeed, the risk of

cracking of the mortars modified with ethylene vinyl acetate is significantly reduced and this effect emphasized when polymer is combined to calcium oxide [1]. Moreover, the combination of CaO and EVA induces the increase of shrinkage in mortar and the decrease of its compressive strength. These results show that high shrinkage alone cannot be considered as a weak point for these repair mortars. However, the results on the adhesion performance were not entirely conclusive. Furthermore, this study has also revealed that the studied properties of these mortars were also depending on the type of cement used in the mortar [2]. And it is also possible that the curing regime affects the performance, since the polymer film formation process requires a low amount of water in the last stage, while the calcium oxide requires water for the hydration [3].

Despite the increase of the good performance brought by using polymers in the formulation of mortars, the intrinsic changes induced by the polymer itself and the polymer combined with the calcium are not fully understood. Even though evidences of interactions between EVA and calcium ions of the cement have been observed [4], the link between the hydration process of these mortars and their properties at early ages has not yet been studied intensively. Moreover, the nature and the mechanism of interaction between the cement and the polymer are not fully known. The hydration process can also affect the ease of use of these mortars such as their possible application on a vertical surface, which could be

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linked to the mortar's stiffness and cohesiveness, and can have an impact on the quality of bond between the repair mortar and the surface to repair. Therefore, it is important to also pay attention to the rheological changes induced by the admixtures.

This article deals with the interactions and modifications that occur in cement pastes in the presence of EVA and CaO. It is well known that the hydration of calcium oxide is an exothermic reaction with a high amount of energy released. Therefore, the heat of hydration of each cement paste was measured through calorimetry. The evaluation of the EVA particles was done using dynamic light scattering (DLS). Furthermore, the evolution of the setting time and the rheological properties of pastes are also discussed in this paper, with the aim to see if these properties could be related to the changes observed intrinsically.

2 Techniques and materials

2.1 Techniques

- The heat of hydration of the cement pastes was measured in a thermal heat flow calorimeter (TAM Air).
- Dynamic light scatter technique (Zetasizer nano ZS) was used to observe the behaviour of the polymers during the first moment of hydration. To do this, a pore solution was extracted from a cement paste and this solution was used as solvent to measure the hydrodynamic radius and the zeta potential of EVA. These analyses were realised on a pore solution with 0.43% of EVA. The hydrodynamic radius gives an estimation of the particle size of the polymer. This optical method called the dynamic light scatter (DLS) is based on the fluctuation of the intensity of a light signal shot into the sample. This light interacts with the particles of polymer in the solution. The hydrodynamic radius R_H is linked to the diffusion coefficient D by the Stokes-Einstein equation given in the equation (1). The zeta potential is the electro kinetic potential in colloidal dispersion, and it is caused by the electrical charges that surround the polymer particles and the other ions in the solution. Therefore, its value depends on the interactions between the ions in the solution.

$$D = \frac{kT}{6\pi\eta R_H} \quad (1)$$

Where: R_H is hydrodynamic radius,
 D is the diffusion coefficient,
 k is the Boltzmann constant,
 η is the medium viscosity,
 T is the temperature.

- A rotational viscometer with a basket probe was used for the rheological tests. Based on some preliminary trials, the test program was set up as shown in Fig. 1.

Fig. 1. Test program for the rheological tests.

2.2 Materials

All the results presented in this article were realised on the cement pastes. Their formulations are presented in Table 1.

Table 1. Formulation of the cement pastes.

	Cement	w:c	EVA:c (%)	CaO:c (%)
Ref	CEM I 42.5 N	0.72	0	0
7 EVA			7	0
14 EVA			14	0
3 CaO			0	3
7 CaO			0	7
10 CaO			0	10
7 EVA - 7 CaO			7	7

EVA:c = EVA to cement weight ratio

CaO:c = CaO to cement weight ratio

3 Results

3.1 Evolution of EVA particles in a pore solution

Fig. 2 presents the zeta potential of a pore solution with EVA. This figure essentially shows a constant value of the zeta potential between -2 mV and -4 mV. This stabilisation can reflect the increase of interaction between EVA particles and the ions in the pore solution. According to previous experiences, these interactions can be the result of two different processes: a complexation of the acetate group of the EVA with calcium ions which produces calcium acetate [4] and/or a physical process where the polymer particles are adsorbed at the surface of the cement grains [5]. On the other side, the stabilisation of the zeta potential can also indicate the imminent precipitation or coagulation which could be agglomeration of EVA particles, which is a part of the process of the film formation (filmification) [6, 7].

Fig. 2. Zeta potential of pore solution that contains EVA.

Regarding the measurement of the hydrodynamic radius in Fig. 3, EVA changes state around an hour after being introduced in the pore solution. The modification could be seen in three phases. Immediately after the introduction the EVA in the pore solution, the particles of the polymer are dissolved in the solution. This is why the intensity of the peak already drops around 10 minutes, after which two main peaks can be identified until approximately 60 minutes. The first group of peaks has a hydrodynamic radius of about 900 nm like the peak between 0 and 10 minutes but with lower intensity. This lower intensity corresponds to a reduced fraction of EVA of that size range. The right side of the diagram in Fig. 3 shows the emergence of a peak with a hydrodynamic radius located around 5500 nm, after approximately one hour. This indicates that the EVA polymers agglomerate with time, which implies a beginning of the formation of a polymer film [6, 7].

Fig. 3. Evolution of the hydrodynamic radius of EVA in the pore solution.

3.2 Impacts of EVA and CaO on the hydration and the setting of the cement pastes

The results of the calorimetry are presented in Fig. 4. It is observed that EVA decreases the heat released during the hydration and it also delays the hydration process. This delay can be explained by the work of Bertoli *et al.* [8] which shows that calcium acetate complex ($\text{Ca}(\text{COO})_2$) formed from the reaction between EVA and the Ca^{2+} from the cement lasts around 24h. Therefore, it is only after the dissolution of the $\text{Ca}(\text{COO})_2$ complex that the calcium

ions are released for the hydration. Furthermore, a second peak occurs on the cement paste curve with 7% of EVA and it is more visible on the curve of the cement paste that contains 14% of EVA after 30 hours. Yet, at this stage, it is not possible explain this peak.

Fig 4. Heat of hydration of different cement pastes.

Fig. 4 also shows that the calcium oxide accelerates the hydration and it increases the heat released by the cement paste, which is an expected outcome since the hydration of calcium oxide is an instant reaction that releases a large amount of energy, as Equation (2) shows.

Regarding the combination of the EVA and CaO (7% of each), the diagram is similar to the one with only 7% of CaO, as if the heat development was not affected by the polymer in presence of CaO.

As shown in Table 2, the setting time of the cement pastes is delayed in the presence of polymers. The spontaneous hydration of calcium oxide induces the acceleration of the setting. However, the setting time of the cement paste that contains both EVA and CaO is similar to the one with EVA alone. The retarding effect of EVA distinctively outweighs the accelerating effect of CaO.

Table 2. Setting time of the cement pastes.

	Initial (h)	Final (h)
Ref	11.1	13.5
7 EVA	12.6	17.1
14 EVA	13.6	16.9
3 CaO	10.6	12.7
7 CaO	9.8	11.8
10 CaO	9.8	11.5
7 EVA - 7 CaO	12.5	16.7

3.3 Impacts of the EVA and the CaO on the rheology the cement pastes

Fig. 5 & 6 present the yield stress and the apparent plastic viscosity of the cement pastes measured over 100 min. These figures reveal that the calcium oxide affects mainly

the yield stress of these pastes while the plastic viscosity is mainly controlled by the amount of polymer and the duration of the mixing. The hydration of CaO produces calcium hydroxide ($\text{Ca}(\text{OH})_2$) particles which are twice as big as the CaO in volume. This could explain the increase of the yield stress. Besides, as mentioned above, the presence of the EVA particles induces more interactions and reactions in the system and these particles are also transformed to become films this, which should induce the variation of the viscosity of the paste. The mixing time does not affect the rheological properties of the cement pastes with CaO during these 100 minutes. However, the viscosity strongly increases for the 20 first minutes of mixing, then decreases in the cement paste with EVA. This effect might still be linked to the filmification of

polymer. However, the combination of EVA and CaO shown on Fig. 7 tends to increase the yield stress but the viscosity has the same order of magnitude than the one with EVA only.

4 Discussion

As stated above the interactions of the polymer EVA and the ions of a pore solution can happen at a chemical level with the complexation of the calcium ions by the acetate groups of the EVA and the absorption of the polymer at the surface of cement particles. In both cases, they lead to the capture of a calcium ion which restricts the initiation of the hydration of the cement.

Fig. 5. Time-development of yield stress and the plastic viscosity of the cement pastes with EVA (time given in minutes).

Fig. 6. Time-development of yield stress and plastic viscosity of the cement pastes with CaO (time given in minutes).

Fig. 7. Time-development of yield stress and plastic viscosity in pastes with a combination of EVA and CaO (time given in minutes).

These results are consistent with the ones observed in the heat of hydration diagrams in Fig. 4 and the setting time in Table 2. Indeed, they show that the hydration and the setting of the cement pastes are delayed in the presence of EVA. Besides, as expected, the rapid reaction of calcium oxide CaO induces the acceleration of the hydration and the beginning and the end of the setting time. However, for these two cases, the combination of the EVA and the CaO (7% of each in the cement paste) reveals that the setting time and the hydration might be governed by only the EVA since the results obtained from the cement paste with EVA and CaO are similar to the ones with only EVA.

On the other hand, the results on the rheology show that the EVA mainly affects the plastic viscosity of the cement paste and that this viscosity depends on the mixing time. It is only after 60 minutes of mixing that the rheological parameters of the cement paste seem to be more stable. This could still be linked to the interactions between EVA and the cement, especially to the absorption of the EVA particles, which combined to network of EVA films in the paste, might modify the viscosity. Besides, the quick reaction of the CaO in contact with water produces calcium hydroxide ($\text{Ca}(\text{OH})_2$) which is twice as big than the starting particle. This might cause the increase of the yield stress. In this case, the rheological behaviour the combination of EVA and CaO tends to be increased.

5 Conclusions

The aim of this study was to investigate the consequences of the intrinsic modification that can occur in a mortar modified with calcium oxide and EVA, and the effects on the properties of this mortar at earlier ages. This article focuses on the heat released during hydration, the behaviour of EVA particles in cement paste, and the changes in the setting time and the rheological properties. The conclusions are as follows:

- The hydration of CaO, which is spontaneous and highly exothermic enhances the energy released during the hydration, accelerates the setting of the mortars, and also increases the yield stress of the paste.
- Part of the calcium ions from the cement are complexed by the EVA to form calcium acetate before being released later in the solution and hydrated. This is shown by the drop of the zeta potential and the delay of setting. Furthermore, the formation of EVA film tends to modify the viscosity of the polymer.
- The combination of EVA and CaO increases the yield stress. However, in this situation, the heat of hydration is similar to that with only CaO, while the viscosity of the cement paste is similar to that with EVA alone.

In conclusion, the use of ethylene vinyl acetate and calcium oxide can affect the workability of mortars. These results show that the combination of these two admixtures can lead to a mortar with a longer setting time, but with lower workability which might affect the adherence properties of the mortar.

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