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Polymer film formation in cement mortars modified with water-soluble polymers**E. Knapen^{*,°,+}, D. Van Gemert[°]**

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Abstract

The modification of cement mortars with small amounts of water-soluble polymers (polyvinyl alcohol-acetate, methylcellulose and hydroxyethylcellulose) is studied. During hardening, two processes can take place, i.e. cement hydration and polymer film or bridge formation. Due to the very low polymer contents, the formation of polymer films is generally not considered. In this paper, evidence is given of the presence of polymer films or bridges in mortars modified with 1% of polyvinyl alcohol-acetate or methylcellulose. A contribution to the flexural strength of these mortars is found. By means of SEM investigation, polymer bridges are detected between the layered $\text{Ca}(\text{OH})_2$ crystals. Additional bonds are created which strengthen the preferential cleavage sites. Furthermore, polymer films or bridges are intergrown within the cement matrix on a submicron scale.

Keywords: Polymer modification, film formation, microstructure, water-soluble polymers, SEM investigation, flexural strength

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1 Introduction

Water-soluble polymers are commonly used in dry set mortars or added to fresh mortar mixtures as rheology modifiers or stabilizing agents. The influence on the rheological properties is extensively reported in literature [1-3], but their use remains essentially empirical. In general, the purpose of modification with water-soluble polymers is the improvement of the fresh mortar properties, whereas the impact on the mechanical properties is considered as a side-effect. However, some authors report a significant beneficial effect on the hardened mortar structure. An increase of the tensile strength is found for some applications [4]. Also, the bond strength between cement paste and aggregates [5, 6], between cement paste and steel fibres [7] and between cement paste and carbon fibres [8] is improved. An enhancement of the interface between aggregates and cement paste can result in a decreasing permeability [1]. Although it is sometimes found that cellulose ethers increase cement paste shrinkage, crack formation is reduced due to an improved cohesion within the cement matrix [9]. The addition of the water-soluble methylcellulose (0.4% by mass of cement) or a polymer dispersion (20% by mass of cement) to cement paste gave similarly significant increases of the shear bond strength between stainless steel fibres and cement paste, in spite of the low concentration and, therefore, lower cost of methylcellulose, when compared to the dispersion [7].

Until now, very little information is available about the effect of water-soluble polymers on the hydration reactions and on the microscopical properties of cement mortars. Recently, there is a growing interest in the polymer-cement interactions and in the effect of polymer solutions on the microstructure formation [9-11], but a large

number of research questions remains unanswered. During hardening of cement mortars modified with water-soluble polymers, two processes could take place, cement hydration and formation of polymer film or bridges. Because of the very low polymer contents (usually below 4% of the cement mass), the formation of polymer films is rarely considered. However, due to the molecular distribution of the water-soluble polymers in the mixing water, an easier and more uniform film formation might take place, in comparison with polymer dispersions. In this paper, polymer film formation in cement mortars modified with water-soluble polymers is investigated. It is found that the polymers do not only act as rheological additives, but that, in some cases, polymer bridges are formed. By means of mechanical strength tests, thermal analysis and microscopic investigation, the presence of the polymer films or bridges in the hardened mortar structure is studied.

2 Experimental program

2.1 Materials and composition

An ordinary Portland cement (CEM I 52.5 N) and CEN-Standard sand DIN EN 196-1 are used. The specifications of the cement are presented in Table 1. Different types of polymers are added to the fresh mixtures: a polyvinyl alcohol-acetate (PVAA, Celvol 805 of Celanese Chemicals), which is a 87-89% hydrolyzed polyvinyl acetate, and two cellulose ethers, methylcellulose (MC, Methocel A15-LV of the Dow Chemical Company) and hydroxyethylcellulose (HEC, Cellosize QP40 of the Dow Chemical Company). All pure polymer solutions form transparent and crack-free films at room temperature.

For the mechanical strength tests and the SEM investigation, mortar beams (40 x 40 x 160 mm) are prepared with a polymer-cement ratio (p/c) of 1%, a water-cement ratio (w/c) of 0.45 and a sand-cement ratio (s/c) of 3. The polymer powders are first dissolved in the mixing water, according to the procedures proposed by the manufacturers, before adding to the sand and cement in the mixer. The mortar beams are covered for 2 d before demoulding. The standard curing implies a storage, after demoulding, in a moist room for 5 d (20°C, 93% R.H.), followed by a dry curing until the moment of testing (20°C, 60% R.H.).

For the thermal analyses, cement pastes with the same composition but without sand are prepared according to the same procedure. The pastes are stored in closed recipients until the moment of testing. Prior to thermal analyses, the free water is removed by vacuum drying for 2 h in a vacuum of 2.5×10^{-2} mbar. Extracted water is continuously collected in an ice condenser at a temperature of -62°C.

2.2 Experiments

Thermal analysis is performed using a Netzsch STA 409 PC, a simultaneous Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) system. The samples are heated from room temperature to 1000°C with a heating rate of 10°C/min in a N₂ atmosphere (60 ml/min). Assuming that all water, which has not yet participated in the hydration reactions, is removed by vacuum drying, the mass loss between 20°C ($m_{20^\circ\text{C}}$) and 1000°C ($m_{1000^\circ\text{C}}$) is a measure of the amount of bound water during hydration and, therefore, of the degree of hydration [12]. The amount of bound water in Formula 1 is corrected for the mass loss due to the decomposition of

the polymers and for the loss on ignition of the cement itself. L_{cem} is the loss on ignition of the unhydrated cement, L_{pol} the loss on ignition of the polymer, both as percentage of the initial mass.

$$\text{Amount of bound water } [\%] = \frac{m_{20^{\circ}\text{C}}(1 - L_{cem}) - m_{1000^{\circ}\text{C}}(1 + \frac{p}{c}L_{pol})}{m_{1000^{\circ}\text{C}}(1 - \frac{p}{c}(1 - L_{pol}))} \quad (1)$$

Compressive and flexural strength tests are carried out, according to the European standard EN 196-1:2005 [13]. The average of three (flexural strength) or six (compressive strength) test results is presented. After mechanical testing, the microstructure of the mortar beams is investigated on freshly broken surfaces, using a Philips XL 30 FEG Scanning Electron Microscope (SEM). In order to render the mortar surface conductive, samples are coated by evaporation with gold.

Because polymer modification favours the stabilization of air voids, due to the surface activity of the polymers, a large amount of closed pores is formed in the polymer modified mortars [14]. Therefore, the total porosity is calculated from the absolute density of the sample that is measured by pycnometry.

3 Results

3.1 Thermal analysis

Thermal analysis is used to study the progress of cement hydration reactions. During the first 24 h, the hydration reactions of the polymer modified pastes are retarded, especially in the HEC modified pastes [14]. The amount of bound water after 24 h, 2

d, 7 d, 28 d and 90 d of hydration is presented in Figure 1. After 2 d of hydration, the bound water content for the paste modified with HEC is the same as for the other pastes, but it still increases significantly between 28 d and 90 d when compared to the other pastes. The PVAA modified paste shows a strong increase of the amount of bound water, and therefore of the degree of hydration, between 24 h and 7 d of hydration. Afterwards, it remains almost constant. After a major increase between 2 d and 7 d, the bound water content of the MC modified pastes follows a similar course as the unmodified paste.

All polymer modified samples show a higher amount of bound water than the reference paste after 90 d of hydration. A possible explanation is the better dispersion of the cement particles in the mixing water in the presence of water-soluble polymers [14]. Water-soluble polymers also show a higher water retaining ability, increasing the final degree of hydration [2]. Because all samples are stored in closed bottles until the moment of testing and evaporation of water is prevented, the latter effect can not be studied.

3.2 Mechanical strength tests

3.2.1 Air entrainment versus compressive strength

The main goal of this study is to investigate the impact of water-soluble polymers on the microstructure formation. Therefore, the mortar composition and mixing procedure are not optimized with respect to the mechanical properties. In general, polymer film formation has only a minor effect on the compressive strength [15]. The compressive strength of polymer modified mortars is usually lower than that of

unmodified mortars, because of the higher air entrainment, which masks possible strengthening of the hydrated cement matrix.

In Figure 2, the compressive strength of the mortars is plotted versus the absolute density. The MC and HEC modified mortars are characterized by a high air entrainment and a low absolute density. The corresponding porosity of the MC and HEC modified mortars, resp. 22.4% and 21.5%, is much higher than that of the unmodified mortars (13.3%), while the porosity of the PVAA modified mortars is only slightly higher (14.8%). The high porosity of the MC and HEC modified mortars explains the low compressive strength.

3.2.2 Influence of curing conditions

The influence of the curing conditions on the mechanical properties is important towards the practical applications of the mortars. Cement hydration is promoted by a wet or moist curing, while a dry curing is needed for a proper polymer film formation [16]. For that reason, film formation can be studied by examining the influence of the curing conditions on the mechanical strength of the mortar beams. Comparison is made between mortars that are standard cured and mortars that are cured at a high relative humidity (93% R.H.) for 28 d. No effect of the curing conditions on the compressive strength of the mortars is found [14].

The flexural strength of the unmodified mortars and the mortars modified with HEC is also not affected by the curing conditions (Figure 3). On the other hand, the flexural strength of the mortars modified with PVAA and MC is increased with 21% and 27% resp. if a dry curing period is included (standard curing). After wet curing, the flexural

strength of the PVAA modified mortar is equal to that of the unmodified mortar. The strength of the MC and HEC modified mortar is lower, probably due to the large air entrainment.

3.2.3 Strength development with hydration time

The evolution of the mechanical strength with hydration time reveals some information on the hydration process and the polymer film formation and is important towards the practical applications. In order to study the mechanical properties with respect to the hydration time, mortar beams are standard cured and stored afterwards at 60% R.H. The compressive and flexural strength is determined after 2 d, 7 d, 28 d, and 90 d. The development of the compressive strength with hydration time is almost similar for all mortar beams. For the mortars modified with MC and HEC, the air entrainment is very high, which greatly reduces the compressive strength [14].

When analyzing the evolution of the flexural strength (Figure 4), the curing conditions should be borne in mind. During standard curing, a dry curing is applied after 7 d of moist curing. The increase of the flexural strength of the PVAA and MC modified mortars between 7 d and 28 d of hydration is much larger than that of the unmodified mortar. The development of the flexural strength of the PVAA and HEC modified beams also seems to be retarded with still a major increase of the flexural strength after 28 d. This phenomenon is much less pronounced for the compressive strength [14].

3.3 SEM investigation

An extensive SEM investigation is carried out. Unfortunately, there are some shortcomings of SEM for the visual detection of water-soluble polymer films in the cement mortar microstructure. Water-soluble polymers are generally added in very low amounts (only 1% of the cement mass). Therefore, and due to their water-solubility, etching with a strong acid in order to remove the cement matrix is not possible. The small polymer films can also be integrated in the cement matrix on a submicrometer scale, which makes detection impossible. Furthermore, the electron beam that bombards the sample during SEM investigation is rather aggressive. Polymer films are reported to be highly sensitive to damage by the electron beam [17]. However, between the layered Ca(OH)_2 crystals and at the air void surfaces, polymer bridges are detected and the presence of polymers in the cement matrix is observed.

3.3.1 Polymer films between the Ca(OH)_2 crystals

In unmodified cement mortars, Ca(OH)_2 crystals are weak and unable to withstand the stresses that are generated during the early hydration when the rearrangement of hydrates takes place in a limited space [18]. However, in the presence of MC, Ca(OH)_2 precipitates as stacks of layered crystals with an undistorted morphology. The crystal structure is strengthened by MC modification. At high magnifications, polymer bridges are detected between the layered Ca(OH)_2 crystals (Figure 5). The bridges are stretched between the layers, acting as an additional bond and gluing the layers together. Because Ca(OH)_2 crystals represent the weak phase in the binder matrix and the surfaces of those crystals form preferred cleavage sites, the strengthening by polymer bridges may improve the overall strength of the binder matrix.

3.3.2 *Polymer films at the air void surfaces*

The presence of water-soluble polymers can be expected at the air void surfaces, because of their strong affinity for the gas-water interface. The polymers serve as surface-active agents that are initially dissolved in the mixing water. During mechanical mixing, they are attached to the air void interface and start to stabilize the entrained air voids in the fresh mixture. An enrichment of polymer at the interface between air void and wet cement paste may be detected, depending on the surface activity of the polymer [17].

In Figure 6, an air void in a MC modified mortar is presented. In the area of interest, $\text{Ca}(\text{OH})_2$ linings cover the air void surface. At high magnifications, polymer bridges are found between the plate-like $\text{Ca}(\text{OH})_2$ crystals, similar to what is observed in Figure 5.

In the MC modified mortar, polymer films are also detected, stretched in the open pore spaces. In Figure 7, the polymer film is partially intermingled with the ettringite needles and other cement hydrates [14]. Additionally, polymer films are observed between the ettringite needles at the air void surface in MC modified mortar (Figure 8). The films cover the C-S-H phase, giving it a more smooth and bright texture.

3.3.3 *Intermingling of polymer films with the cement matrix*

In the PVAA and HEC modified mortars, polymer film formation is not so easily detectable by SEM investigation. Nevertheless, it is possible that polymer films or bridges are present in the finer capillaries and intergrown within the cement matrix on a submicron scale, which makes them much more difficult to detect, but which may

be even more important for the overall properties of the material. Therefore, the effect of under water storage is studied.

Water-soluble polymers are highly sensitive to moisture and water [19]. During storage under water, the polymer films can be redissolved in water and transported throughout the mortar matrix. For this reason, samples are studied before and after vacuum saturation and storage under water. Mortar beams are sawn to small beams of approximately 1 x 1 x 5 cm, vacuum saturated with water and stored under water and vacuum for 7 d. Afterwards, they are dried at 50°C. Freshly broken surfaces are prepared and samples are coated with gold.

In Figure 9, an aggregate surface in a 1% PVAA modified mortar is presented, before and after wetting. The freshly broken surface is partially covered with C-S-H phase, which has a typical reticular or honeycomb structure. After storage under water, the C-S-H phase is covered with a smooth polymer film. The PVAA film seems to be leached from the cement matrix during under water storage and is deposited on top of the C-S-H phase during the subsequent drying. This is supported by mechanical strength data. A strong decrease of the flexural strength of polymer modified mortars is found after storage under water, which is not found for unmodified mortars [14].

4 Discussion

Until now, little information is available about the effect of water-soluble polymers on the microstructure of polymer modified cement mortars, and particularly about the polymer film formation. For polymer dispersions, a polymer-cement ratio higher than

5% is necessary for an adequate film formation throughout the cement matrix. If the polymer-cement ratio is lower than 5%, the polymer acts as an admixture for the ordinary cement mortar and no continuous polymer film is formed [16]. Because of the low amounts of water-soluble polymers that are added to the fresh mixture ($p/c=1\%$), these polymers are generally considered as rheological additives and polymer film formation is not mentioned. However, in contrast to polymer dispersions, water-soluble polymers are added on a molecular scale, allowing the polymer film or bridge formation to proceed more easily and possibly at lower polymer-cement ratios. In this paper, evidence is given of the formation of polymer bridges in mortars modified with 1% of water-soluble polymers and of their contribution to the mechanical strength of the mortars.

For the formation of polymer films with a sufficiently high strength, a dry curing period is needed [16]. PVAA and MC modified mortars show a 21%, resp. 27% higher flexural strength if a dry curing is introduced after 7 d of hydration, compared to the mortars that are wet cured for 28 d (Figure 3). Without dry curing period, the flexural strength of unmodified and PVAA modified mortars is comparable and the influence of the curing conditions on the flexural strength of the unmodified mortars is negligible. Additionally, it is shown that a strong increase of the flexural strength of polymer modified mortars takes place when the dry curing starts, i.e. after 7 d of hydration (Figure 4).

As a measure of the degree of cement hydration, the amount of bound water is calculated. By comparing the evolution of the flexural strength with the degree of hydration at certain time intervals, polymer film formation can be studied as the

bridging behaviour of the polymer films strengthens the microstructure [15]. Thermal analysis showed that the amount of bound water for 1% PVAA modified pastes remains almost constant after 7 d of hydration (Figure 1). The evolution of the amount of bound water for the pastes modified with 1% MC is similar to that of the unmodified pastes. Therefore, the large increase of the flexural strength after 7 d is a strong indication of the formation of a polymer film which contributes to the flexural strength of the PVAA and MC modified mortars. Film formation in the HEC modified mortar is less clear, because still a major increase of the amount of bound water is measured after 28 d of hydration.

The presence of the polymer films in PVAA and MC modified mortars is confirmed by SEM investigation. In MC modified mortars, polymer bridges are detected between the $\text{Ca}(\text{OH})_2$ crystals (Figures 5 and 6) and at the air voids (Figures 7 and 8). Even though no continuous network of polymer films is found, the presence of discontinuous polymer films or bridges at weak interface, such as $\text{Ca}(\text{OH})_2$ crystal surfaces, can strengthen the microstructure and improve the overall properties. After leaching due to storage under water, PVAA films are found on top of the cement hydrates (Figure 9). Because of the impact of the polymer film formation on the mechanical properties and the sensitivity of the polymer films to water and moisture, further research is needed to investigate the effect of moisture and under water storage on the bridge formation in mortars modified with water-soluble polymers [14].

In HEC modified mortars, polymer film formation is less clear. The influence of possible film formation on the mechanical properties is often masked by the high air entrainment and the strong retardation of the hydration reactions. Additionally, pure

HEC films have a lower tensile strength than PVAA and MC films and are highly sensitive to moisture [19].

5 Conclusion

Polymer film formation in mortars modified with 1% of PVAA, MC and HEC is studied by SEM investigation, mechanical strength tests and thermal analysis. SEM investigation on MC modified mortars shows the presence of polymer bridges between the Ca(OH)_2 crystals, acting as an additional bond between the crystal layers and strengthening the crystal structure. Furthermore, at the air void surfaces of MC modified mortars, the presence of polymer films or bridges is detected at several places, e.g. between Ca(OH)_2 crystals, stretched in open pore spaces and partially intermingled with the ettringite needles and the C-S-H phase. In PVAA modified mortars, the visual detection is much more difficult, possibly due to an intermingling with the cement hydrates on a submicron scale. However, after extensive storage under water, PVAA films are found to be leached from the cement matrix and deposited on top of the cement hydrates during the subsequent drying. In HEC modified mortars, polymer film formation is less clear.

Additionally, the presence of polymer films and their contribution to the strength are investigated by mechanical strength tests. When a dry curing period is introduced, which is necessary for the polymer film formation, a much higher flexural strength is measured for PVAA and MC modified mortars, compared to mortars that are wet cured. On the other hand, the curing conditions do not influence the flexural strength of unmodified mortars, nor the compressive strength of both unmodified and polymer

modified mortars. Furthermore, by comparing the evolution of the flexural strength with the degree of hydration at certain time intervals, strong indication is found of polymer film or bridge formation in the PVAA and MC modified mortars which contributes to the flexural strength of those mortars.

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Tables

Table 1: Chemical composition of cement CEM I 52.5 N (provided by manufacturer).

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	Cl ⁻	Loss on ignition	Insoluble residue
Wt. %	61.7	17.2	5.7	3.9	0.8	0.41	0.77	3.1	0.04	1.6	0.7

Figure Captions

Figure 1. Amount of bound water after 24 h, 2 d, 7 d, 28 d and 90 d of hydration for unmodified pastes and pastes modified with 1% PVAA, MC and HEC ($w/c=0.45$)

Figure 2. Compressive strength versus absolute density measured by pycnometry for unmodified mortars and mortars modified with 1% PVAA, MC and HEC ($w/c=0.45$)

Figure 3. Influence of curing conditions on flexural strength of unmodified mortars and mortars modified with 1% PVAA, MC and HEC ($w/c=0.45$) after 28 d. The error bars represent the standard deviation.

Figure 4. Flexural strength after 2 d, 7 d, 28 d, and 90 d of hydration for unmodified mortars and mortars modified with 1% PVAA, MC and HEC ($w/c=0.45$)

Figure 5. Polymer films between layered $\text{Ca}(\text{OH})_2$ crystals in 1% MC modified mortars ($w/c=0.45$)

Figure 6. Polymer bridges at the edge of air bubble surfaces in 1% MC modified mortars

Figure 7. Polymer film stretched in open space in 1% MC modified mortar

Figure 8. Polymer film, covering the C-S-H phase between the ettringite needles in 1% MC modified mortar

Figure 9. C-S-H phase on top of an aggregate in 1% PVAA modified mortar before storage under water (a). After storage under water for 7 d, a polymer film covers the C-S-H phase (b).

Figure 5a

Polymer bridges

Acc.V	Spot	Magn	Det	WD	Exp
10.0 kV	3.0	15000x	SE	12.0	1

2 μ m

Figure 5b

Polymer bridges

Acc.V	Spot	Magn	Det	WD	Exp		
10.0 kV	3.0	25000x	SE	11.1	1	1 μm	

Figure 6a

Figure 6b

Polymer bridges

Acc.V	Spot	Magn	Det	WD	Exp
10.0 kV	3.0	16000x	SE	11.9	1

2 μ m

Figure 7

Discontinuous
polymer films

Acc.V	Spot	Magn	Det	WD	Exp
10.0 kV	3.0	6400x	SE	11.3	1

5 μ m

Figure 8a

Acc.V	Spot	Magn	Det	WD	Exp	Scale Bar	2 μm
10.0 kV	3.0	9000x	SE	12.1	1		

Figure 8b

Polymer films

Acc.V	Spot	Magn	Det	WD	Exp		
10.0 kV	3.0	25600x	SE	12.1	1	1 μm	

Figure 9a

Acc.V	Spot	Magn	Det	WD	Exp		1 μm
10.0 kV	3.0	21000x	SE	11.5	1		

Figure 9b

Acc.V Spot Magn Det WD Exp |——| 1 μm
10.0 kV 3.0 20000x SE 12.1 1