Cement and Concrete Research 39 (2009) 6–13

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Cement hydration and microstructure formation in the presence of water-soluble polymers

E. Knapen [a,b,*], D. Van Gemert [a]

[a] *Department of Civil Engineering, Building Materials and Technology Division, Kasteelpark Arenberg 40 (2448), 3001 Heverlee, Belgium*
[b] *De Nayer University College, Materials and Structures Research Group, J. De Nayerlaan 5, 2860 Sint-Katelijne-Waver, Belgium*

ARTICLE INFO

Article history:
Received 31 January 2008
Accepted 2 October 2008

Keywords:
Retardation (A)
Hydration products (B)
Microstructure (B)
SEM (B)
Polymers (D)

ABSTRACT

Hardening of cement mortars modified with small amounts of water-soluble polymers implies both cement hydration and polymer film formation. In this paper, the effect of the presence of water-soluble polymers on the cement hydration reactions is investigated by means of isothermal calorimetry, thermal analysis, FT-IR spectroscopy and SEM investigation. In spite of an initial retardation of the hydration reactions, a higher degree of hydration is found after 90 days for 1% PVAA, MC and HEC modified mortars, due to a better dispersion of the cement particles in the mixing water. MC also affects the morphology of the $Ca(OH)_2$ crystals. Polymer bridges are detected between the layered crystals, gluing the layers together and strengthening the microstructure. Additionally, the internal cohesion of all bulk polymer modified cement pastes is improved. In the presence of the polymers, a more cohesive microstructure with a smaller amount of microcracks is created.

1. Introduction

Water-soluble polymers are frequently added to cement mortars in order to improve the fresh mixture properties. Mortars modified with water-soluble polymers show a higher water retention than ordinary cement mortars. The hydrophilic parts of the polymers fix the water molecules in the fresh mixture, preventing the dry-out by evaporation and absorption into the surrounding porous material [1]. The water-retaining capacity also often results in a thickening and viscosity enhancing behaviour. Because of the increased viscosity of the cement paste, less free water is available for bleeding and the segregation tendency decreases. The homogeneity of the mortar is improved [1–3]. Also, a better dispersion of carbon and steel fibres in the cement paste is realized [4]. Although the consistency of the mortars is often reduced in the presence of water-soluble polymers, the easiness to apply the fresh mixtures is markedly improved, because of the plasticizing, lubricating and air-entraining effects of the polymers.

Whereas the effect of polymer dispersions on the microstructure formation is frequently studied [5], only little information is available about the effect of polymer solutions. In contrast to polymer dispersions, water-soluble polymers are dissolved in the mixing water on a molecular scale and no surfactants are needed. However, the addition of small amounts of water-soluble polymers (usually below 4%) also influences the properties of the hardened material [6]. During hardening, two processes can take place, i.e. cement hydration and polymer film formation. In spite of the very low polymer concentrations, polymer films are detected in mortars modified with 1% of polyvinyl alcohol-acetate (PVAA) and methylcellulose (MC). A major contribution of the films to the strength of these mortars is observed [7]. Furthermore, the cement hydration reactions can be influenced by the presence of the polymers. In this paper, the rate and degree of cement hydration and the nature and amount of hydration products that are formed are determined. Additionally, the morphology of the hydrate crystals and the microstructure of the hardened cement matrix are 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. 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). The solubility of the polymers in water is mainly determined by the viscosity of the solution. The polymers are dissolved in water, according to the specifications and at the concentrations proposed by the manufacturer. All polymer solutions are found to form transparent and crack-free films at room temperature.

For the SEM investigation, mortar beams (40×40×160 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

---

[*] Corresponding author. Department of Civil Engineering, Building Materials and Technology Division, Kasteelpark Arenberg 40 (2448), 3001 Heverlee, Belgium. Tel.: +32 16321678; fax: +32 16321976.
E-mail address: Elke.Knapen@bwk.kuleuven.be (E. Knapen).

0008-8846/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.10.003

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 days before demoulding. The curing implies a storage, after demoulding, in a moist room for 5 days (20 °C, 93% R.H.), followed by a dry curing until the moment of testing (20 °C, 60% R.H.).

For the thermal analyses and FT-IR spectroscopy, cement pastes without sand and with a polymer–cement ratio of 1% and a water–cement ratio of 0.45 are prepared. The polymer powders are first dissolved in the mixing water before adding to the cement in the mixer. The pastes are stored in closed recipients until the moment of testing. The addition of polymers significantly reduces the risk of bleeding. Additionally, for all analyses, samples are taken at the centre of the paste specimens. Prior to the analyses, the free water should be removed. After being crushed to fine powder, the cement pastes are vacuum dried for 2 h. The samples are introduced in an Alpha 1-2 LD Martin Christ type freeze-dryer without prefreezing. Round bottom flasks containing the samples are connected to a vacuum device consisting of a vacuum chamber that allows applying a vacuum of 2.5×10^{-2} mbar. Extracted water is continuously collected in an ice condenser at a temperature of −62 °C. Due to the exposure to the high vacuum, drying starts immediately and at high drying rate. A large amount of heat is needed for the evaporation of water and is extracted from the environment. Therefore, the sample is cooled down quickly, the available water freezes and hydration is stopped within minutes.

2.2. Experiments

Isothermal calorimetry measurements are carried out on a TA Instruments TAM Air Calorimeter at 20 °C. Cement pastes are mixed before inserting in the measuring unit. The sample mass is 7±0.5 g.

For the thermal analyses, a Netzsch STA 409 PC, a simultaneous Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) system, is used. The samples are heated from room temperature to 1000 °C with a heating rate of 10 °C/min in a N_2 atmosphere (60 ml/min). Assuming that all water which has not yet participated in the hydration reactions is removed by vacuum drying [8], the weight loss between 20 °C and 1000 °C is a measure of the amount of bound water during hydration and, therefore, of the degree of hydration. However, it also incorporates the mass loss due to the decarbonation of the carbonate phases, resulting in a small overestimation of the amount of bound water. The amount of bound water in Eq. (1) is corrected for the weight 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 and L_{pol} the loss on ignition of the polymer, both as percentage of the initial weight.

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

The weight loss in the temperature interval around 450 °C is mainly due to the dehydration of $Ca(OH)_2$. The $Ca(OH)_2$ content is calculated according to Eq. (2).

$$\mathrm{Ca(OH)_2}[\%] = \mathrm{WL_{Ca(OH)_2}}[\%] \cdot \frac{\mathrm{MW_{Ca(OH)_2}}}{\mathrm{MW_{H_2O}}} \tag{2}$$

$\mathrm{WL_{Ca(OH)2}}$ is the weight loss during the dehydration of $Ca(OH)_2$ as percentage of the ignited weight, determined according to the method described by Taylor [9]. $\mathrm{MW_{Ca(OH)2}}$ and $\mathrm{MW_{H_2O}}$ represent the molecular weight of resp. $Ca(OH)_2$ and water.

FT-IR spectra are taken in a Perkin Elmer 1725× spectrometer. Powdered samples are mixed with KBr and pressed into pellets. The analyses are carried out in the frequency range of 400–4000 cm^{-1}, using 4.0 resolution and 128 scans.

The microstructure of the mortar beams is investigated with a Philips XL 30 FEG Scanning Electron Microscope (SEM). For the analysis in the secondary electrons (SE) mode, freshly broken surfaces are prepared. Polished surfaces are analyzed in the backscattered electrons (BSE) mode. The final polishing stage is carried out with a 1 μm diamond paste. In order to render the mortar surface conductive, samples are coated by evaporation with gold prior to the SEM investigation.

3. Results

3.1. Isothermal calorimetry

The heat evolution, measured by isothermal calorimetry measurements, is presented in Fig. 1. It is observed that the start of the acceleration stage of hydration is postponed by ~30 min in the PVAA and MC modified pastes and by more than 5 h in the HEC modified paste. Not only the induction or dormant period is extended, but also

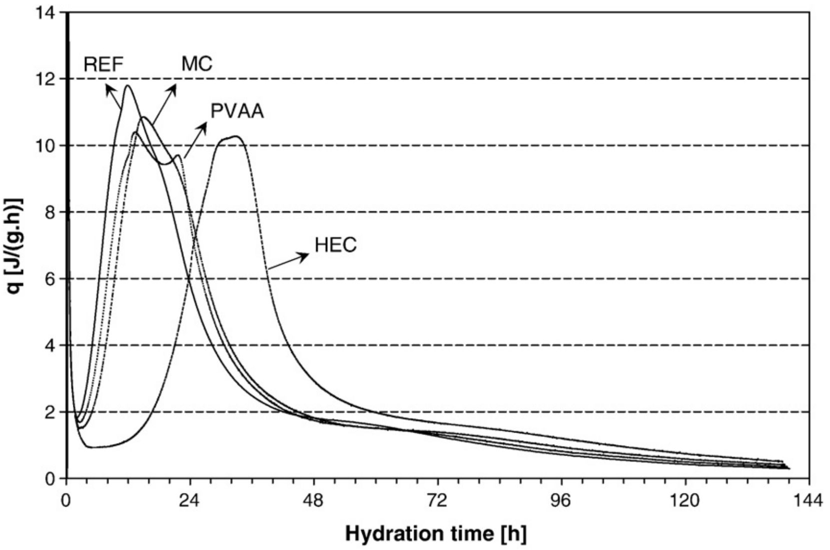

Fig. 1. Rate of heat evolution at 20 °C for unmodified and 1% PVAA, MC and HEC cement pastes (*w*/*c*=0.45).

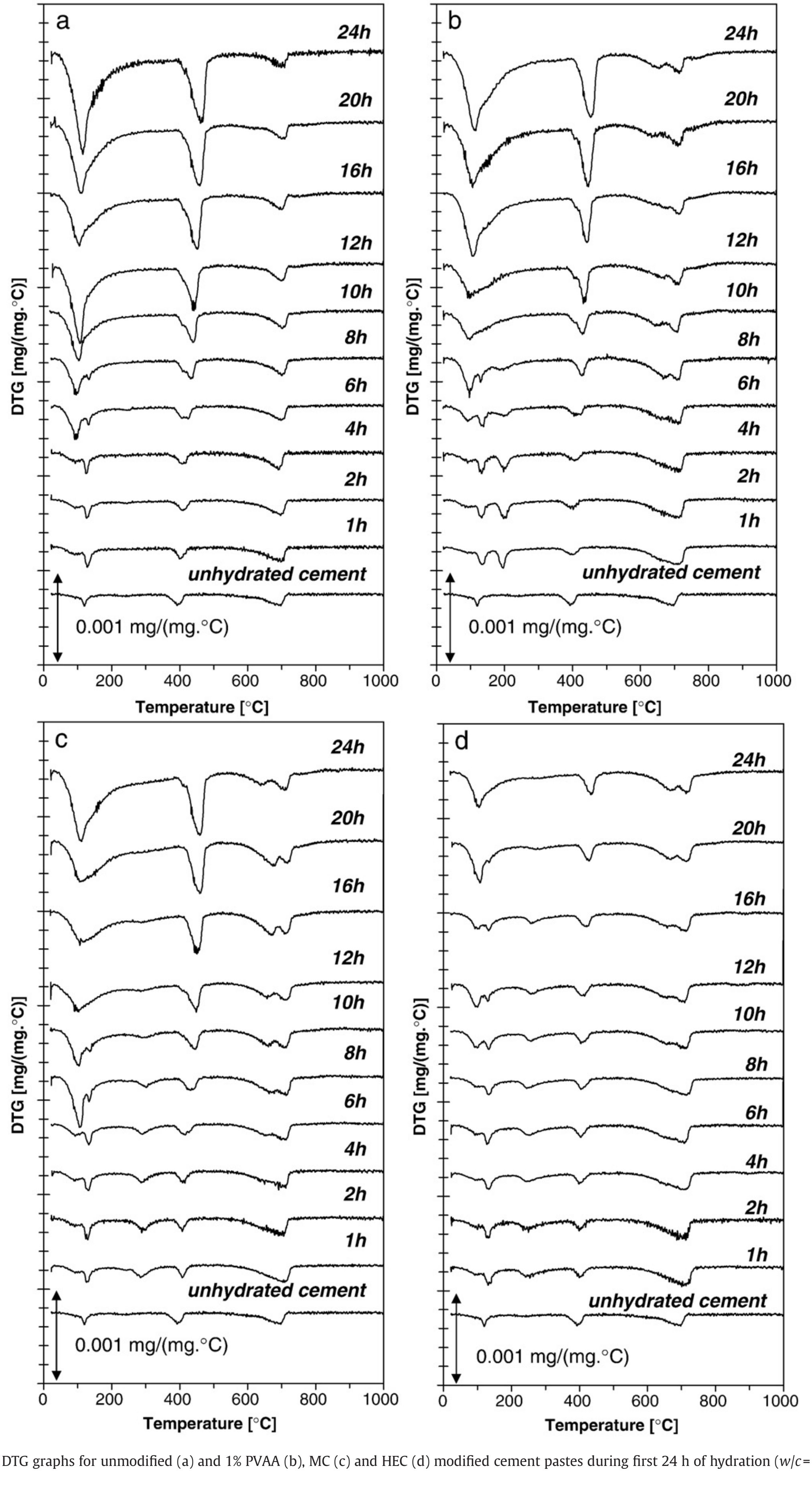

Fig. 2. DTG graphs for unmodified (a) and 1% PVAA (b), MC (c) and HEC (d) modified cement pastes during first 24 h of hydration (w/c = 0.45).

Table 1
Amount of bound water and $Ca(OH)_2$ content for unmodified and 1% PVAA, MC and HEC modified pastes (w/c=0.45)

	Amount of bound water [% of ignited mass]				$Ca(OH)_2$ [% of ignited mass]			
	4 h	12 h	24 h	90 days	4 h	12 h	24 h	90 days
REF	1.2%	7.9%	13.4%	23.6%	1.4%	5.8%	11.9%	16.9%
PVAA	1.1%	5.3%	12.5%	24.6%	1.0%	5.0%	9.6%	15.7%
MC	1.0%	4.7%	11.9%	24.8%	1.3%	3.6%	9.5%	16.3%
HEC	1.1%	2.1%	4.5%	26.7%	1.1%	1.5%	2.7%	15.4%

the rate of the following hydration reactions is slowed down. This is illustrated by lower values of the maximum heat release and broader exothermal peaks in the isothermal calorimetric curves of the polymer modified pastes.

3.2. Thermal analysis

The results of thermal analyses during the first 24 h of hydration are given in Fig. 2. Gypsum dehydrates at ~125 °C, generating a small mass loss, in the DTG graphs of the unhydrated and early-age cement pastes. Additional small mass losses appear at ~400 °C ($Ca(OH)_2$) and at ~700 °C ($CaCO_3$), because of partial hydration and carbonation during storage.

During the first hours of hydration, the DTG graphs remain almost unchanged. After 6 h of hydration, the unmodified cement paste shows a large peak at ~100 °C, due to the dehydration of C–S–H. This peak increases with hydration time. At the same time, gypsum is consumed by the formation of ettringite, resulting in a decrease of the peak at ~125 °C. The ettringite peak cannot be clearly distinguished because of overlapping with the C–S–H peak [10]. $Ca(OH)_2$ formation starts. The decomposition temperature of the relatively large $Ca(OH)_2$ crystals formed during cement hydration is slightly higher than the one of the smaller $Ca(OH)_2$ crystals formed during storage [9]. In the temperature range of ~600–800 °C, carbonate phases decompose.

After 6 h of hydration, only a small C–S–H peak is present in the DTG graphs of the PVAA modified paste. In the MC modified pastes, the accelerated formation of cement hydrate products seems to start at 8 h. After HEC modification, almost nothing happens during the first 8 h and even afterwards the formation of C–S–H and $Ca(OH)_2$ is rather slow. A double peak appears in the DTG graphs of the polymer modified pastes in the temperature range where the carbonate or carbonate-like phases decompose (~600–800 °C), whereas the DTG graphs of unmodified pastes only show a single peak at high temperatures. Additionally, an extra peak is detected at ~200 °C (PVAA), ~300 °C (MC) and ~260 °C (HEC) at early ages. The temperature of this peak does not correspond to the decomposition temperature of the pure polymer solutions (320 °C (PVAA), 355 °C (MC) and 305 °C (HEC)). The extra peaks start to disappear from the moment the hydration is accelerated and C–S–H and $Ca(OH)_2$ start to form. Measurements at later ages (up to 90 days) do not reveal the presence of new phases.

The amount of bound water and the $Ca(OH)_2$ content of the pastes after 4 h, 12 h, 24 h and 90 d of hydration are presented in Table 1. At early ages, a lower amount of bound water is found for the polymer

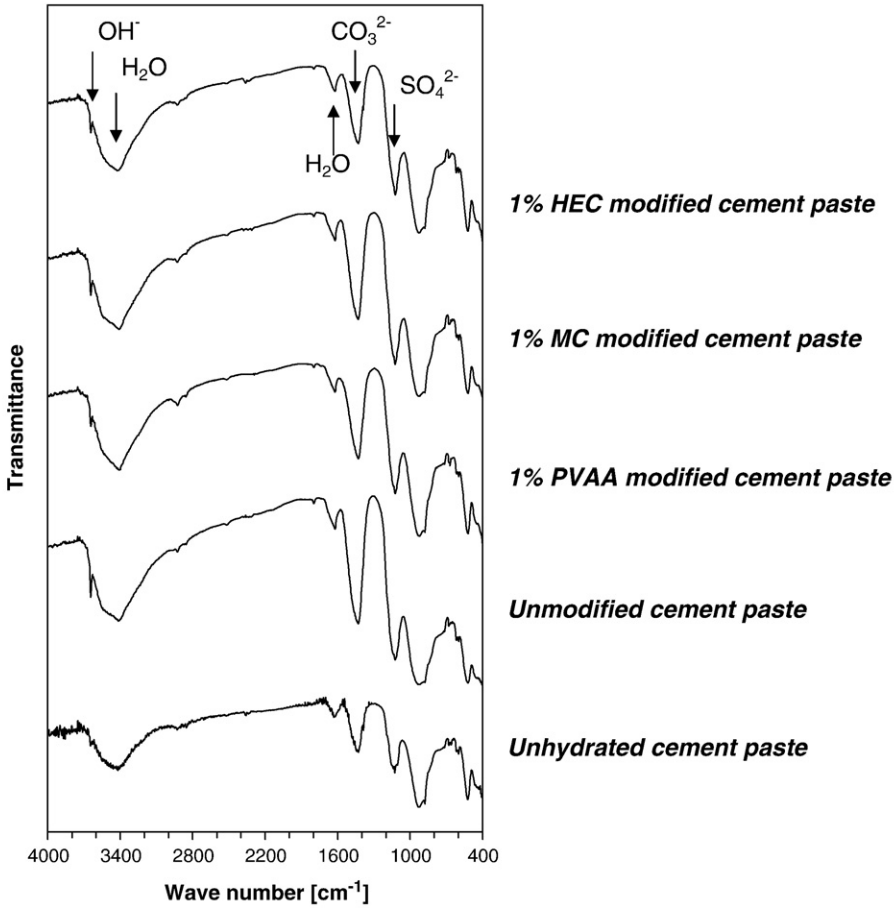

Fig. 3. FT-IR spectra for unmodified pastes and pastes modified with 1% PVAA, MC and HEC after 4 h of hydration (w/c=0.45).

modified pastes. After 24 h, the bound water content for the unmodified and PVAA and MC modified pastes is resp. 57%, 51% and 48% of the water content after 90 days, whereas a much lower value (17%) is measured for the HEC modified paste. Nevertheless, after 90 days of hydration, polymer modification results in a higher amount of bound water. The $Ca(OH)_2$ content is the highest for the unmodified pastes at all ages.

3.3. FT-IR spectroscopy

In Fig. 3, the FT-IR spectra of unmodified and polymer modified pastes are compared after 4 h of hydration. In the range between 3100–3700 cm^{-1}, the H_2O and OH stretching bands appear. They are also present in the spectrum of the unhydrated paste, because of the high hygroscopicity of the KBr pellets. A small increase of the OH^- band, associated with the $Ca(OH)_2$ molecules, is recorded at 3642 cm^{-1}, when compared to the unhydrated paste. The ν_3 S–O vibrations are found in the range between 1100 and 1170 cm^{-1}. In the unhydrated cement powders, several bands are present between 1106 and 1152 cm^{-1}. Peaks at ~1122 cm^{-1} are detected after 4 h of hydration, pointing to the early formation of ettringite. An increased intensity of this band is recorded for the unmodified paste. The progress of hydration is also characterized by a shift of the Si–O asymmetric stretching vibration (ν_3) to higher wave numbers (926 to 970 cm^{-1}), due to the polymerization of the SiO_4^{2-} units during C–S–H formation. However, at 4 h of hydration no polymerization of the silicate phase is detected yet. Carbonates are characterized by a $\nu_2+\nu_3$ band at 1428 cm^{-1}, a ν_4 band at 878 cm^{-1} and a ν_4 shoulder at 736 cm^{-1}. The bands, associated with the polymer itself, cannot be detected, because of the very low polymer contents and the partial overlapping with the bands of the unhydrated and hydrated phases.

3.4. SEM investigation

The results of the SEM investigation shown in this paper are part of a larger microscopical study in which the cement hydration as well as the polymer film formation are studied [11]. Although water-soluble polymers are added at very low polymer–cement ratios, polymer film formation is detected [7,11]. In the following sections, the morphology of the $Ca(OH)_2$ crystals and the microstructure of the cement matrix are analyzed.

3.4.1. Freshly broken surfaces in SE mode

The morphology of the $Ca(OH)_2$ crystals is studied on freshly broken surfaces in the SE mode. The addition of small amounts of methylcellulose results in the formation of stacks of layered and undistorted $Ca(OH)_2$ crystals at the air void surfaces (Fig. 4). Moreover, at high magnifications, polymer bridges are detected between the $Ca(OH)_2$ layers, which act as an additional bond, gluing the layers together. The polymer bridges are present between all $Ca(OH)_2$ crystals in MC modified mortars, stretched between the crystal layers. Due to the different orientation of the $Ca(OH)_2$ crystals in PVAA and HEC modified mortars, the inspection of the interlayer spaces and, therefore, the detection of possible polymer bridges is impossible.

3.4.2. Polished surfaces in BSE mode

In Fig. 5, the polished surfaces of unmodified and polymer modified mortars are compared in the BSE mode. Unhydrated cement

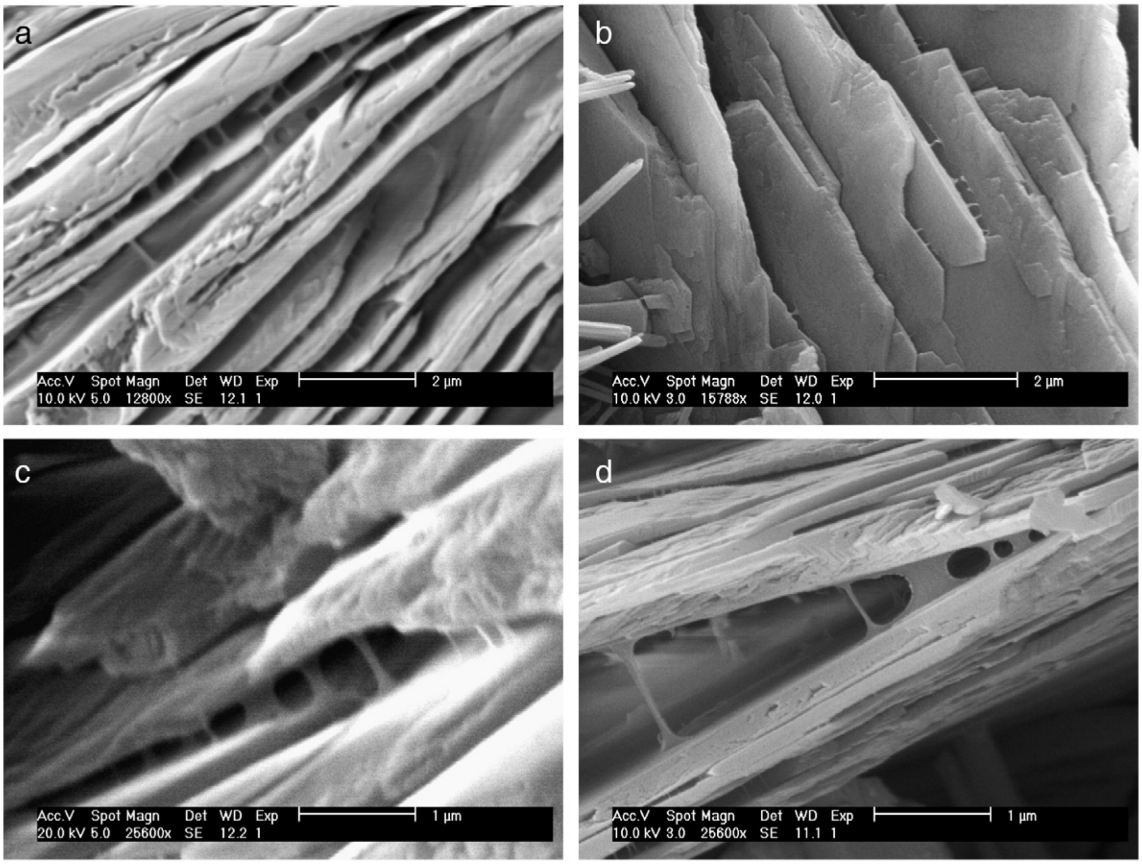

Fig. 4. Secondary electrons (SE) image of stacks of layered $Ca(OH)_2$ crystals in 1% MC modified mortars. Between the crystal layers, polymer bridges are detected.

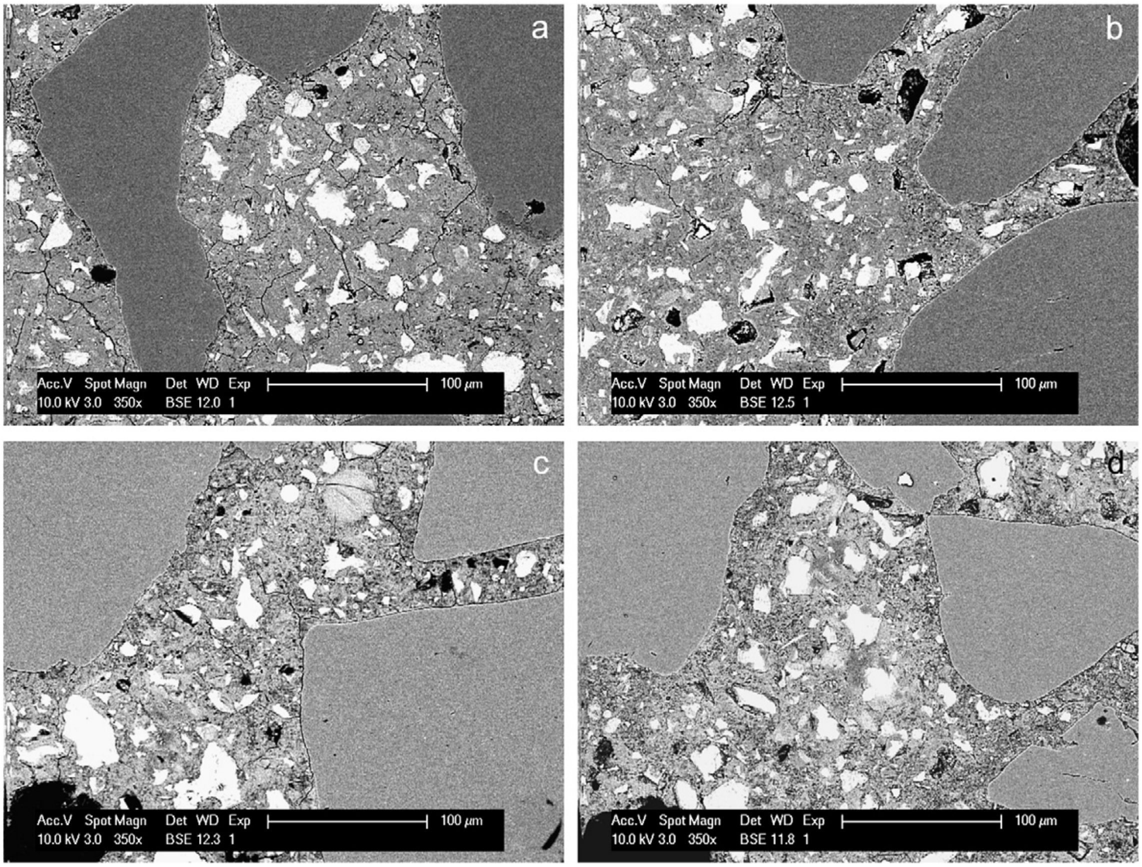

Fig. 5. Backscattered electron (BSE) image of crack formation in unmodified mortars (a) and mortars modified with 1% PVAA (b), MC (c) and HEC (d).

grains appear as bright areas in BSE images, epoxy impregnated pores and cracks as black spots. The large, uniformly grey zones represent the sand particles, the lighter zones in between are cement hydrates. Among the cement hydrates, $Ca(OH)_2$ is significantly brighter than the other phases.

A difference in adhesion between the aggregates and cement paste of the different mortars is difficult to detect. However, polymer modification improves the cohesion of the bulk cement paste: a lower amount of microcracks is observed for the polymer modified mortars on all analyzed surfaces.

4. Discussion

The presence of water-soluble polymers in cement mortars influences the rate and degree of cement hydration and the nature and amount of hydration products that are formed. Additionally, the morphology of the hydrate crystals and the microstructure of the cement paste are changed.

4.1. Retardation of cement hydration

A retardation of cement hydration is observed by isothermal calorimetry (Fig. 1), thermal analysis (Fig. 2) and FT-IR (Fig. 3). Especially the hydration reactions of the pastes modified with HEC are retarded significantly. The water-soluble polymers extend the induction period and interfere with the early cement hydration reactions. By analyzing the different hydration theories, several explanations can be found for the retardation of the cement hydration reactions in the presence of organic compounds, such as adsorption [12], nucleation control and poisoning of the crystal growth [13], complexation of the rate-controlling alkalis [14], precipitation of insoluble complexes hindering the water transport [15], incorporation in the protective membrane around the cement particles [16] and decreased ion mobility [17]. Probably, not just one mechanism is sufficient to explain all aspects of retardation, but a combination of interactions takes place [14].

Polymers can be adsorbed on the unhydrated cement particles, preventing the attack by water [12]. The water-soluble polymers, used in this research, contain a lot of hydroxyl groups, which are able to form hydrogen bonds with the oxygen ions on the surfaces of the anhydrous compounds [18,19]. However, a reduced polyvinyl alcohol and polyethylene oxide adsorption on silica is observed at higher pH values due to the deprotonation of surface hydroxyl groups, which results in a decrease in the number of specific hydrogen bonding sites [20,21]. A strong adsorption of cellulose ethers on C_3S is found, associated with the retarded hydration of this phase [22]. On the other hand, Banfill and Saunders [13] found poor correlation between the retardation and adsorption of several retarders on the unhydrated cement compounds.

Besides the adsorption on the unhydrated particles, adsorption on the hydrating compounds can occur. The adsorption of the polymers on the $Ca(OH)_2$ and C–S–H nucleation sites can poison the growth of those phases [14]. Cellulose ethers are reported to strongly adsorb on $Ca(OH)_2$ crystals [22]. In Fig. 4, the presence of MC bridges between the layered $Ca(OH)_2$ crystals is observed, pointing to the strong affinity of the polymers for this phase.

Another assumption is the complexation of the metal ions in the pore water by the water-soluble polymers. By complexing these ions, the solubility of the ions increases, the early precipitation of hydration products is prevented and more cement compounds should be dissolved before hydration barriers are set up [14]. Pourchez et al. [23] showed that the ability of cellulose ethers to complex calcium ions is negligible. Additionally, because of the high concentration of calcium ions, the amount of polymers in solution should be high in order to have a significant influence on the calcium ion equilibrium. Complexing of the aluminate, ferrite or silicate ions may have a larger influence because of their much lower concentration in solution [14].

Some authors attributed the retardation of the cement hydration to the decreased ion mobility in the pore water [17]. Water-soluble polymers increase the viscosity of the mixing water, which restricts the movement of ions and decreases the dissolution rate of the unhydrated phases and the precipitation of hydrates. The polymer solution with the highest viscosity (HEC solution) has the largest effect on the rate of hydration, followed by the lower viscosity solutions of MC and PVAA. The assumption of a diffusion barrier induced by the highly viscous solution of cellulose ethers is doubted by Pourchez et al. [24].

4.2. Hydration products

The composition of the hydrated cement matrix in unmodified and 1% polymer modified cement pastes is quantitatively studied by thermal analysis and semi-quantitatively by FT-IR at several time intervals. Special attention is paid to the total amount of bound water, the $Ca(OH)_2$ content, the carbonate or carbonate-like phases and the possible formation of new products.

4.2.1. Amount of bound water

Because the amount of bound water is an empirical measure of the degree of hydration, the initial retardation of hydration is illustrated by the evolution of the amount of bound water (Table 1). However, after 90 days of hydration, a slightly higher amount of bound water is found for the polymer modified pastes. This can be attributed to a better dispersion of the cement particles in the mixing, which results in a higher degree of hydration. Water-soluble polymers are also reported to increase the degree of hydration, due to their water-retaining properties. Because all pastes are stored in closed bottles until the moment of testing, the water-retaining effect cannot be investigated.

4.2.2. $Ca(OH)_2$ content

By thermal analysis, a slightly lower amount of $Ca(OH)_2$ is found for the polymer modified pastes than for the unmodified pastes at all ages (Table 1). A possible explanation can be the adsorption of the polymers on the $Ca(OH)_2$ nucleation sites, which prevents the growth of these crystals. However, it will be demonstrated in the next paragraph that the real $Ca(OH)_2$ content of polymer modified pastes can be underestimated by thermal analysis, because of an interaction with the polymers upon heating.

4.2.3. Carbonate or carbonate-like phases

After polymer modification, a double peak appears in the DTG graphs during the decomposition of the carbonate or carbonate-like phases and the corresponding mass loss is much larger than for the unmodified pastes (Fig. 2). PVAA modified pastes show on average a mass loss of 1.9%, the MC and HEC modified pastes a mass loss of 1.8%. For the unmodified cement paste, the average mass loss during the decomposition of carbonate phases is 1% of the ignited mass.

In contrast to the findings by thermal analysis, the intensity of the carbonate bands in the FT-IR spectrum is slightly higher for the unmodified paste (Fig. 3). It is assumed that at least part of the carbonate or carbonate-like phases are formed during thermal analysis. Upon heating, polymers or their decomposition products can react with the unhydrated cement particles, the hydrated compounds or the released OH^- ions, resulting in the formation of carbonate or carbonate-like phases. Similar results were obtained by thermal analysis carried out on cement pastes that are treated with solvents [8]. The high amount of carbonates, determined by thermal analysis, could not been verified with other techniques, while an increase of the carbonate content is measured upon heating. Therefore, care should be taken when quantitatively interpreting the results of thermal analysis in the presence of polymers or other organics. The real content of certain phases, such as the $Ca(OH)_2$ content, can be underestimated. This phenomenon becomes much more important at high polymer–cement ratios. The higher carbonate content for the unmodified paste, detected by FT-IR, can be attributed to the sample preparation. During sample preparation, carbonation is favoured in pastes in which crushing is more time-consuming, because setting has already started, but which still contain a large amount of free water.

4.2.4. New products

At early ages, new peaks are detected in the DTG graphs of the polymer modified pastes at temperatures which do not correspond to the decomposition temperature of the pure polymers (Fig. 2). Afterwards, the extra peaks disappear and no additional peaks are observed.

Alkaline degradation of the polymers can be propounded, but it is contradictory to what is found in literature [22,23,25]. It also does not explain the first reduction in decomposition temperature, followed by the disappearance of the peak when the hydration proceeds. Polyvinyl alcohol–acetate can undergo saponification [5], but the PVAA used in this study is already hydrolyzed for 87–89% before addition to the alkaline mixing water. Moreover, mechanical strength tests and SEM analysis gave evidence of the existence of the polymers in the cement matrix at later ages [7].

The new peak can be the result of an interaction between the polymers and the cement compounds or hydrates. There seems to be a connection between the progress of cement hydration and the disappearance of the peak. The peak disappears from the moment that the cement hydration reactions are accelerated. The more the hydration reactions are retarded, the longer the peak remains. After 24 h, the peak has disappeared in all pastes. Because no new phases are detected by XRD [11], the product should be amorphous in nature. Furthermore, no significant differences between the FT-IR spectra of unmodified and polymer modified pastes are found (Fig. 3). Further research, by means of additional analytical techniques, such as NMR spectroscopy, is needed to identify the nature of this product.

4.3. Microstructure of cement mortars

4.3.1. Morphology of the $Ca(OH)_2$ crystals

It has been shown by several authors [26–29] that the presence of organics can significantly influence the morphology of $Ca(OH)_2$ in cement matrices, depending on the type of polymer, the brand of polymer, the polymer-cement ratio or a combination of all these factors. In the absence of polymers, crystals of $Ca(OH)_2$ 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. However, in the presence of polymer dispersions, the structure of $Ca(OH)_2$ is modified to the extent that the crystals become capable of withstanding those stresses [30]. The addition of polymer dispersions is reported to result in a layered deposition of $Ca(OH)_2$ crystals, arranged in stack, without deformations [31]. It is assumed that the polymer particles act as a kind of a bonding agent between the different layers, increasing the interparticle bonding [26], but the presence of the polymers between the crystal layers could not been observed.

Although a lot of research is carried out on the influence of the addition of polymer dispersions on the microstructure, less is known about the effect of water-soluble polymers on crystal formation. Mikhail et al. [29] found an orientation and layered deposition of $Ca(OH)_2$ crystals and attributed this to chemical bond formation between the water-soluble polymers and $Ca(OH)_2$. However, until now, no evidence was found in literature of the action of the water-soluble polymers as bonding agents.

In Fig. 4, the bridging behaviour of the water-soluble polymers is demonstrated. By gluing the crystal layers together, the microstructure is strengthened. 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 improves the overall strength of the binder matrix.

4.3.2. Cohesion of the microstructure

Irrespective of the crack formation mechanism, a much higher amount of microcracks is detected in the bulk paste of the unmodified mortar (Fig. 5). Cracks can be initiated during shrinkage, mechanical testing, sample preparation or SEM analysis, but all samples are subjected to the same treatment. The presence of the polymers strengthens the cement matrix and increases the internal cohesion. Similar conclusions were drawn by Müller by means of ultrasonic measurements [22].

5. Conclusion

The presence of small amounts of water-soluble polymers (1% of the cement mass) is found to influence the cement hydration reactions. A small decrease in the rate of hydration of pastes modified with PVAA and MC is observed during the first hours of hydration, while the cement hydration in HEC modified pastes is strongly retarded. Despite of the retardation at early ages, the amount of bound water of the polymer modified pastes is higher than that of the unmodified paste after 90 days of hydration, due to a better dispersion of the cement particles in the mixing water. The $Ca(OH)_2$ content, determined by thermal analysis, is found to be slightly lower after polymer modification, but, due to an interaction between the polymers and the hydration products, the unhydrated cement particles or the released OH^- ions upon heating, the real $Ca(OH)_2$ content can be underestimated in the presence of polymers. No new phases are detected by FT-IR. On the other hand, new peaks are observed in the DTG graphs of the polymer modified pastes at early ages. Further research is needed to identify the nature of these peaks and to explain their disappearance at early ages.

The presence of water-soluble polymers influences the morphology of the $Ca(OH)_2$ crystals. The addition of MC results in a layered deposition of $Ca(OH)_2$, arranged in stack without deformations. Polymer bridges are found between the layered $Ca(OH)_2$ crystals, acting as a kind of a bonding agent between the different layers, increasing the interparticle bonding and producing a better structure. Water-soluble polymers are also found to improve the internal cohesion of the bulk cement paste. The strengthening of the bulk paste results in a significantly lower crack formation.

Acknowledgement

The grant offered by the Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT-Vlaanderen) is gratefully acknowledged. The authors would like to thank José Barroso de Aguiar for the interesting discussions about the thermal analyses. The Department of Metallurgy and Materials Engineering (MTM) and the Applied Geology & Mineralogy Research Group of K.U.Leuven are acknowledged for the use of the SEM and thermal analysis systems and the Department of Chemical Engineering (CIT) of K.U.Leuven for the use of the FT-IR spectrometer.

References

[1] H. Paiva, L. Silva, J. Labrincha, V. Ferreira, Effects of a water-retaining agent on the rheological behaviour of a single-coat render mortar, Cem. Concr. Res. 36 (7) (2006) 1257–1262.
[2] K. Khayat, Viscosity-enhancing admixtures for cement-based materials — an overview, Cem. Concr. Compos. 20 (2–3) (1998) 171–188.
[3] T. Soshiroda, K. Hayakawa, K. Yoda, M. Tanaka, Effects of cellulose ether on the homogeneity of concrete in structures — relating quality variations and construction joints, in: H. Sasse (Ed.), Adhesion between polymers and concrete, Proceedings of international symposium organized by Rilem Technical Committee, vol. 52, 1986, pp. 125–133.
[4] X. Fu, X. Fu, W. Lu, D. Chung, Improving the bond strength between carbon fiber and cement by fiber surface treatment and polymer addition to cement mix, Cem. Concr. Res. 26 (7) (1996) 1007–1012.
[5] Y. Ohama, Handbook of polymer-modified concrete and mortars, Noyes Publications, 1995.
[6] D. Chung, Review: use of polymers for cement-based structural materials, J. Mater. Sci. 39 (2004) 2973–2978.
[7] E. Knapen, D. Van Gemert, Polymer film formation in mortars modified with water-soluble polymers, Cem Concr Compos (submitted for publication).
[8] E. Knapen, O. Cizer, K. Van Balen, D. Van Gemert, Comparison of solvent exchange and vacuum drying techniques to remove free water from early age cement-based materials, in: J. Marchand, B. Bissonnette, R. Gagné, M. Jolin, F. Paradis (Eds.), Proceedings of the 2nd International RILEM Symposium on Advances in Concrete through Science and Engineering, Quebec, Canada, 2006, CD-ROM, 2006.
[9] H. Taylor, Cement Chemistry, Academic Press Limited, London, 1990.
[10] I. Odler, S. Abdul-Maula, Possibilities of quantitative determination of the AFt-(ettringite) and AFm-(monosulphate) phases in hydrated cement pastes, Cem. Concr. Res. 14 (1) (1984) 133–141.
[11] E. Knapen, Microstructure formation in cement mortars modified with water-soluble polymers, Ph.D. thesis, K.U.Leuven (2007).
[12] W. Hansen, Actions of calcium sulfate and admixtures in Portland cement pastes, in: A. S. T. M. S. T. Publ. (Ed.), Effect of Water-Reducing Admixtures and Set-Retarding Admixtures on Properties of Concrete, vol. 266, 1960, pp. 3–25.
[13] P. Banfill, D. Saunders, The relationship between the sorption of organic compounds on cement and the retardation of hydration, Cem. Concr. Res. 16 (3) (1986) 399–410.
[14] J. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, Cem. Concr. Res. 2 (4) (1972) 415–433.
[15] N. Thomas, J. Birchall, The retarding action of sugars on cement hydration, Cem. Concr. Res. 13 (6) (1983) 830–842.
[16] N. Thomas, D. Double, Calcium and silicon concentrations in solution during the early hydration of Portland cement and tricalcium silicate, Cem. Concr. Res. 11 (5–6) (1981) 675–687.
[17] D. Silva, H. Roman, V. John, Effects of EVA and HEC polymers on the Portland cement hydration, in: M. Maultzsch (Ed.), Proceedings of 11th Congress on Polymers in Concrete, Berlin, 2004, pp. 91–97.
[18] C. Sawyer, J. Reed, Adsorption of hydroxypropyl methyl cellulose in an aqueous system containing multicomponent oxide particles, J. Am. Ceram. Soc. 84 (6) (2001) 1241–1249.
[19] H. Steinour, Discussion of "actions of calcium sulfate and admixtures in Portland cement pastes" by W. C. Hansen, in: A. S. T. M. S. T. Publ. (Ed.), Effect of Water-Reducing Admixtures and Set-Retarding Admixtures on Properties of Concrete, vol. 266, 1960, pp. 25–37.
[20] J. Rubio, J. Kitchener, The mechanism of adsorption of poly(ethylene oxide) flocculant on silica, J. Colloid Interface Sci. 57 (1) (1978) 132–142.
[21] T. Tadros, Adsorption of polyvinyl alcohol on silica at various pH values and its effect on the flocculation of the dispersion, J. Colloid Interface Sci. 64 (1) (1978) 36–47.
[22] I. Müller, Influence of cellulose ethers on the kinetics of early Portland cement hydration, Ph.D. thesis, Westfälische Wilhelms-Universität Münster (2006).
[23] J. Pourchez, A. Govin, P. Grosseau, B. Guilhot, B. Ruot, Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration, Cem. Concr. Res. 36 (7) (2006) 1252–1256.
[24] J. Pourchez, P. Grosseau, R. Guyonnet, B. Ruot, HEC influence on cement hydration measured by conductometry, Cem. Concr. Res. 36 (9) (2006) 1777–1780.
[25] A. Peschard, A. Govin, E. Fredon, P. Grosseau, G. Fantozzi, Influence of polysaccharides on cement hydration, Key Eng. Mater. 264–269 (2004) 2141–2144.
[26] M. Afridi, Y. Ohama, M. Iqbal, K. Demura, Behaviour of $Ca(OH)_2$ in polymer modified mortars, Int. J. Cem. Compos. Lightweight Concr. 11 (4) (1989) 235–244.
[27] A. Barker, Structural and mechanical characterization of calcium hydroxide in set cement and the influence of various additives, World Cem. 15 (1) (1984) 25–31.
[28] R. Berger, J. McGregor, Effect of temperature and water solid-ratio on growth of $Ca(OH)_2$ crystals formed during hydration of Ca_3SiO_5, J. Am. Ceram. Soc. 56 (2) (1973) 73–79.
[29] R. Mikhail, M. Shater, T. Al-Akkad, Studies on premix water-soluble polymer cement pastes - I, Cem. Concr. Res. 13 (2) (1983) 207–215.
[30] M. Afridi, Y. Ohama, M. Iqbal, K. Demura, Morphology of $Ca(OH)_2$ in polymer-modified mortars and effect of freezing an thawing action on its stability, Cem. Concr. Compos. 12 (3) (1990) 163–173.
[31] A. Beeldens, Influence of polymer modification on the behaviour of concrete under severe conditions, Ph.D. thesis, K.U.Leuven (2002).