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The influence of polymers on the hydration of portland cement phases analyzed by soft X-ray transmission microscopy

Denise A. Silva [a,*], Paulo J.M. Monteiro [b]

[a] W.R. Grace & Co., Cambridge, MA, USA
[b] Department of Civil and Environmental Engineering, University of California at Berkeley, CA, USA

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Abstract

The soft X-ray transmission microscope, which allows the in situ observation of wet samples of cement at normal pressures with high spatial resolutions (25 nm), was used to observe and compare the effects of two polymers — a water soluble polymer (HPMC — hydroxypropyl methylcellulose) and a latex [EVA-poly(ethylene-*co*-vinyl acetate)] on the early hydration of C_3S and C_3A. These polymers are used to modify the properties of fresh and hardened mortars and concretes, especially when adhesive characteristics are required. The images show that the cellulose ether delays the hydration of the cementitious particles and promotes the formation of inner products rather than outer products. On the other hand, EVA particles agglomerate around the hydrating C_3S grains, and act as nucleation agents in the development of the composite microstructure. While HPMC slightly changed the aspect of C_3A hydration, EVA inhibited or even prevented the formation of ettringite crystals during the early stage of hydration, and resulted in a cloud of small, bright particles concentrated around the hydrating C_3A grains.

Keywords: Ca_3SiO_5; $Ca_3Al_2O_6$; Hydration; Polymer; Soft X-ray transmission microscopy

1. Introduction

Nowadays, the addition of chemical admixtures to concrete is almost as usual as the presence of aggregates. Regardless of the nature of the chemical product, changes in the hydration reactions of the cement are expected, because physical and chemical interactions occur between the hydrating cement and the admixtures. As a result, the kinetics of the hydration reactions and the morphology of the hydration products may be altered. Microstructural characteristics and performance of the concrete are thus affected.

Since the '40s, different types of synthetic and semi-synthetic polymers have been added to cement-based materials in order to modify important characteristics and properties of fresh and hardened mortars and concretes, such as rheology, water retention ability, cohesion, adhesion, and toughness. Two major families are studied in this article: water soluble cellulose ethers and water redispersible latex.

Cellulose ethers are semi-synthetic, water-soluble polymers whose hydrophilic groups adhere to the water molecules by hydrogen bonding, modifying the rheology of mortars and concretes [1]. Due to the resulting higher viscosity, water retention ability and adhesion, these polymers are currently used to produce rendering mortars and adhesive mortars for ceramic tiles installation. The higher resistance to bleeding and wash-out also encourages their use as pumping agents and in underwater applications. Along with superplasticizer and antifoaming agents, cellulose ethers have recently been used to produce self-compacting concretes due to their higher resistance to segregation [2].

Poly(ethylene-*co*-vinyl acetate) or EVA copolymer is mainly used as a modifier of hardened mortar and concrete properties, such as elastic modulus, toughness, permeability and bond strength to various substrates [3]. These changes are produced by a film formed by the copolymer that creates a network inside the cement matrix, partially covering hydrated and anhydrous cement particles, sealing pores and bridging microcracks. Due to improved adhesion, it is also used in conjunction with cellulose ethers for the production of dry-set mortars for ceramic tile installation.

Many articles can be found in the literature dealing with the engineering properties of mortars and concretes containing

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* Corresponding author.
E-mail addresses: denise.a.silva@grace.com (D.A. Silva), monteiro@ce.berkeley.edu (P.J.M. Monteiro).

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Table 1
Characteristics of EVA redispersible polymer powder

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

cellulose ethers and polymeric latexes. On the other hand, little information is available on the effects of the polymers on the microstructure of such materials. In summary, these microstructural studies report that the amount of calcium hydroxide is depleted and the morphology of AFt and AFm phases are changed when EVA is present [4–8]. Recently, Silva and Monteiro [9,10] reported the effects of EVA on the hydration of cement minerals using soft X-ray transmission microscopy.

Regarding the effects of cellulose ethers on the microstructure of cement-based materials, Silva [8] reported a tendency for the formation of C–S–H types III and IV in cement pastes with hydroxyethyl cellulose, a type of cellulose ether. The microstructure of mortars containing hydroxymethylethyl cellulose (HMEC) studied by Jenni et al. [11] focused mainly in the distribution of the polymer along thin bed mortars. Some studies have also been conducted by Drabik and co-workers, and by Majumdar [12–14]. However, they were concerned with MDF (macro-defect-free) cements, which have very low water–cement ratio and require special production procedures (heating and compression), inducing severe changes in the chemical reactions and hence in the microstructure of the composite. No other information on the microstructure of cement-based materials containing cellulose ethers could be found in the literature.

Although the abovementioned research improved the knowledge of mortars and concretes modified with polymers, the need for further research on the microstructural aspects of such materials is evident. Moreover, the techniques used so far have not clarified the effects of the polymers on the cement hydration mechanism and products before the cement setting, when the interaction of the materials is expected to be significant.

The soft X-ray transmission microscopy described in this paper permits the dissolution of anhydrous cement phases and the development of hydrated particles to be followed in real time, as early as a few minutes after the contact with water. The hydration mechanisms of two major clinker constituents, C_3S and C_3A, and the effects of EVA and HPMC polymers were observed in wet samples at normal pressures. Thus, the technique has proven to be an important tool to fill the gap in the knowledge regarding cement–polymer composites. Although the effects of EVA on the hydration of C_3S and C_3A based on soft X-ray transmission microscopy have been explored by the authors in previous publications [9,10], the most interesting aspects of the study are emphasized in this article for comparison purposes to the effects of HPMC.

Table 2
Characteristics of the cellulose ether HPMC

Powder	
Hydroxypropyl methylcellulose	85–99%
Water	1–10%
Sodium chloride	0.5–5%
Proprietary polyglycol, carboxylic acid, and aldehyde	<5%
Aqueous solution	
Surface tension at 25 °C, 0.05% solution	43–55 dyn/cm
Specific gravity at 4 °C, 1% solution	1.0012
Typical viscosity (Brookfield RVT, 20 rpm, 20 °C, 2% solution)	3800 mPa s
pH, 2.5% solution	4.26

2. Soft X-ray transmission microscopy

The soft X-ray transmission microscope (XM-1) used in this research was built and is operated by the Center of X-ray Optics (Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California). The Advanced Light Source is a synchrotron facility that generates intense radiation in the ultraviolet and soft X-ray regimes. The optics of the microscope are based on the use of mirrors and Fresnel zone plate lenses to guide and focus the radiation generated by the facility, and to form high spatial resolution images from the samples. XM-1 was first used to study cement-based materials by Kurtis in 1998 [15]. The technique allows the observation in situ of wet samples at normal pressures with high spatial resolutions (25 nm). The incident X-rays pass through the sample where they are partially absorbed with a spatial variation dependent on the atoms present (atomic number Z), their distribution and the wavelength of the incident rays (λ) [16]. The microscopy was carried out using a photon energy of 517 eV, above the K absorption edge for carbon (284.2 eV), making EVA particles opaque to soft X-rays. They can be identified by their shape (spherical) and low contrast to water. Calcium, aluminium, sulphur, carbon and silicon absorb almost the same radiation, but the contrast of the phases containing such elements to water depends on the composition of the phase (content of each element) and the thickness of the particles. For the samples analyzed here, polymeric particles have low contrast while Ca-, Al-, S- and Si-bearing phases are dark.

Soft X-rays transmission microscopy is a powerful technique used to study the hydration of cement grains as early as 6 min after mixing, depending on the ability of the experimenter. The effects of admixtures on the kinetics of hydration and formation of hydrated phases have already been studied using the technique; see

Table 3
List of samples analyzed and corresponding images

C_3S + solution (solution/C_3S = 5 cm^3/g)	Fig. 1
C_3A + solution (solution/C_3A = 5 cm^3/g)	Fig. 2
C_3S + EVA + solution (solution/C_3S = 5 cm^3/g; EVA/solution = 0.02 g/cm^3)	Fig. 3
C_3A + EVA + solution (solution/C_3A = 5 cm^3/g; EVA/solution = 0.02 g/cm^3)	Fig. 4
C_3S + HPMC + solution (solution/C_3S = 5 cm^3/g; HPMC/solution = 0.002 g/cm^3)	Fig. 5
C_3A + HPMC + solution (solution/C_3A = 5 cm^3/g; HPMC/solution = 0.002 g/cm^3)	Fig. 6

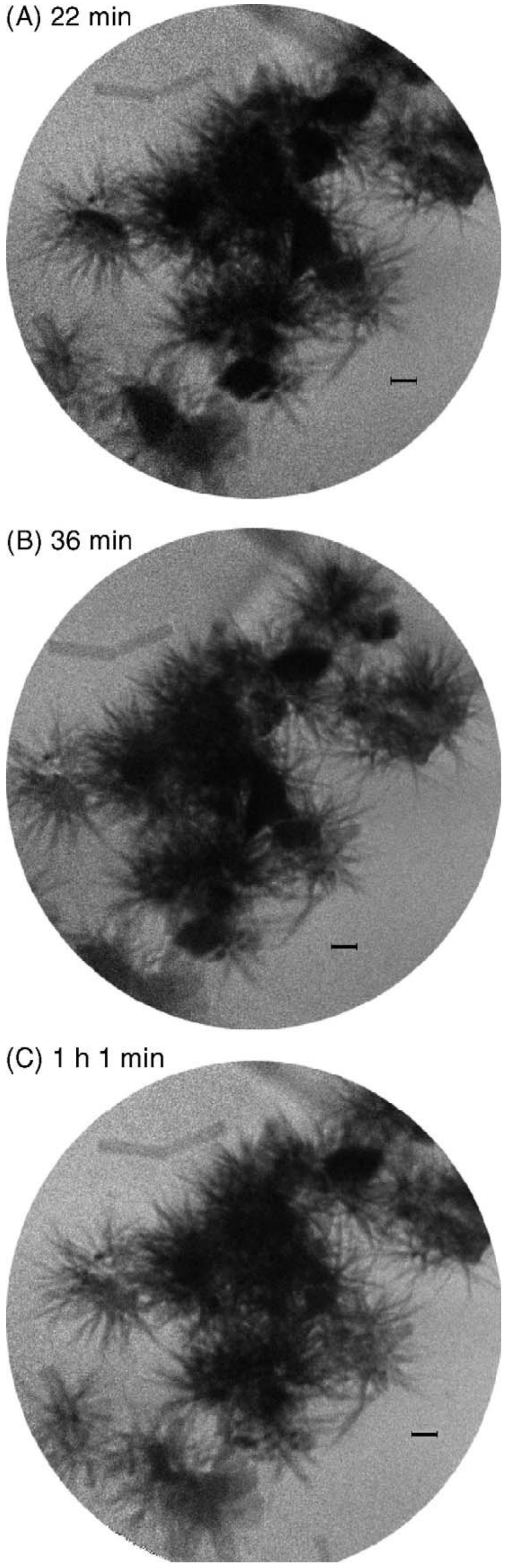

Fig. 1. Soft X-ray images of hydrating C_3S without EVA in the saturated solution from 22 min to 1 h after mixing (scale bar is 700 nm).

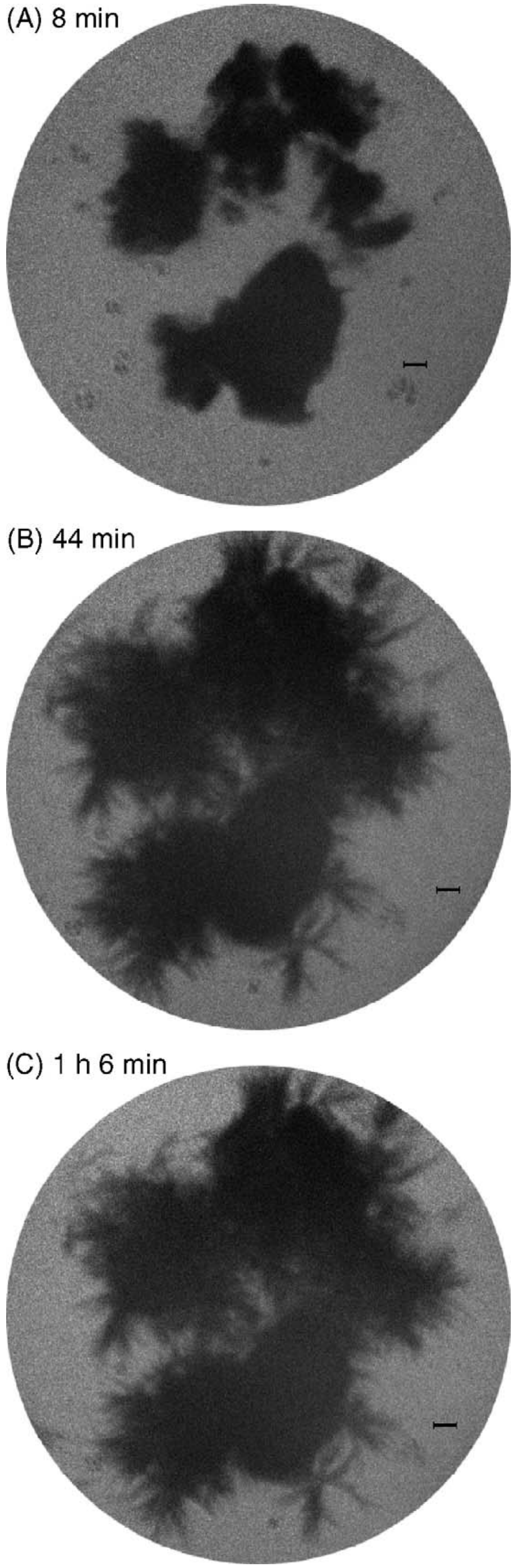

Fig. 2. Soft X-ray images of C_3A-saturated solution sample from 8 min to approximately 1 hr after mixing (scale bar is 700 nm).

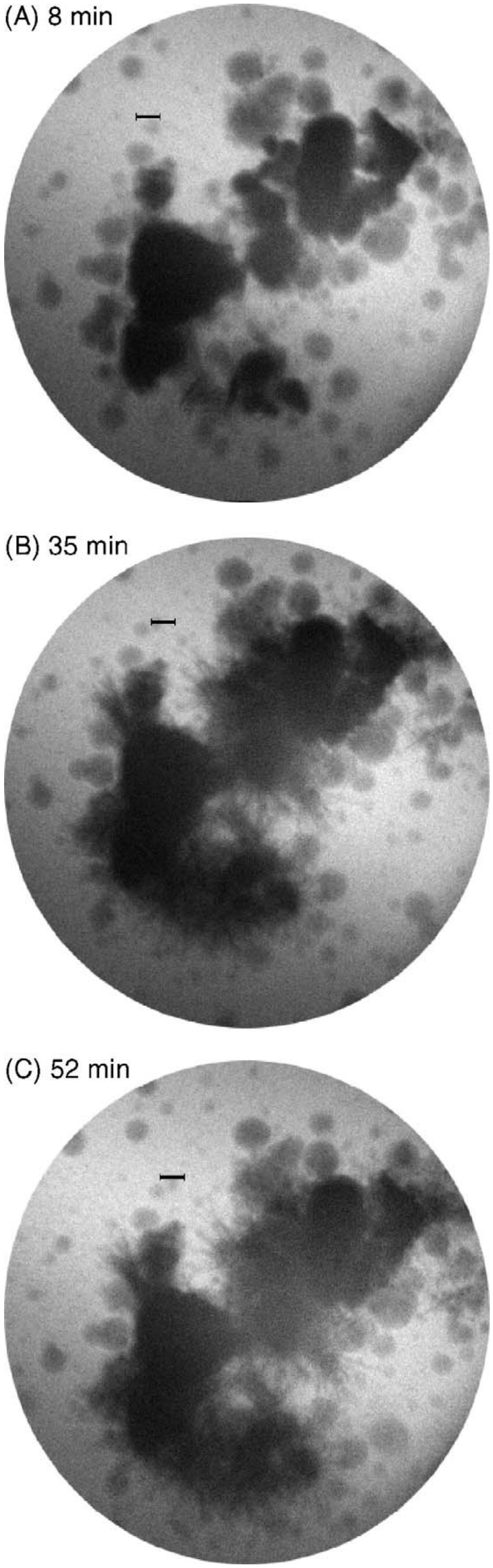

Fig. 3. Soft X-ray images of hydrating C_3S with EVA in the saturated solution from 22 to 52 min after mixing (scale bar is 700 nm) [9].

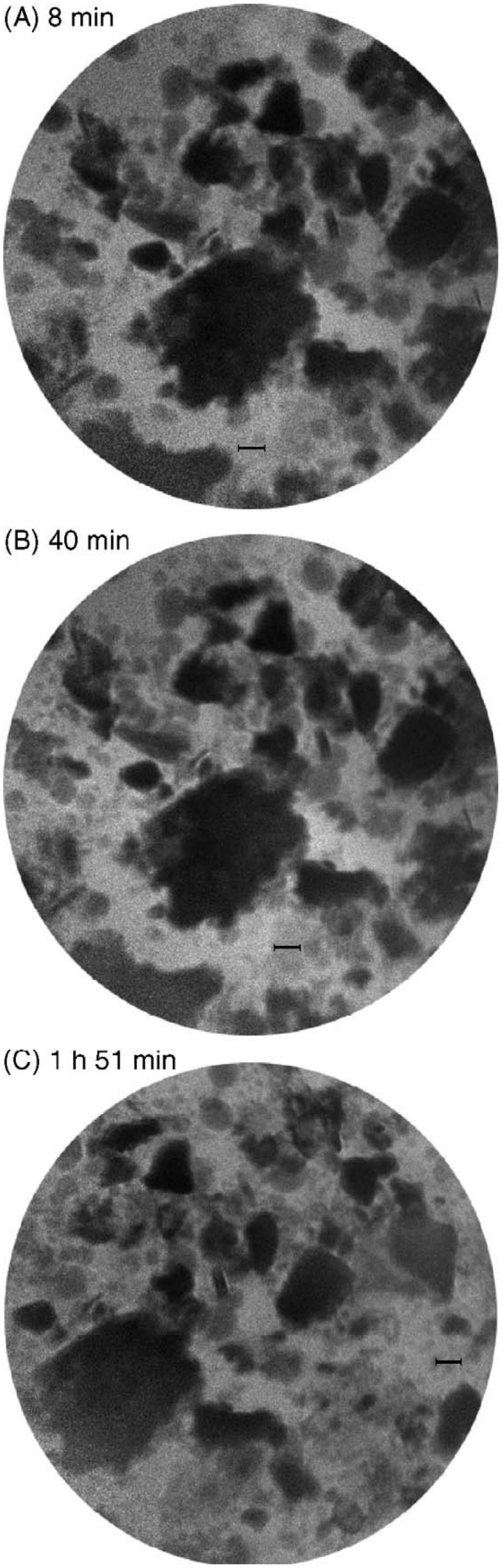

Fig. 4. Soft X-ray images of C_3A-EVA-saturated solution sample from 9 min to almost 2 hr after mixing (scale bar is 700 nm).

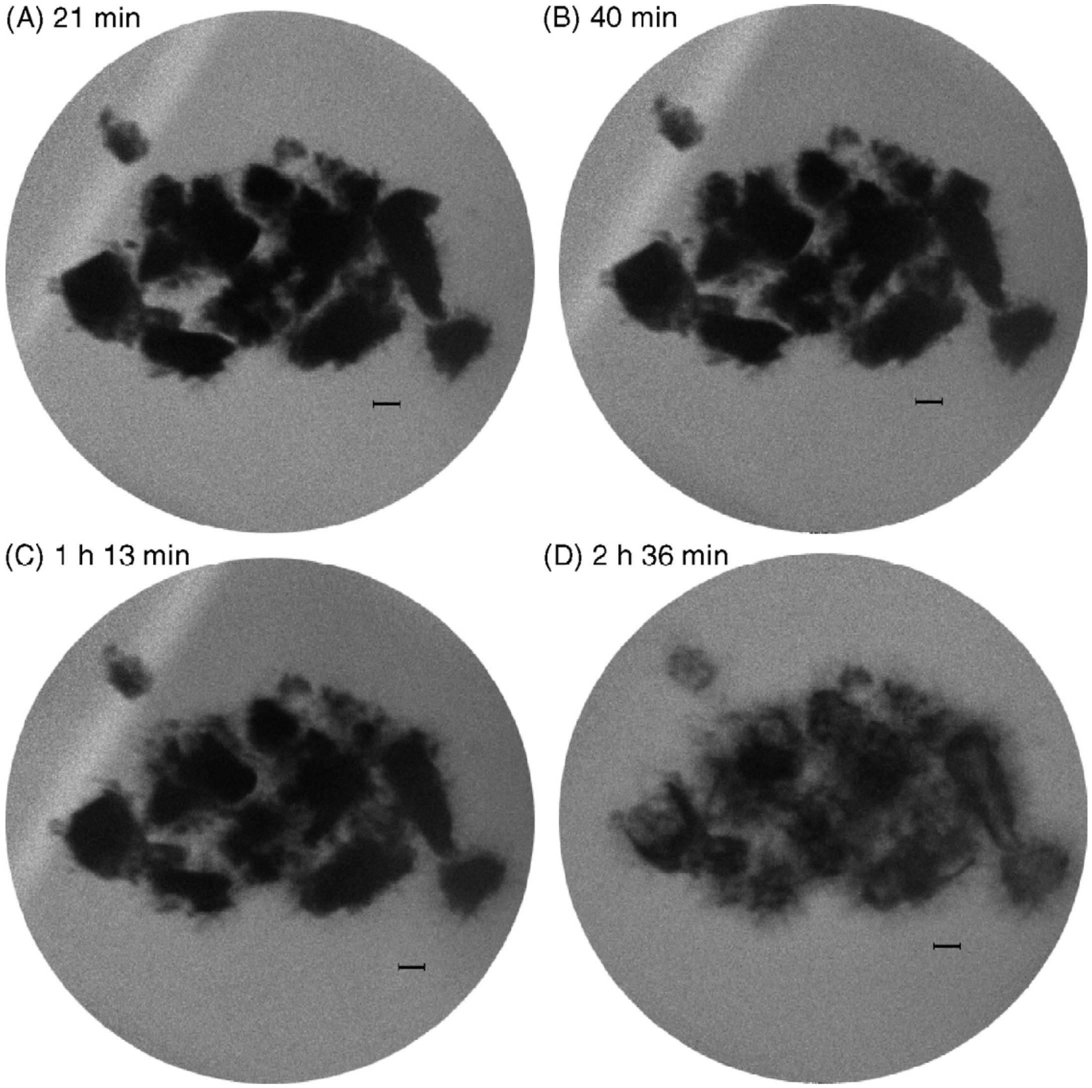

Fig. 5. Soft X-ray images of C_3S particles in the saturated solution with HPMC, hydration time indicated (scale bar is 700 nm).

[9,10,17,18]. Because of the high magnification (2400×) and high spatial resolution, the images obtained clearly show nucleation and growth of crystals.

3. Experimental

In order to better understand the influence of the polymers on portland cement hydration, two of its main compounds — C_3S and C_3A — were synthesized, ground and sieved, and particles smaller than 75 μm were selected for the analyses.

Commercial polymers — hydroxypropyl methylcellulose (HPMC) and poly(ethylene-*co*-vinyl acetate) (EVA) — were used for this study. The characteristics of the polymers are presented in Tables 1 and 2. The inorganic part (ash content) of the EVA contains the minerals magnesite (37% mass of the inorganic compounds), dolomite (13%), calcite (14%), talc (16%) and kaolinite (20%), identified and semi-quantified using XRD analysis.

The samples must be highly diluted for the transmission of the X-rays. In order to retard the dissolution of C_3S and C_3A in the highly diluted samples, and to provide SO_4^{2-} ions for the reactions, a solution saturated with $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ was used as the liquid media (pH = 12.3). The solution was prepared using freshly boiled, deionized water inside a glove bag filled with nitrogen gas to avoid carbonation. Teflon and polyethylene flasks were used to prepare the solution to avoid alkali–silica reaction.

The solid particles (C_3S, C_3A, and the polymers) were mixed in the solution (w/c ratio was approximately 5) for 10 s inside a test tube and approximately 2 ml of the mixture was centrifuged for 25 s. A small droplet — around 2 μl — was taken from the supernatant with a micropipette and squeezed between two silicon nitride windows in a metallic sample holder that was then placed in the microscope for examination. Further details on the preparation procedure are described by Juenger et al. [17,18]. The study concentrated primarily on the morphology of the hydrated phases, the rate of particle dissolution and growth, and the overall particle distribution.

Table 3 gives details of the six different mixtures, which are presented in this paper. However, due to centrifugation, the

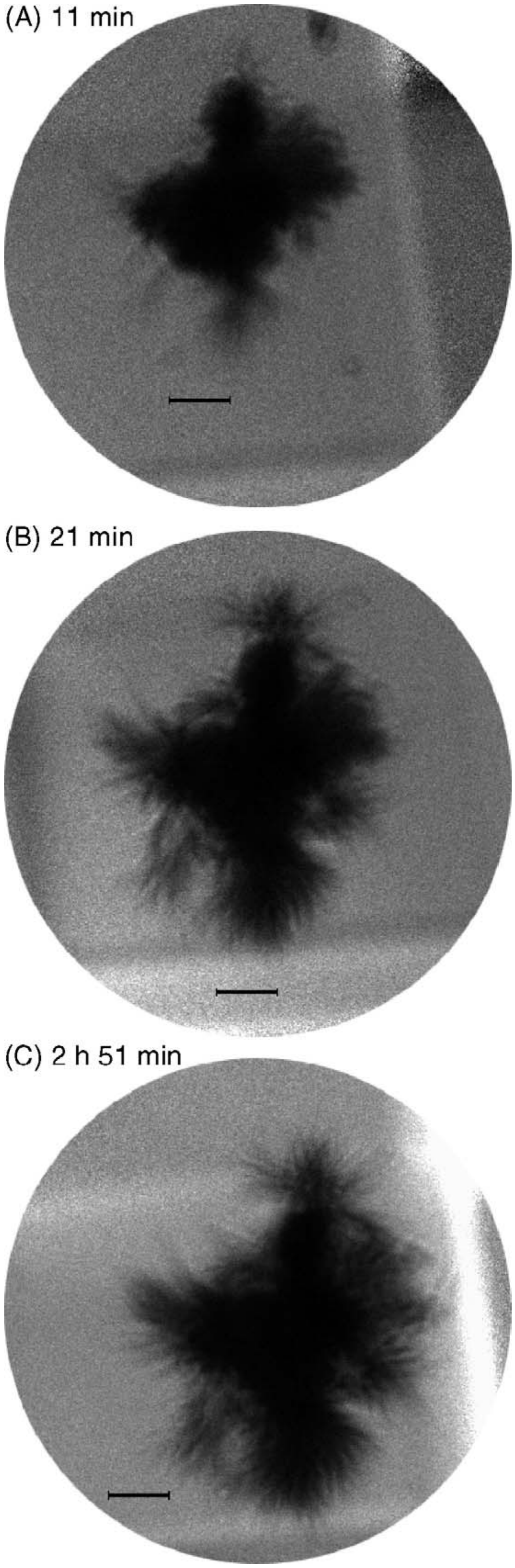

Fig. 6. Soft X-ray images of C_3A particles in the saturated solution with HPMC, hydration time indicated (scale bar is 1.14 μm).

initial solid particle/solution ratios will differ from those in the supernatants, from where the samples were taken.

The polymers were mixed in the solution before the addition of the cementitious particles. The hydration times presented in this article refer to the time after the addition of the cementitious particles to the liquid. The samples were centrifuged just before observation.

4. Results

Pure C_3S and C_3A systems, i.e., with no polymeric admixtures, are shown in Figs. 1 and 2, respectively. The effects of EVA on C_3S and C_3A hydration can be observed in Figs. 3 and 4, respectively. Samples of C_3S and C_3A hydrating with HPMC are imaged in Figs. 5, 6, respectively. The images were taken from 21 min to around 3 h after mixing in order to allow the observation of the kinetics of dissolution and formation of hydrates, with the intention to compare the effects of the admixtures at a given hydration time.

A detailed description of EVA effects on C_3S and C_3A hydration is reported in a previous works [9,10]. In summary, EVA particles tend to concentrate around the cementitious grains from very early times, retarding the dissolution of C_3S and the growth of hydrates for at least one hour after mixing. It is likely that EVA acts as a nucleation agent for C–S–H particles. As early as 4 h after mixing, there is formation of a film in locations where the concentration of EVA particles was high enough for their coalescence.

As for C_3A hydration, EVA hinders the formation of ettringite crystals, leading to the formation a cloud of small and semitransparent particles concentrating around C_3A grains. It is evident that EVA has a stronger effect on the hydration of C_3A than on that of C_3S (comparison of Figs. 3 and 4).

Fig. 5 shows images of C_3S hydrating in a HPMC solution, where thin and short hydrate fibers are seen growing outwards from the surface of the particles during the first minutes of hydration. The reactions then slow down until a further hydration reaction period at approximately 1 h after mixing (Fig. 5C), leading to the development of hydrate fibers in between the C_3S grains. The dissolution–precipitation mechanism of hydration develops inwards from the original boundaries of the grains, followed by the formation of inner products. The overall kinetics of C_3S hydration seems to be strongly delayed by the polymer. The aspect of the C_3A particles hydrating in the solution with HPMC is shown in Fig 6. Thin hydrated needles are observed to exist on the surface of the particles as soon as 11 min after mixing. For the next 10 min, there is a quick development of hydrates, as can be seen in Fig. 6B. Following this, only slight signs of a further hydration were observed up to the end of the analysis, around 3 h after mixing (Fig. 6C).

5. Discussion

The polymers HPMC and EVA have distinct effects on C_3S and C_3A hydration. Because the cellulose ether is water-soluble, it cannot be seen in the images. On the other hand, the dispersed EVA particles are readily recognized by their size, shape and contrast to the aqueous phase.

Although it is not possible to see the dissolved HPMC particles, the main effect of the polymer on hydration of C_3S and C_3A is evidently the retardation of reactions. However, it is not possible to state from the images whether the retardation is caused by physical or chemical adsorption of the polymer onto cementitious grains, by ionic motion hindrance, or by chemical interactions. Other complementary tests should be carried out in order to obtain such information. On the other hand, adsorption and agglomeration of EVA particles on and around C_3S grains are clear in Fig. 3. Retardation of hydration is also evident from the images. Chemical interaction between EVA and the hydrating C_3S system was demonstrated by the authors in a previous publication [9].

The polymers have distinct effects on the cementitious phases. HPMC seems to stimulate the formation of inner products rather than outer products in C_3S particles. The opposite effect is observed for C_3A hydration, i.e., no inner products were seen.

While C_3S hydrate morphology seems to be more affected by the cellulose ether than by EVA, C_3A is more sensitive to EVA. HPMC does not change the morphology of C_3A hydrates, but there is clearly a strong interaction between EVA and hydrating aluminates, where no ettringite was produced during the observation period.

6. Conclusion

Soft X-ray transmission microscopy proved to a powerful technique for the comparison of the effects of two commonly used chemical admixtures on (HPMC and EVA) on the hydration of two cement phases (C_3S and C_3A). The high resolution of the microscope allowed the observation of nucleation and growth of hydrates, as well as the effect of the polymers on the hydration. However, because no chemical analysis can currently be obtained from the microscope, other analytical techniques are needed to complement the characterization.

From the images of C_3S and C_3A samples with HPMC and EVA polymers, the following conclusions can be drawn:

- Both HPMC and EVA affect the hydration of C_3S and C_3A from the first few minutes after mixing. They retard the kinetics of hydration and affect the morphology of the hydrates.
- EVA particles tend to concentrate around the C_3S grains during hydration. The polymeric particles, which are less than 1 μm in diameter, seem to act as nucleation sites for C–S–H from solution. On the other hand, HPMC retards the kinetics of C_3S hydration, and favors the formation of inner rather than outer C_3S hydrates.
- In C_3A samples, EVA prevents the formation of ettringite crystals during the first few hours of hydration, and a cloud of small particles concentrates around the hydrating C_3A grains. Conversely, the effect of HPMC on C_3A hydration resides on kinetics retardation.

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References

[1] K.H. Khayat, Viscosity-enhancing admixtures for cement-based materials: an overview, Cem. Concr. Compos. 20 (1998) 171–188.
[2] K.H. Khayat, J. Assaad, Air-void stability in self-consolidating concrete, ACI Mater. J. 99 (2002) 408–416.
[3] S. Chandra, Y. Ohama, Polymers in Concrete, CRC, Boca Raton, 1994.
[4] M.U.K. Afridi, Y. Ohama, M.Z. Iqbal, K. Demura, Behaviour of $Ca(OH)_2$ in polymer modified mortars, Int. J. Cem. Compos. Lightweight Concr. 11 (1989) 235–244.
[5] M.U.K. Afridi, Y. Ohama, M.Z. Iqbal, K. Demura, Morphology of $Ca(OH)_2$ in polymer-modified mortars and effect of freezing and thawing action on its stability, Cem. Concr. Compos. 12 (1990) 163–173.
[6] M.U.K. Afridi, Z.U. Chaudhary, Y. Ohama, K. Demura, M.Z. Iqbal, Effects of polymer modification on the formation of high sulphoaluminate or ettringite-type (AFt) crystals in polymer-modified mortars, Cem. Concr. Res. 24 (1994) 1492–1494.
[7] M.U.K. Afridi, Z.U. Chaudhary, Y. Ohama, K. Demura, M.Z. Iqbal, Morphological characterization of low sulphoaluminate-type (AFm) crystals, hollow tubules and hollow crystals in polymer-modified mortars, Cem. Concr. Res. 25 (1995) 271–275.
[8] D.A. Silva, Effects of EVA and HEC polymers on the microstructure of portland cement pastes, UFSC/PGMAT Dissertation, Florianopolis — Brazil, 2001 (in Portuguese).
[9] D.A. Silva, P.J.M. Monteiro, Hydration evolution of C_3S–EVA composite analyzed by soft X-ray microscopy, Cem. Concr. Res. 35 (2005) 351–357.
[10] D.A. Silva, P.J.M. Monteiro, Analysis of C_3A hydration using soft X-ray transmission microscopy: effect of EVA (available online 17 May 2005, www.sciencedirect.com).
[11] A. Jenni, L. Holzer, R. Zurbriggen, M. Herwegh, Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars, Cem. Concr. Res. 35 (2005) 35–50.
[12] M. Drábik, L. Gáliková, P. Zimmermann, Attack by moisture on advanced cement-based microscopic defect-free material — a thermoanalytical study, J. Therm. Anal. Calorim. 56 (1999) 117–124.
[13] M. Drábik, S.C. Mojumdar, L. Gáliková, Changes of thermal events of macrodefect free (MDF) cements due to the deterioration in the moist atmosphere, Cem. Concr. Res. 31 (2001) 743–747.
[14] S.C. Majumdar, Processing-moisture resistance and thermal analysis of macro-defect-free materials, J. Therm. Anal. Calorim. 64 (2001) 1133–1139.
[15] K.E. Kurtis, Transmission soft X-ray microscopy of the alkali–silica reaction, Ph.D. dissertation, Dept. of Civil and Envir. Engrg., Univ. of Calif., Berkeley, Calif., 1998.
[16] D. Atwood, Soft X-ray and Extreme Ultraviolet Radiation: Principles and Applications, Cambridge University Press, University of California at Berkeley/LBNL, 1999.
[17] M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, G.P. Denbeaux, Using soft X-raystransmission microscopy to examine cement hydration in the presence of retarders, Proc. 11th. Int Congr Chem Cem (ICCC), Durban (South Africa), 2003, pp. 249–258.
[18] M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, G.P. Denbeaux, A soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration, Cem. Concr. Res. 35 (2005) 19–25.