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Influence of carboxylated styrene–butadiene latex copolymer on Portland cement hydration

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ABSTRACT

The influence of carboxylated styrene–butadiene (SB) latex on the hydration of ordinary Portland cement was investigated by means of isothermal heat flow calorimetry, in-situ X-ray diffraction, electroacoustic zeta potential measurement and ion analysis of the cement pore solution. In particular, to assess the influence of the spraying aids polyvinyl alcohol (colloidal stabilizer) and kaolin (anti-caking agent) on cement hydration, the impact of the liquid SB latex was compared with that of its redispersible powder. It was found that anionic SB generally retards both the aluminate and silicate reactions. This effect can be ascribed to adsorption of SB particles onto positively charged clinker or hydrate phases and the chelation of calcium ions present in cement pore solution by the carboxylate groups of the SB sample. SB powder exhibits a lower anionic charge density due to PVOH coating, thus interacts less strongly with cement and retards slightly less, compared to liquid SB latex.

1. Introduction

The hydration of ordinary Portland cement (OPC) represents a complex process that originates from the reactions of the two main cement constituents, the silicate and the aluminate phases. Owing to its complexity, it still is the subject of scientific papers which contribute to an increased understanding of this process [1]. The silicate and especially the aluminate reactions may significantly be impacted by the presence of admixtures such as superplasticizers, retarders, accelerators etc., as has been reported in numerous previous studies [2,3].

Latex polymers represent key components in many drymix mortar formulations, e.g. in repair mortars, tile adhesives and grouts, in waterproofing membranes or self-leveling underlayments (SLUs) [4]. They provide cohesion of the fresh mortar and good adhesion on various substrates. Additionally, latex polymers increase the flexural strength of hardened mortar due to the formation of elastic polymer films within the inorganic mortar matrix [5].

For drymix mortar applications, the latex mother liquors are transformed into powders. There, the liquid latex is spray dried under the addition of spraying aids (a colloidal stabilizer and an anti-caking agent) that prevent coalescence of the latex particles during the drying process and provide a non-compacting powder [6]. Typically, partially hydrolyzed, water-soluble polyvinyl alcohol (PVOH) is used as a protective colloid while inorganic compounds such as clays (e.g. kaolin), diatomaceous earth, microsized silica or calcium carbonate serve as anti-caking agents. In a previous study, we have reported about the effects of the spraying aids PVOH and kaolin on the colloidal properties of carboxylated SB and ethylene-vinyl acetate latexes [7]. They increase the colloidal stability of the re-dispersed latex powder and promote its film formation. In the present study, the influence of latex mother liquor and of the re-dispersible latex powder on cement hydration was investigated.

In the literature, many articles on the interaction between polymers and mineral phases in general can be found. For example, *Jansen* et al. [8,9] examined the impact of polyvinyl alcohol and of poly diallyl dimethyl ammonium chloride (PDADMAC) on the formation of cement hydrates using quantitative X-ray diffraction. *Plank* and *Gretz* [10] confirmed the adsorption of anionic and cationic latex particles onto cement via zeta potential and adsorption measurements. *Su* et al. [11] reported that styrene–acrylate or vinylpropionate–vinylidenechloride latex

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dispersions retard the setting and hydration of cement. *Larbi* and *Bijen* [12] investigated the influence of the same polymers on the composition of cement pore solution and showed that Ca^{2+} ions are chelated by the polymers. *Betioli* et al. [13] and *Silva* et al. [14] examined the interaction between ethylene–vinylacetate copolymers and Portland cement via thermogravimetric analysis. They presented that upon EVA hydrolysis in alkaline cement pore solution, calcium acetate is formed and as a result the calcium hydroxide content in the fresh and hardened cement paste decreases. *R. Wang* et al. [15–19] investigated the effect of liquid styrene–butadiene rubber (SBR) latex and powder on ettringite and portlandite formation via X-ray diffraction, and of C–S–H formation via environmental scanning electron microscopy. They found that both liquid SBR latex and powder promote ettringite formation, whereas C–S–H and portlandite crystallization are reduced. However, in these works no information on the specific composition (e.g. charge character or spraying aids) of the latex polymers was given.

Despite these previous efforts, no work exists that reflects the different colloidal properties of liquid latexes and their re-dispersible powders, the consequences for their presumably different interaction with cement and their overall influence on cement hydration. However, the colloidal properties of latex particles such as surface charge or particle size are most critical for their interaction with mineral phases or ions in cement pore solution. The chemical composition of the polymer appears to be less relevant here, because the electrokinetic surface properties represent the main driving force behind such physical interactions [20].

Therefore, in this work we focused on the surface properties of carboxylated styrene–butadiene latex and powder and the impact of the spraying aids polyvinyl alcohol and kaolin on the hydration of OPC. Their influence was tracked via isothermal heat flow calorimetry. Time-dependent evolution of the main hydration phases ettringite and portlandite was monitored via in-situ X-ray diffraction. Complementarily, the SO_4^{2-} and Ca^{2+} ion concentrations present in cement pore solution were quantified via ion chromatography (SO_4^{2-}) or atomic absorption spectroscopy (Ca^{2+}). Electroacoustic zeta potential measurements of cement slurries were performed in order to investigate adsorption of the latex particles on cement. From these experiments, it was envisioned to obtain a thorough understanding of the colloidal properties of liquid SB latex and powder, their interaction with specific cement hydrates, and a mechanistic view of the processes involved in these interactions.

2. Materials and methods

2.1. Materials

The cement used in this study was an ordinary Portland cement CEM I 52.5 N from Heidelberg Cement, Geseke plant, Germany that is commonly used as the base cement in drymix mortar formulations. Its phase composition as determined by quantitative X-ray diffraction (Bruker AXS D8 Advance, Karlsruhe, Germany) using *Rietveld* refinement (software Topas 4.0) is shown in Table 1.

Average particle size (d_{50} value) of the cement sample measured via laser granulometry (Cilas 1064, Cilas Company, Marseille, France) was found to be 11.8 μm. Specific density of the cement was 3.2 kg/L as obtained by Helium pycnometry (Ultrapycnometer 1000, Quantachrome Instruments, Boynton Beach, USA).

Liquid (solid content 45 wt.%) and powder SB latex samples were provided by Dow Olefinverbund GmbH, Schkopau, Germany. The SB re-dispersible powder was produced by spray drying of an SB mother liquor under addition of polyvinyl alcohol (~10 wt.%) as colloidal stabilizer and kaolin (~12 wt.%) as anti-caking agent. Polyvinyl alcohol (Mowiol 4 – 88) was purchased from Kuraray Europe, Frankfurt/Germany and kaolin (KAMIN HG 90) was obtained from KaMinLLC, Macon, GA, United States.

Table 1
Phase composition of the CEM I 52.5 N sample, as was determined via Q-XRD using *Rietveld* refinement.

Phase	Content [wt.%]
C_3S	57.91
C_2S	23.47
C_3A, cubic	4.38
C_3A, orthorhombic	3.58
C_4AF, orthorhombic	2.49
CaO (free lime)	0.28
MgO (periclase)	0.14
$CaSO_4$	2.08
$CaSO_4 \cdot 0.5H_2O$[a]	0.38
$CaSO_4 \cdot 2H_2O$[a]	0.66
Calcite	3.33
Quartz	0.82
Arcanite	0.48

[a] Measured via thermogravimetry.

Table 2 summarizes the main properties of the liquid and powder SB latex samples. Particle size, zeta potential, anionic charge density, glass transition temperature (T_g) and minimum film forming temperature (MFFT) of the liquid and powder SB samples were determined as described in a previous paper [7].

2.2. Preparation of polymer-modified cement pastes

Hydration of CEM I 52.5 N was monitored in the presence and absence of SB polymer, PVOH and kaolin using isothermal heat flow calorimetry, in-situ X-ray diffraction, electroacoustic zeta potential and analysis of the chemical composition of the cement pore solution.

For all experiments, cement pastes were prepared at a constant water-to-cement (w/c) ratio by weight of 0.5 using the following procedure: first, the liquid SB latex or SB powder or kaolin were added to deionized mixing water and sonicated for three min. In this way, the latex powder or kaolin are fully dispersed into their primary particles. Second, cement powder was added to the SB or kaolin dispersion and shaken on a vortex shaker (Reax, VWR International, Darmstadt, Germany) for one minute. In additional experiments with PVOH, this polymer was completely dissolved under stirring in the mixing water before it was mixed with cement as described above.

SB polymer dosages (stated by weight of cement) were chosen at 5, 10 or 20% bwoc respectively. Thus, cement pastes modified with powder SB contained additional PVOH and kaolin, and the same amount of SB polymer as contained in the liquid SB. For the investigation on the impact of spraying aids, the respective amounts of PVOH or kaolin contained in the SB powder were applied.

2.3. Isothermal heat flow calorimetry

Hydration of CEM I 52.5 N in the presence and absence of SB polymer was tracked via heat flow calorimetry using a TAM Air isothermal heat conduction calorimeter from Thermometric, Järfälla, Sweden.

In a typical experiment, 4 g of cement powder were mixed at a w/c ratio of 0.5 in a 10 mL tubular glass ampoule with water holding the SB latex either in liquid or powder form. The glass ampoules were sealed with a metal lid, shaken for 1 min on a vortex mixer to homogenize the paste and transferred into the instrument. Heat flow curves were recorded for 72 h at 20 °C.