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Effect of highly carboxylated colloidal polymers on cement hydration and interactions with calcium ions

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ABSTRACT

Polymer latexes are often found to retard cement hydration. Interaction of polymer particles with Ca^{2+} in pore solution and adsorption of polymer on cement were proposed as possible mechanisms for the retardation effect. This paper aims at disclosing the retardation mechanism of colloidal polymers using a highly carboxylated polystyrene latex. Interaction between colloidal particles and Ca^{2+} was studied by post-treatment of the latex with $\text{Ca}(\text{NO}_3)_2$. Techniques including calorimetry, adsorption test, ICP-OES, SEM, are involved to investigate effects of the post-treated latexes on hydrations of cement and C_3S . It is found that enrichment of Ca^{2+} on surface of colloidal particles doesn't contribute to the retardation effect of polymer on cement hydration. Furthermore, the acceleration effect of the two-step treated latex using $\text{Ca}(\text{NO}_3)_2$ and Na_2SiO_3 suggests that nucleation inhibition of the adsorbed polymer layer on cement surface is the more conceivable mechanism responsible for the retardation effect of the highly carboxylated latex.

1. Introduction

Polymer latexes such like styrene-acrylate (SA) latex [1,2], styrene-butadiene rubber (SBR) [3] and vinyl acetate (VAc) based polymers [4,5], representing a big class of chemical admixtures for cement mortar and concrete, are popularly used in cementitious materials to improve various properties including ductility, adhesion to substrate, and durability etc. [6–9]. Polymers, in the forms of either liquid latexes or re-dispersible dry powders are regularly incorporated in the formulations of repair mortar, ceramic tile adhesives, water proofing membrane etc. [10–12]. Despite the gains in many superior properties, an often observed drawback of the addition of latex polymers is the retardation effect on cement hydration, which frequently leads to retarded setting and slowed early strength growth of the polymer modified mortar and concrete [13]. A huge effort has been paid to understand the mechanisms underlying the retardation effect of the colloidal polymers on cement hydration [1,14–17] and hitherto two possible mechanisms are proposed [14–18]: 1) Driven mainly by the electrostatic interaction between the colloidal particles and the surface of cement grains, polymer particles are largely adsorbed onto the surface of cement grains and hence the formed polymer covering layer on the one hand may hinder the dissolution of cement phases and/or on the other hand may act as nucleation inhibitor for generation of hydration products, such as C–S–H; 2) Complexation of carboxylate groups

contained in the colloidal particles with the Ca^{2+} ion present in the pore solution of cement pastes may decrease the Ca^{2+} ion concentration in the pore solution and thus delay the precipitation of hydration product due to the prolonged time to reach the necessary super-saturation for hydration products.

Complexation of carboxylate group contained in polymers with calcium ions has been observed by many researchers [16,19,20]. It has been frequently reported that the retardation effect of the carboxylate group containing polymers, such as polycarboxylate superplasticizers (PCE) [17,21] and acrylate-based latex [16,22], may originate from the complexation between R-COO^- and Ca^{2+} ions in pore solution of cementitious system. However, on the other hand, some other researchers argued that the tiny amount of R-COO^- groups introduced into cement pastes by the polymers seems hard to explain their strong and continuous retardation effect on cement hydration [23]. Besides, no direct relationship between the retardation effect of chemical admixtures on cement hydration and their complexation ability [24] was found. So far, no conclusive evidences confirming the role of complexation in cement hydration are obtained. With respect to another possible mechanism for the retardation effect of polymers, adsorption of polymers on mineral surfaces, it is still unclear how the adsorbed polymers retard the cement hydration process at different stages, either by hindering the dissolution process of cement phases or by inhibiting the nucleation and growth of the hydration products.

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In our previous studies [22,25], it has been clearly demonstrated that when polymer latexes are incorporated into hydrating cement systems, instead of the bulk composition of the polymer particles, the type and the amount of surface charge of the colloidal particles, originating from either the emulsifiers or the water soluble functional monomers such as acrylic acid used in the synthesis of the latexes [26], are the decisive factors for their retardation effect on cement hydration. Besides, compared to the sulfonated polymer latex and the lower charged latex with poly (ethylene oxide) (PEO) hairy layer covering on colloidal surface, the carboxylated polymer latex exhibits much stronger retardation and the retardation effect is somehow proportional to the amount of carboxylate groups introduced by the latex polymer into cement pastes [22]. Contrarily, in some cases, it was also found that the presence of $R-COO^-$ groups may promote cement hydration to some extent. Nalet et al. [27] found that the maximum hydration rate of C_3S paste is enhanced in the presence of the organic acid, although the induction period is prolonged. Our previous study [28] also showed that larger amount of carboxylate groups generated on the surface of polymer particles due to the hydrolysis of butyl acrylate unit in the latex of styrene-butyl acrylate co-polymer, lead to higher but delayed hydration peak in comparison with those polymer particles with lower amount of carboxylate groups.

These abovementioned conflicting results indicate the limited understanding on the retardation effect caused by the addition of polymers and the role of carboxylate groups contained in the polymers in cement hydration process. In this context, a highly carboxylated polystyrene latex was synthesized by using a large amount of methacrylic acid (8 wt%) as the water soluble co-monomer via conventional emulsion polymerization. The effect of the latex on cement hydration was investigated by calorimetry. The interaction of the colloidal particles with Ca^{2+} , namely the Ca^{2+} capturing capacity of the colloidal particles was investigated using ICP-OES measurement by adding $Ca(NO_3)_2$ into the dialysis purified latex sample. If the complexation effect of $R-COO^-$ with Ca^{2+} is the dominating mechanism of the retardation effect of latex on cement hydration, the mitigation of the retardation effect should be observed using the Ca^{2+} treated latex, in comparison with the pure latex. Adsorption of the polymer in cement pastes was measured by the depletion method. A Ca-Si bearing latex was prepared by subsequently adding $Ca(NO_3)_2$ and Na_2SiO_3 into the purified latex, with expectation of modification of the colloidal surface by forming a calcium silicate precipitate surrounding layer on top of the surface of the colloidal particles. Nucleation poisoning effect of the adsorbed polymer particles is expected to be eliminated by using such calcium silicate precipitate modified latex. By systematically comparing the effects of the above prepared latex samples, namely the purified polymer latex with high amount of $R-COO^-$, the Ca treated and the Ca-Si treated latex samples, it is expected to disclose the retardation mechanisms of the carboxylated polymer latex on cement hydration and to draw a clear conclusion to the question, whether the complexation or the adsorption is the dominating mechanism in the retardation effect.

2. Experimental

2.1. Materials

Styrene (St), methacrylic acid (MAA), sodium persulfate (SPS), sodium hydroxide, calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) were used as received (all > 98% purity). Isoprenyl oxy poly(ethylene glycol) macromonomer (TPEG) with weight average molecular weight (M_w) of 2400 was provided by Liaoning Kelong Fine Chemical Co., Ltd., China. Two kinds of emulsifiers, MS-1 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}COC_3H_6SO_3Na$, 40 wt% aqueous solution) and OP-10 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$, 40 wt% aqueous solution), were provided by Hai'an petrochemical factory. Deionized (DI) water was used in all experiments. Defoamer (FoamStar ST 2111, provided by BASF) was used in the preparation of

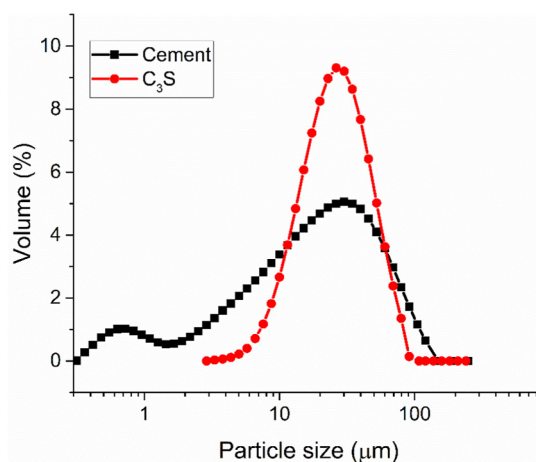


Fig. 1. Particle size distribution of the cement and the C_3S pure clinker.

cement mortars for mechanical tests in order to control the air content in the mortar specimens.

Commercial reference cement P-I 42.5 complying with the Chinese standard GB8076-2008 and pure clinker C_3S provided by University of Erlangen-Nuremberg were used in this study. Specific surface area and particle size for the two materials were measured by Malvern laser particle size analyzer (Malvern Mastersize 2000, UK). The measured specific surface area values of cement and C_3S are $0.35 m^2/g$ and $0.31 m^2/g$ respectively. The particle size distributions for the two materials are shown in Fig. 1. Chemical composition of the cement was measured by X-ray fluorescence spectrometry (LAB Center XRF-1800, Shimadzu) and mineralogical composition of the cement was determined by XRD using Rietveld refinement (D8 diffractometer, Bruker). The results are summarized in Table 1. The pure clinker C_3S was characterized by XRD as shown in Fig. 2.

2.2. Synthesis of the polymer latex

Polystyrene latex was synthesized by conventional emulsion polymerization in a 1 L three necks glass flask. Two dosing units were used for dropwise addition of the pre-emulsion of all monomers and the initiator solution. The reaction temperature was kept constant at $90^\circ C$ during the whole polymerization period. The mass composition of the monomers was shown in Table 2. Specifically, in total, 8.0 g TPEG, 32.0 g MAA and 360.0 g St were used for the synthesis of the latex.

Initiator solution was prepared by dissolving 2.7 g SPS in 248.0 g DI water. Pre-emulsion of monomers was prepared by thoroughly mixing all monomers as shown above, emulsifiers (5.3 g MS-1 and 3.2 g OP-10) and 172.0 g DI water using a high-shear mixer at 10,000 rpm. 6.5 g MS-1 and 136.0 g DI water was firstly charged into the three necks glass flask and the pre-charge was then heated up to $90^\circ C$ by water bath under stirring and kept for 5 min. The monomer emulsion and the initiator solution were separately dosed into the flask at constant dosing rates over 3.5 h and 4.0 h respectively. Before finishing the synthesis, the reactant was kept at $90^\circ C$ under stirring for another 0.5 h to complete the polymerization. In this way, a milky polymer dispersion with solid content of ca. 40 wt% was prepared.

In the obtained polymer latex, a tiny amount of residual monomers, free surfactants and salts are still present in the serum phase, which may have unneglectable impacts on cement hydration [18]. For investigation of the colloidal particles on cement hydration, it is necessary to minimize the disturbance of the serum components. Therefore, in this study, dialysis was carried out to remove the residuals in the serum of polymer latex. Detailed description of the dialysis process can be found in our previous publication [25]. The solid content of the dialyzed latex marked as L0 was 21.6%. The cleaned polymer latex was

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