Construction and Building Materials 132 (2017) 112–123

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effects of organosilane-modified polycarboxylate superplasticizer on the fluidity and hydration properties of cement paste

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HIGHLIGHTS

- Organosilane-modified PCEs are made by inserting 3-(trimethoxysilyl) propyl methacrylate.
- Partially organosilane-modified PCEs enhance adsorption and dispersing properties.
- Adding organosilane-modified PCEs rarely changes the morphology of hydrates.

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 19 August 2016
Accepted 24 November 2016

Keywords:
Organosilane-modified polycarboxylate superplasticizer
Synthesis procedures
Adsorption behavior
Dispersing property
Cement hydration
Microstructure

ABSTRACT

A series of organosilane-modified polycarboxylate (PCE) superplasticizer were synthesized, in which acrylic acid (AA) was partially or completely substituted by 3-(trimethoxysilyl) propyl methacrylate. This study mainly investigated their adsorption behavior, dispersing performance as well as their effects on cement hydration process. Results indicate that partially silylated PCEs exhibit larger adsorption than the reference PCE, decrease zeta potential of cement paste to a larger negative value and improve the fluidity properties of cement paste. The fluidity retention property of organosilane-modified PCEs is weaker, and the viscosity and the yield stress increase more steeply with time. Partially silylated PCEs can accelerate the cement hydration rate, and the mechanical strength is higher at 3 d due to accelerated hydration as well as improved pore structures.

1. Introduction

Polycarboxylate superplasticizers (PCE) are widely used nowadays to improve the workability of fresh concrete [1–5]. The dispersing function of PCE is mainly achieved through adsorption on the cement particles and the steric hindrance effect produced by polyethylene glycol (PEG) side chains [6]. Generally, in cement paste, silicate phases have negative zeta potential, while aluminate phases have positive zeta potential. The negatively charged PCEs adsorb onto positively charged aluminate phases via electrostatic forces [7,8], and adsorb on silicate surfaces through the complexation bonding between $-COO^-$ and Ca^{2+} [9,10]. Due to the difference of zeta potential in mineral surfaces, much higher adsorption takes place on C_3A and C_4AF phases than on C_2S and C_3S phases [7,8]. Furthermore, the adsorption behavior of PCE on cement particles is quite sensitive to interference factors [11,12]. For example, PCE polymer can desorb if there is high content of sulfate ions in pore solutions, which therefore significantly decreases the dispersing performances of PCEs [12–15]. Otherwise, PCE polymers can also desorb at relatively high temperature, which remarkably reduces the dispersing effect in hot environment [16].

To address the problem of unstable adsorption behavior of PCEs, a large number of researches have been carried out [3,6,13,17,18]. It was found that the adsorption equilibrium of PCE can be modified by regulating its molecular structure and charge density, for example, by decreasing PEG side chain length or increasing ionic groups in PCE backbones [19]. However, PCE exhibiting excessive adsorption is disadvantageous to fluidity retention, due to the fact that the residual amount of non-adsorbed PCEs is not sufficient to compensate for the increase of solid surface due to hydration [6]. And the use of a PCE designed for particular cement may result in problems when used in a different kind of cement [6]. Therefore,

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http://dx.doi.org/10.1016/j.conbuildmat.2016.11.122

it is necessary to improve the adsorption performance of PCE through more robust interaction effects.

Some researchers have found that a new layered calcium organosilicate hybrid can be formed with covalently linked organic functionalities, and their silylated hydrosoluble polymers can be covalently bonded to C–S–H gel [6,20]. And this kind of organosilane-modified PCE superplasticizer has been developed by incorporating organosilane functions into PCE polymers [6,17]. The silylated groups in the backbone of PCE can solidly interact with negatively charged phases, for example C_3S and C_2S, and hence improve the adsorption capability of PCE polymers on cement grains [21,22]. Moreover, this kind of organosilane-modified PCE superplasticizer contributes to a higher resistance against competitive adsorption of sulfate ions [6].

However, organosilane-modified PCE may affect the interaction of polymers with cement, and thus exert an influence on rheological properties and cement hydration. In this study, a series of PCEs modified by insertion of trimethoxysilane groups were synthesized, and detailed research was carried out on their interaction with cement, including adsorption behavior, dispersing capability, cement hydration process, pore structure in hardened cement paste, morphology and composition of hydrates as well as mechanical properties of hardened cement mortar.

2. Experimental

2.1. Materials

2.1.1. Cement and sand

Ordinary Portland cement classified as 42.5R was applied in this study. Chemical composition, mineral composition as well as physical performance of the cement are shown in Table 1. The contents of oxides were measured through X-ray fluorescence. The content of f-CaO was analyzed by the Franke method. The mineral phases were calculated by the Bogue method. The China ISO standard sand compling with GB/T 17671-2005 was used to prepare cement mortar.

2.1.2. Materials for PCE synthesis

Analytical grade acrylic acid (AA, 99%, Acros, stabilized with 250 ppm of methylethylhydroquinone), ammonium persulfate (APS), 3-mercaptopropionic acid (MPA), 3-(Trimethoxysilyl) propyl methacrylate, tetrahydrofuran (THF) and methyl allyl polyethenoxy ether (HPEG, Mn ~1600 g mol^{-1}) were used without further purification.

2.2. Synthesis of organosilane-modified PCE

Radical copolymerization of HPEG, AA and MAPTMS were initiated by APS at 80 °C with a chain transfer agent (3-(Trimethoxysilyl) propyl methacrylate). Certain molar ratios of HPEG, MAPTMS and APS were mixed with 40 g THF, and the molar ratios of HPEG, MAPTMS and APS were tabulated in Table 2. The mixture was bubbled under argon for 10 min to remove oxygen. 3-(Trimethoxysilyl) propyl methacrylate and AA were then injected into the mixture through micro-syringes respectively. The flask was placed in a water bath thermostated at 80 °C and the polymerization was kept for 24 h under argon. Copolymers were then directly isolated by evaporation of THF.

To remove un-reacted monomers from the samples, a cellulose ester semipermeable membrane with nominal molecular weight cut-off of 7000 Da was used to purify co-polymers [10]. The synthesized polymers were introduced into the dialysis bag. Then the sealed dialysis bags were put in a vessel full of deionized water for 7 days.

2.3. Analytical methods

2.3.1. Evaluation of PCE chemical structure

The proportion of alkoxysilanes in the synthesized polymers was verified by TGA and quantitative ^{29}Si NMR. ^{29}Si NMR experiments were conducted by a Bruker Avance 500 MHz spectrometer in a 7 mm diameter probe [6]. Thermogravimetric measurements (TGA) were carried out under N_2 atmosphere up to 1000 °C, at a heating rate of 10 °C min^{-1}. Size exclusion chromatography (Viscotek GPCmax) were applied to measure the weight-average molar masses (M_w) and their distribution (PDI = M_w/M_n, the polydispersity index) under the condition of 35 °C using a 0.5 mol L^{-1} $NaNO_3$ aqueous solution as eluent [6].

2.3.2. Properties of cement paste

Cement paste was prepared with a water/cement ratio (W/C) of 0.29, using a blade-type high shear blender. Before mixing, PCE solution was prepared with deionized water. With the addition of PCE solution, cement paste were mixed for 2 min at low speed and then 2 min at high speed.

The fluidity of cement paste was measured using a mini-slump cone according to Chinese standard GB/T 8077-2000 [23].

For the rheology experiments, a Bohlin C-VOR shear rheometer equipped with a Vane geometry was used. The Vane tool diameter is 25 mm, the outer cup diameter is 50 mm, and its depth is 60 mm. The cup of the rheometer was filled with cement paste and then measurement sequence was started. The measurement was performed 15 min after mixing by preshearing the cement paste at a shear rate of 100 s^{-1} for 1 min. a decreasing shear rate was then directly applied from 100 s^{-1} to 1 s^{-1} (with a logarithmic distribution of shear rates) for 200 s. The yield stress was calculated by fitting the rheogram data according to the Hershey-Buckley model [6].

Table 1
Chemical composition, mineral composition and physical properties of cement.

Chemical composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	TiO_2	K_2O	Na_2O	$(Na_2O)eq.$[a]	LOI[b]
(%)	63.3	21.4	5.6	2.7	1.9	3.4	0.4	0.7	0.12	0.58	0.48
Mineral composition			C_3S		C_2S			C_3A			C_4AF
(%)			57.34		18.9			6.47			11.25
Physical properties	Specific gravity (g/cm^3)		Mean size (μm)	Fineness (cm^2/g)		Setting time (min)		Mortar compressive strength (MPa)		Mortar flexural strength (MPa)	
						Initial	Final	3 days	28 days	3 days	28 days
	3.12		26.6	3570		90	175	33.2	58.5	6.5	8.2

[a] $(Na_2O)eq. = (Na_2O)+0.658(K_2O)$.
[b] LOI = loss of ignition.