



Modified poly(carboxylate ether)-based superplasticizer for enhanced flowability of calcined clay-limestone-gypsum blended Portland cement



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ABSTRACT

Supplementary materials that are utilized to replace ordinary Portland cement (OPC) decrease the workability of the cementitious mixtures and superplasticizers are usually added to cement to control their fluidity. In general, current superplasticizers are solely optimized for single component systems such as OPC. Here, we report the performance of a series of a modified poly(carboxylate ether)-based superplasticizers (PCEs) in a ternary OPC-calcined clay-limestone blend. We have utilized: i) a co-monomer with high ionic character, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) to be incorporated into the acrylic acid backbone of PCEs and ii) low density of polyethylene glycol (PEG) grafted chains < 0.01 mol/mol. The optimized polymer does not intercalate into the layered structure of calcined clay and preserves its steric size in the presence of high concentration of sulfate ions.

1. Introduction

Ordinary Portland cement is the most produced human-made material and its production is responsible for approximately 8% of total anthropogenic CO₂ emissions [1]. Materials with lower emissions, such as pozzolans, clays, fly ash, blast-furnace slag, and silica fume are suggested to replace OPC [2–6]. However, this replacement is often associated with reduction of strength at early ages. Recently, introduction of limestone to these blends have been reported to remedy this problem through improving the reactivity of the system [7,8]. Scrivener et al. [9,10] and Habert et al. [11] have shown that the substitution of OPC, up to 50%, with a combination of calcined clay, limestone, and gypsum offers an energy/cost-effective solution along with mechanical properties that are comparable to plain cement.

The utilization of supplementary materials has significant impact on fluidity of blended cement and thereby, an increase in water to binder ratio (w/b) is required to maintain necessary fluidity of these mixtures [12]. Similar to plain cement, high range water reducer agents, known as superplasticizers, are added to these blends to limit the amount of mixing water while retaining the workability at low w/b ratios. Latest generation of superplasticizers, PCEs, which exhibit superior dispersing ability compared to other types of superplasticizers (e.g., sulfonated naphthalene formaldehyde and sulfonated melamine formaldehyde) adsorb onto cement particles through the carboxylic groups present in

the backbone. The side chains based on polyethylene glycol (PEG) are responsible of the steric hindrance [13–15]. Despite the superior performance of PCEs in forming workable mixtures, their interaction with clay minerals and sulfate ions (SO₄²⁻) still leads to a loss in fluidity or a higher water demand to achieve the same levels of workability of plain cement [15–17]. Based on the specific properties of clay minerals (e.g., layered structure and swelling ability), different type of clays can potentially increase the dosage of PCEs due to consumption of superplasticizers through intercalation [18]. Therefore, highly-substituted mixtures require advanced superplasticizers that can address the high surface area and layered structure of the incorporated clay minerals as well as high concentration of sulfate ions in the pore solution.

Here, we pursued a step-wise approach in developing such a superplasticizer. Although substituted, the major component of blended cements is still OPC; therefore, we first developed a modified poly(carboxylate ether)-based grafted copolymer that remains effective in plain OPC paste at high concentrations of sulfate ions and low water content. A monomer with high ionic character, AMPS, was utilized as the co-monomer of acrylic acid (AA) in the backbone of PCEs. We tracked the performance of this type of superplasticizer in OPC systems at different i) co-monomer/monomer ratios, ii) density of side chains, and iii) molecular weights. Among optimized superplasticizers, to be then used in blended systems, we chose one with a density of PEG grafted chains < 0.01 mol PEG/mol (AA + AMPS) to avoid

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intercalation of the copolymer into clay minerals. The effect of this modified grafted copolymer (hereafter, referred to as AMPS-PCEs) on adsorption behavior, workability, and hydration of blends that are substituted up to 50 wt% with calcined clay (28–45 wt%), limestone (0–15 wt%) and gypsum (0–5 wt%) were demonstrated. Incorporation of 1 wt% of AMPS-PCEs to the blends led to high initial workability with no reduction in slump flow diameter during 60 min after the first touch of water. This superplasticizer, to the best of our knowledge, is the first customized PCE-based copolymer that can concurrently accommodate i) layered structure of clay, ii) surface charge density and, thus initial water demand of limestone, and iii) high concentration of sulfate ions of OPC-clay-limestone-gypsum blended cement. The workability retention and dispersing ability of AMPS-PCEs were linked to gradual adsorption of copolymer molecules onto the surface of particles while preserving their steric size in the presence of high concentration of sulfate ions.

2. Materials and proportioning

OPC-CEM 1 42.5 R was provided by a local cement company (AKCANSAs). Calcium carbonate (CaCO_3) was purchased from Sigma-Aldrich. The clay was calcined at 800 °C in a semi-industrial rotary kiln with a residence time of 15 min. The Rietveld analysis on calcined clay showed that it contains 42% calcined kaolinite (metakaolin) and the rest is uncalcined kaolinite, quartz (16%), and traces of illite, anatase, and hematite (in total < 2%). We also observed the layered structure in clay particles after the calcination (Fig. S1). Chemical composition (from X-ray fluorescence analysis) and physical properties of OPC, calcined clay, and CaCO_3 were listed in Tables 1–3. The specific surface area of calcined clay particles was measured as 9 m²/g by N₂ adsorption method.

AA (99%), AMPS (99%), and potassium persulfate (KPS, ≥ 99.0%) obtained from Sigma-Aldrich. Polyethylene glycol with a molecular weight of 1000 g (PEG1000), maleic anhydride (MA, 99%), and sodium hydroxide (NaOH, ≥ 97%) were purchased from Merck. All of the reagents were used as received without further purification. The AMPS-PCEs were synthesized by aqueous free radical polymerization of AA, AMPS, and esterified-PEG1000 [19]. After cooling down the reaction to room temperature, copolymers were precipitated in ethanol and dried under vacuum at 50 °C until reaching a constant weight. Chemical structure of AMPS-PCEs is shown in Fig. 1a and characteristic properties of the copolymers (quantitative H¹-NMR, Fig. 1b) are listed in Table 4.

Different amounts of calcined clay, limestone, and gypsum were first dry-mixed with OPC for 5 min to formulate binders of varying compositions (Table 5). Certain amounts of these blends were then

Table 1
Chemical analysis of OPC and clay.

	OPC	Clay
Chemical composition (%)		
SiO ₂	13.37	53.46
Al ₂ O ₃	4.68	34.87
Fe ₂ O ₃	3.35	3.39
CaO	63.08	0.13
MgO	1.42	0.09
SO ₃	2.71	0.03
Na ₂ O	0.29	0.17
K ₂ O	0.63	0.23
Cl	0.009	
TiO ₂		2.35
P ₂ O ₅		0.16
Mn ₂ O ₃		0.1
ZrO ₂		0.25
Loss on ignition		4.75

Table 2
Physical properties of OPC.

Density (g/cm ³)	3.15
Fineness (Blaine) (cm ² /g)	3275
BET surface area (m ² /g)	1.65
Initial setting time	155
Final setting time	250
Residue in 45 μm sieve (%)	0.0
Residue in 90 μm sieve (%)	0.3

Table 3
Physical and chemical properties of CaCO₃.

Density (g/cm ³)	2.93
BET surface area (m ² /g)	8.2
Sulfate (SO ₄ ²⁻)	≤ 0.01%
Chloride	≤ 0.001%
Fluoride	≤ 0.0015%
K	≤ 0.01%
Na	≤ 0.1%
Impurities	≤ 0.03%

charged to 100 ml of polymer solutions containing 0–15 mg/g AMPS-PCEs/binder (0–1.5 wt%) to cast pastes with water to binder ratio (w/b) of 0.4. For mechanical and thermo-gravimetric analysis, binder with 45 wt% quartz substitutions was prepared as control sample without addition of superplasticizer. All binders were first hand-mixed for 30 s and then stirred by Heidolph RZR 2102 mixer equipped with a 4-blade stainless steel propeller for 5 min at 1000 rpm. Such a high-shear mixing regime was used to ensure good dispersion of particles and homogeneous pastes.

3. Experimental methods

3.1. Dispersing performance of AMPS-PCEs in pastes

In order to determine the workability of pastes, mini slump test was carried out at 22 ± 2 °C according to ASTM C143. In this test, a cone with bottom diameter, top diameter, and height of 40 mm, 20 mm, and 60 mm, respectively, is filled with the paste and spread diameter is recorded after pulling out the cone. Average value of two crossing spread diameters after 2 times repetition of each test was reported as the test result. Time dependent workability tests (slump retention) were performed at the intervals of 15, 30, 45, and 60 min after the first touch of water. Four different batches were prepared and sealed to prevent the evaporation of water. The pastes, were, then stirred at 300 rpm for 30 s and slump tests were conducted after 15 s of resting time of the pastes in the slump cone.

3.2. Adsorption behavior of AMPS-PCEs on components

Adsorption of AMPS-PCEs on different components was evaluated using depletion method in synthetic pore solution prepared from 0.6 g/l CaSO₄·2H₂O, 5.2 g/l NaOH, 17.9 g/l KOH, and 2.4 g/l Ca(OH)₂ in 1 l of deionized water (pH of ~13.5) [20]. Suspensions of OPC, clay, and limestone with 0–10 mg/g AMPS-PCEs/particle at a pore solution to particle ratio of 2 were prepared. Although this w/b ratio is not similar to that of workability test, utilization of synthetic pore solution mimics the ionic composition of the cement pore solution and compensates the difference between solid fractions of suspensions in different tests [21]. After 15 min of stirring, the suspensions were centrifuged at 10,000 rpm for 10 min to separate the particles. The liquid phase was diluted by 1/2 (vol/vol) with 1.5 M HCl and filtrated through a 0.2 μm filter to remove any contaminants. The amount of adsorbed polymer was quantified by measuring the difference between intensity value of the scattered light (Zetasizer ZS, Malvern Instruments) of supernatant and bulk concentration of the polymer before addition of particles [22].

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