Journal of Industrial and Engineering Chemistry 55 (2017) 80–90

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Novel designs of polycarboxylate superplasticizers for improving resistance in clay-contaminated concrete

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ARTICLE INFO

Article history:
Received 15 April 2017
Received in revised form 12 June 2017
Accepted 18 June 2017
Available online 27 June 2017

Keywords:
Polycarboxylate superplasticizer
Clay
Molecular design
Concrete
Dispersion

ABSTRACT

Certain clays attached around the aggregates contaminate the concrete and also greatly affect the concrete workability, the mechanism of which was investigated through calculating the volume change of solid and liquid phases of concrete mixture containing clay. To minimize this detrimental effect, two novel designs based on the transfer of theory and techniques from polymer science, i.e., molecular design of polycarboxylate superplasticizer (PCE), were proposed. The one was "intercalator" synthesized via Hofmann rearrangement and cationization, and the other was "star-shaped polycarboxylate superplasticizer (SPCE)" synthesized via a route of "core first and arm second". The results of Infrared Spectroscopy (IR) and ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) confirm the designed structures. The applications of these polymers in clay-contaminated cement paste and concrete were tested. The results showed that, the dispersing capacities of "Intercalator + Comb-shaped polycarboxylate superplasticizer (CPCE)" and SPCE were less affected by adding clay in both cement paste and concrete. Adsorption and X-ray diffraction (XRD) experiments revealed less harmful intercalation for SPCE and preferential occupation in the interlayer space of clay for intercalator to protect other workable PCEs. It is interesting that optimizing charge characteristic and "disassembling-assembling" molecular arrangement can contribute to excellent resistance towards clay. The aim of this study is to offer two promising alternatives, which attractively provide the theoretical basis and technological application in researching advanced materials in clay-contaminated concrete.

Introduction

High-performance concrete (HPC) that includes high-fluidity concrete and high-strength concrete only can be produced with advanced concrete admixtures [1,2]. Polycarboxylate superplasticizer (PCE) makes up a class of concrete admixtures that exhibit a unique comb or brushlike structure, consisting of a trunk chain holding carboxylate groups and of pendant chains that are made of poly ethylene oxide (PEO). Because there are many advantages of PCE molecules which are easy to adjust, PCE is widely used to improve the workability of concrete [3–5] by dispersing agglomerated hydrating cement particles present in cement paste [6] and concrete applications, which have attracted great research attention in recent years [7–13].

Recently, researchers found that PCEs had strong sensitivity to clays which were attached around the aggregates to contaminate concrete, resulting in a loss in workability [14–16]. Consequently, their dispersing force decreases significantly in presence of clay [14,17–19]. Clay is a mineral aggregate of layered or layer-chained silicate with cohesiveness and plasticity [20]; in particular, montmorillonite clay has a 2:1 type structure consisting of two silicon–oxygen tetrahedral sheets sandwiching one alumina octahedral sheet. This structural characteristic leads to its expanding lattices promoting intercalation and cation exchange [21,22], which is found to be harmful to concrete fluidity. The design and tailoring of novel molecular structures for PCEs are used to solve some application problems [23–26]. In this way, we expect to explore new PCEs possessing high resistance toward montmorillonite clay.

There are some researches regarding the adsorption of PCE on clay [27,28] and the effect of clay on the durability of concrete containing PCE [29]; however, the understanding of clay-PCE interaction is unthorough. The current accepted mechanism is that

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http://dx.doi.org/10.1016/j.jiec.2017.06.031
1226-086X/

the PEO side chains intercalate in between the alumosilicate layers of montmorillonite clay [15]. However, the workability of concrete still decreases if we use the clay possessing different structure such as kaolin [30] and muscovite [31] or the superplasticizer free of side chains such as naphthalene superplasticizer [18], which cannot be explained by the above mechanism. In authors' opinion, the fluidity of concrete is mainly contributed by the flowable water, and thus the mechanism should also be proposed in terms of the effects of clay on the volume change of solid and liquid phases of concrete mixture, but there have been few studies on this. Furthermore, the reported approaches to minimize this detrimental effect are shortening [16,32] or discarding [25] PEO side chains, whereas they also result in a decrease in dispersing ability of PCE. In addition, other solutions such as increasing PCE dosage or adding polyethylene glycol (PEG)-grafted-lignin [7] or adding pure PEG [15] which will increase the cost, have little innovation. Therefore, by means of molecular design, new PCEs possessing modified chemical structure for enhanced robustness towards clay together with high dispersing force need to be studied, which have been scarcely investigated.

In this study, the mechanism of the decline in concrete workability was clarified by measuring the volume changes of solid and liquid phases of concrete mixture before and after adding montmorillonite clay. Then, two approaches to enhancing clay tolerance were proposed. One was that partial CPCE was replaced by cationic polycarboxylic intercalator synthesized via Hofmann rearrangement and cationization based on optimization of charge characteristic; the other was that entire CPCE was replaced by novel PCE possessing star-shaped structure (namely SPCE) synthesized via esterification and polymerization based on optimization of molecular structure. The molecular structures were characterized by IR, ^{1}H NMR and molecular weight measurements. The dispersing capacities were also tested in absence and presence of clay, followed by adsorption and XRD experiments to reasonably summarize the mechanisms of interaction between new superplasticizers and clay. The overall goal of this study was to provide and evaluate two approaches of synthesizing novel PCEs through innovative molecular design, which possessed high resistance to clay and still strong dispersing power. This finding offers not only a new direction for exploring clay-resistant PCEs but also a theoretical basis for minimizing the negative impact of clay.

Materials and measurements

Materials

Chemicals

Acrylic acid (AA), acrylamide (AM), ammonium persulfate (APS), *p*-toluene sulfonic acid, hydroquinone (all ≥99% purity, purchased from Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), pentaerythritol, sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), thioglycolic acid (TGA) and toluene (all ≥98% purity, purchased from Beijing Chemical Works, Beijing, China) were used in the study without further purification. Isobutenyl polyethylene glycol (IPEG, Mw = 2400 g/mol) consisting of 53 ethylene oxide units was received from Liaoning Oxiranchem, Inc (Liaoning, China).

Component materials of concrete

Reference cement P.I.42.5, fly ash, slag, sand and gravel were supplied by China Building Materials Research Institute (Beijing, China), which chemical and mineral compositions are illustrated in Table 1. The gravel with a continuous grading of 5–20 mm had a density of 2670 kg/m^3 and a bulk density of 1540 kg/m^3; the sand with a fineness modulus of 2.7 had a density of 2650 kg/m^3 and a bulk density of 1460 kg/m^3. Clays were montmorillonite, kaolinite, muscovite and feldspar with a fineness of 0.074 μm. The chemical compositions of these powders are listed in Table 2.

Synthesis

Synthesis of intercalator

The AM and TGA were dissolved in water and then added to a four-neck round-bottom flask which was placed in a constant temperature bath at 70 °C with stirring. Then, AA and APS aqueous solutions were dropwise added to the mixture (AA: AM: APS = 1:1:0.04) for 2.5 h, followed by cooling to room temperature and adding NaOH aqueous solution to adjust pH value to 7–8. Thereafter, NaOCl was added with stirring for 30 min and then heated for 2 h at 70 °C. At last, the mixture was cooled to room temperature and then acidified to adjust pH value to 5. This final product was designated as intercalator.

Synthesis of SPCE

AA, pentaerythritol, *p*-toluene sulfonic acid, hydroquinone and toluene were added to a four-neck round-bottom flask (Pentaerythritol: AA = 1:5) with stirring at 115 °C. The reaction lasted for 7 h and the produced water was uninterruptedly separated. Then, the esterification product obtained by removing toluene was added to the flask containing IPEG aqueous solution (Esterification product: IPEG = 1:15) at 65 °C with stirring. Thereafter, AA, APS and TGA aqueous solutions (APS: TGA: AA: IPEG = 0.28:0.18:3.3:1) were dropwise added to the vessel for 5 h, followed by adjusting pH value to 6–7. This final product was designated as SPCE, which detailed synthesis process was described in our patent [33].

The specimens for all the characterizations and measurements were subjected to several cycles of centrifugation and repeated

Table 1
Chemical and mineral compositions of reference cement.

Cement	SiO_2(%)	Al_2O_3(%)	Fe_2O_3(%)	CaO(%)	MgO(%)	SO_3(%)	Na_2O(%)
Reference cement	22.93	4.29	2.89	66.23	1.92	0.35	0.70
Cement	Loss(%)	f-CaO(%)	C_3S(%)	C_2S(%)	C_3A(%)	C_4AF(%)	
Reference cement	1.48	0.64	58.78	21.38	6.49	8.77	

Table 2
Chemical compositions of powders.

Powder	CaO(%)	SiO_2(%)	Al_2O_3(%)	MgO(%)	Fe_2O_3(%)	SO_3(%)	R_2O(%)
Fly ash	2.42	40.4	48.5	0.64	3.55	0.41	1.44
Mineral powder	40.8	32.6	13.0	9.30	0.56	2.48	0.59
Montmorillonite	1.50	71.0	12.0	2.30	0.95	0.03	1.16
Kaolinite	0.10	49.0	35.0	0.20	0.28	0.05	2.4
Muscovite	0.43	44.5	33.22	0.63	4.24		10.47
Feldspar	0.25	65.5	18.0	0.1	0.12		14.5