Effect of sodium gluconate on dispersion of polycarboxylate superplasticizer with different grafting density in side chain

Fubing Zou[a], Hongbo Tan[a,*], Yulin Guo[a], Baoguo Ma[a], Xingyang He[b], Yang Zhou[a,c]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China
[b] School of Civil Engineering, Architecture and Environment, Hubei University of Technology, Wuhan 430070, PR China
[c] College of Water and Architectural Engineering, Shihezi University, Shihezi 832000, PR China

ABSTRACT

Sodium gluconate is a commonly used retarder, and the incorporation of SG has been accepted as the most efficient way to improve the basic performance of polycarboxylate superplasticizer (PCE) system in real concrete. However, this improvement cannot be always achieved, and the main reason for this uncertainty is because the interaction between PCE and SG has not completely understood. In order to gain deeper insight into this interaction, adsorption behavior and dispersion mechanism of PCE-SG system involved in two kinds of PCE with different grafting density of carboxyl groups in side chain have been investigated. Specifically, the dispersion was assessed with the fluidity of the cement paste, and adsorption behavior was estimated with total organic carbon and zeta potential. The combination between PCE and SG was characterized with conductivity, dynamic light scattering, and X-ray photoelectron spectroscopy. Finally, several models were proposed to illustrate the mechanism behind. The results show that gluconate grafted as side chain of PCE and the increase in length of PEO chain caused by addition of SG can provide contribution to dispersion. Competitive adsorption between SG and PCE would take place to reduce the dispersion, and the declining degree depends on the relative adsorption between PCE and SG. Dispersion of PCE-SG is not only dependent on added dosage of SG, but also decided by molecular structure of PCE. This result provides guidance on how to promote the basic performance of the PCE-retarder system in real engineering practice.

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Introduction

Superplasticizer is increasingly attracting the attention in research area and industrial area, mainly because it is one of the independent components to ensure that high fluidity of the cement-based materials, especially in case of low cement/water ratio, can be achieved [1,2]. In research area, most of previous studies, as reported, have focused on relationship between molecular structure and basic performance, and these discussions are involved in dispersion mechanism, adsorption behavior, and effect of polymer on cement hydration [3–6]. The main goal of these studies is to obtain the polymers with the high dispersion efficiency, which means that higher fluidity of the cement paste can be achieved with less dosage of polymers. However, it is generally believed in industrial area that high dispersion efficiency

of superplasticizer system can be gained with the addition of retarders, which means that the incorporation of retarder can significantly enhance the dispersion ability of the superplasticizer system [7–9]. It has been reported that tripolyphosphate, hydroxyl-carboxylate salt, and carbohydrates can obviously contribute to the initial dispersion or dispersion retention of superplasticizer system, mainly because these retarders can reduce the consumption amount of free water and superplasticizer by delaying the cement hydration [8,10,11]. However, more important thing is often ignored: retarder can also perturb the adsorption process of superplasticizer, known as the competitive adsorption, which would affect the dispersion ability as well [12–15]. These results would help us to understand the interaction between superplasticizer and retarders.

Currently, polycarboxylate superplasticizer (PCE), known as a comb type polymer, is one of the most popular superplasticizers [16–18], and sodium gluconate (SG) is one of the most popular retarders in cement-based materials [19]. Generally, these two kinds of chemical additives are employed together to efficiently

* Corresponding author.
E-mail address: thbwhut@whut.edu.cn (H. Tan).

disperse the cement particles, thereby achieving the high fluidity of the cement-based materials. That is to say, the presence of SG can significantly improve the dispersion ability of the super-plasticizer system. However, our recent studies show that the dispersion ability of PCE-SG is decided by the added dosage of SG: only the dosage of SG less than 0.10% can enhance the dispersion; while when the dosage more than 0.10%, a negative effect on dispersion can be found [20]. The enhancement is mainly because of the plasticizing effect of SG and the combination of SG with carboxyl groups, and the negative effect is attributed to the competitive adsorption between these two additives. This combination results in the SG grafted as long side chain of PCE to provide steric hindrance; probably, the long side chain (i.e. polyethylene oxide, PEO) of PCE may exert negative effect on this combination, because PEO, with much bigger conformation size than carboxyl group in solution, may hinder the SG molecules from approaching to the carboxyl groups in PCE.

Furthermore, the relative adsorption ability is one of the key factors determining the competitive adsorption ability. If the adsorption ability of PCE were much weaker than SG, the adsorption of PCE would be significantly hindered; and in that case, a very small dosage of SG would reduce the dispersion ability of PCE system. Nevertheless, as reported in study about adsorption behavior of PCE, adsorption ability depends on the grafting density of carboxyl groups in side chain, and more grafting density results in stronger adsorption ability [21,22]. According to this theory, in the presence of SG, the different adsorption behaviors may be observed among those PCEs with the different grafting density of carboxyl groups in side chain. Based on discussion above, with different molecular structure of PCE, effect of SG on dispersion of PCE system would be expected to be considerably different [2,4,23].

In this study, two kinds of PCE, with the main difference in grafting density in side chain, were synthesized with isopentenol polyoxyethylene ether (IPEG) and acrylic acid (AA); and the different mole ratio of PCE2 is 1:2, and 1:6 for PCE6. To obtain deeper insight into the effect of grafting density of PCE on dispersion of PCE-SG system, the interaction between PCE and SG was investigated. Specifically, the dispersion ability was assessed with the fluidity, and adsorption behavior was analyzed with total organic carbon and zeta potential. The combination between PCE and SG in pore solution was verified with conductivity, X-ray photoelectron spectrometer and dynamic light scattering. The dispersion model was then proposed to illustrate the mechanism behind. Such results were expected to provide guidance on the design of high efficient superplasticizer-retarder system in real engineering practice.

Experimental

Materials

Cement

A Portland cement (42.5, Wuhan Yadong Cement Co., Ltd, Wuhan, China) in accordance with the requirements of Chinese standard GB175-2007 was used. The content of $CaSO_4$ in the cement is 4.0 wt%. The density is 3.12 g/cm^3, and the specific surface area is 350 m^2/kg. The chemical composition was obtained with X-ray Fluorescence (XRF, Axios advanced, made by PAN-alytical B.V., Holland), and the results are shown in Table 1.

Additives

PCE was synthesized with isopentenol polyoxyethylene ether (IPEG, commercial product, its purity is more than 99.0%; the degree of polymerization is about 48–52) and acrylic acid (AA,

Table 1
Chemical composition of cement.

	Loss	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	CaO	MgO	K$_2$O	Na$_2$O
Cement wt%	3.82	24.08	4.72	2.46	2.31	58.24	1.95	1.02	0.27

reagent grade, made by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The synthesis process can be described as follows:

IPEG and water were added to a 500 mL four-neck round-bottom flask with a stirrer, and the temperature was slowly raised to approximately 50 °C. And then, hydrogen peroxide (for PCE6: 1.0 wt% of IPEG; for PCE6, 0.25 wt% of IPGE) was added into the flask, and the temperature was kept constant. AA solution was added slowly and evenly, and at the same time, the initiator (i.e. vitamin C; 2.0 wt% of AA) and chain transfer agent solution (i.e. mercaptoethanol; for PCE6, 4 wt% of AA; for PCE2, 2 wt% of AA) were also added with the same speed as AA. These solutions were added out within 3 h. After they were finished, the temperature was kept constant for 1 h. Finally, NaOH (reagent grade, made by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used to balance the pH (pH = 7.0) to neutralize the solution, with a solid content of 40 wt%. The main difference in these two kinds of PCE is the mole ratio of carboxyl groups and PEO in side chain: that for PCE2 is 2:1, and 6:1 for PCE6, as shown in Fig. 1. And the basic performance of these two kinds of PCE is shown in Table 2.

An industrial-grade sodium gluconate (SG, white powder, ≥98.0% purity) were used; and a reagent-grade calcium hydroxide (CH), calcium gluconate (CG), and polyethylene glycol (PEG, the degree of polymerization is 22–24; made by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were adopted in this study. Additionally, the added dosage of these additives was recorded as the solid amount.

Test methods

Fluidity of cement paste

PCE2-SG solutions (PCE2: 0.13 wt%; SG: 0–0.50 wt%) and PCE6-SG solutions (PCE6: 0.07 wt%; SG: 0–0.50 wt%) were prepared in advance. The cement paste was prepared with a water/cement weight ratio of 0.29:1 (water: 87 g; cement 300 g), in accordance with the requirements of Chinese standard GB 8076-2008. A flow cone (height 60 mm, top diameter 36 mm and bottom diameter 60 mm) specified in Chinese standard GB/T 8077-2012 was filled with a sample on a glass plate. After the cone was slowly removed from the sample, the maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured. The average of these two values was defined as the fluidity value.

Competitive adsorption between SG and PCE

The carbon content of PCE or SG solution (0.20 g/L, 0.60 g/L, 1.0 g/L, 1.6 g/L, 2.0 g/L) was measured with total organic carbon analyzer (TOC, Liquid TOC II, made by Elementar, Germany). The results are shown in Fig. 2. Based on these results, the concentration of SG or PCE can be obtained with TOC results.

PCE (PCE2 or PCE6, 0.2–2.0 g/L) and SG (0.2–2.0 g/L) solutions were prepared, respectively. Cement (1.0 g) was mixed with these solutions (20.0 g) respectively, and then stirred for 5 min. After that, the mixture was separated by centrifugation at 3000 r/min. The carbon content in upper supernatant was measured by TOC. Based on the results shown in Fig. 2, the residual concentration of PCE or SG in upper supernatant was obtained. The adsorption amount of PCE or SG (mg/g–cement) was calculated as follows:

Adsorption amount = $V (C_0 - C)/m$