Effect of sodium tripolyphosphate on adsorbing behavior of polycarboxylate superplasticizer

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HIGHLIGHTS

- The multiple-adsorption layer is responsible for the excellent retarding performance of STPP.
- Preferential adsorption of STPP in PC-STPP system was confirmed.
- The multiple-adsorption layer contains several layers of STPP inside and a PC layer outside.

ARTICLE INFO

ABSTRACT

Sodium tripolyphosphate (STPP) is usually employed as an auxiliary material in superplasticizer system, because the presence of STPP in superplasticizer system can significantly improve the workability of the fresh concrete. Generally, the retarding effect of STPP on cement hydration can obviously delay the formation of hydration products and cut down the consumption amount of free water and superplasticizer at the very beginning, which is accepted as the main reason for the enhanced dispersing ability of the superplasticizer system. However, the adsorbing behavior, not only including the adsorption amount but also the thickness of adsorption layer, is of great importance to the performance of polycarboxylate superplasticizer (PC). The aim of the paper is to explain why the presence of STPP can obviously enhance the initial dispersing ability of PC system from the point of view of adsorbing behavior. Specifically, adsorption amount of PC and STPP in PC-STPP system was tested with the Total Organic Carbon analyzer (TOC) and Inductive Coupled Plasma Emission Spectrometer (ICP); the thickness of adsorption layer was analyzed with X-ray photoelectron spectroscopy (XPS). The adsorption models were then proposed to reveal the relationship between the adsorbing behavior and the dispersing ability. The result shows that in STPP single system, the multiple-adsorption layer formed by STPP and Ca^{2+} are inferred to be the main reason for the excellent retarding effect. In PC-STPP system, adsorbing ability of STPP is considerably stronger than that of PC, which results in the preferential adsorption of STPP; the multiple-adsorption layer containing several layers of STPP inside and a PC layer outside is inferred responsible for the thicker adsorption layer than that of the single system PC. The results also suggest that the dispersing ability of the multicomponent superplasticizer system with the retarder is closely related to the thickness of adsorption layer rather than the superficial adsorption amount.

1. Introduction

Superplasticizer has been widely employed in high performance concrete and is considered as an indispensable component of cement-based materials [1–3], not only because of the improvement in fluidity of fresh cement paste and concrete [4–6] but also the decreased porosity of the hardened concrete by using less water to reach the high workability [7]. Polycarboxylate superplasticizer (PC), consisting of a main chain and many side chains including the short side chains (carboxyl group and sulfonic acid group) and the long side chains of neutral polyether groups (polyethylene oxide, PEO) [8–10], is accepted as the main direction of the development of superplasticizer. The steric hindrance provided by the long side chain of PEO is mainly responsible for the excellent dispersing ability, and adsorbing onto the surface of the cement particle is the prerequisite condition for the dispersion [11–14].

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Generally, the dispersing ability of PC is dependent on the adsorbing behavior, and more adsorption amount of PC results in a stronger dispersing ability [15–17].

The multicomponent superplasticizer system consisting of copolymer and retarder is commonly employed as the main commercial product, and the practical experience shows that the presence of the retarder can significantly improve the dispersing ability of the PC system; those salts, such as sodium citrate, sodium tartrate, sodium tripolyphosphate (STPP) and so on, are usually used as the auxiliary material in PC system to improve the workability of fresh concrete; generally, the main reason is that the retarding effect on cement hydration can obviously cut down the consumption of superplasticizer and free water as well as delay the formation of the hydration products at the very beginning. In the first few minutes, however, the adsorbing behavior of PC is mainly responsible for the initial dispersing ability, which has been confirmed by other researchers [11,13,18]. In PC-STPP system, the adsorbing process of PC is obviously impeded because of the competitive adsorption between PC and STPP [19–21], and the decreased adsorption amount of PC should weaken the initial dispersing ability of the system [20,22], which is contradictory with the practical experience. It is inferred that the reason for this contradictory result is that the dispersing ability of PC is not only dependent on the superficial adsorption amount but also the adsorption layer; and the adsorption layer [23], which is often ignored, is probably more important to the performance of PC system.

To find the truth, the competitive adsorbing behavior between STPP and PC in the multicomponent superplasticizer system, not only including the superficial adsorption amount but also the component and thickness of adsorption layer was discussed. Specifically, the superficial adsorption amount of PC and STPP was test with Total Organic Carbon analyzer (TOC) and Inductive Coupled Plasma Emission Spectrometer (ICP) respectively, and the adsorption ratio was inferred from the results of the adsorption amount. The thickness of adsorption layer was analyzed with X-ray photoelectron spectroscopy (XPS). The adsorption models were then proposed to reveal the relationship between the adsorbing behavior and dispersing ability. Finally, it is expected to explain why the presence of STPP can significantly improve the dispersing ability of the superplasticizer system.

2. Experimental methods

2.1. Materials

2.1.1. Cement

An ordinary Portland cement (42.5, Wuhan Yadong Cement Co., Ltd., China) in accordance with the requirements of Chinese GB 8076 standard was used. The cement chemical composition was shown in Table 1. The content of $CaSO_4$ in the cement is 4.2%. The density is 3.10 g/cm^3, and the specific surface area is 350 m^2/kg.

2.1.2. Sodium tripolyphosphate

$Na_5P_3O_{10}$ (made by Sinopharm Chemical reagent Co., Ltd., China): impurity content is shown in Table 2, and the molecular structure is shown in Fig. 1.

2.1.3. Polycarboxylate superplasticizer

The molecular structure of PC is shown in Fig. 2. The molecular weight (Mw, Mn) and poly-dispersity index (PDI) were determined with Gel Permeation Chromatography (GPC, Agilent 1260-RID, made in USA). The eluent is 0.1 mol/L $NaNO_3$; current speed is 1.0 mL/min. The concentration of sample is 0.5 wt%. The results have been shown in Table 3.

2.2. Measurements

2.2.1. Adsorption amount and adsorption ratio

PC solution (20 g, 0.20 g/L) with different dosages of STPP (0.00~0.20%, 0.000~0.002 g) was prepared in advance, respectively. Cement (1.0 g) were then mixed with the solution by magnetic stirrer. After stirred for 5 min, the mixture was separated by centrifugation at 3000 r/min for 4 min. And then, the upper solution was prepared for the measurement. The solid of mixture was dried in a vacuum drier at 25 °C, which was prepared for XPS measurement.

Total Organic Carbon Analyzer (TOC, Multi N/C 2100, made in Jena, Germany) and Inductive Coupled Plasma Emission Spectrometer (ICP, Optima 4300 DV, made by Perkin Elmer Ltd., USA) were used to test the concentration of organic carbon and phosphor in upper solution, respectively. Measurements were generally repeated three times and the average was the result. The residual concentration of PC or STPP was inferred from the results of TOC or ICP, and the adsorption amount and adsorption ratio of PC or STPP were calculated from the residual concentration as follow:

$$\text{Adsorption amount of PC or STPP (mg/g-cement)} = V(C_0 - C)/m$$

$$\text{Adsorption ratio of PC or STPP} = (C_0 - C)/C_0$$

where C_0 is the initial concentration (g/L) of PC or STPP before adsorbing; C is the residual concentration (g/L) after adsorbing; V is volume of the solution (mL); m is the mass of the cement (g).

2.2.2. X-ray photoelectron spectroscopy

The dried solid powder was prepared for XPS (X-ray photoelectron spectroscopy, VG Multilab 2000X) measurements, and the silicon, oxygen, phosphor and calcium were tested. Aluminum was used as an anode target (hv = 1486.6 eV); energy resolution was 0.05 eV; XPSPEAK 4.1 was used to process the data of XPS.

3. Results and discussion

3.1. Competitive adsorption

Fig. 3 shows adsorption amount of PC (0.2 g/L) with varied dosages of STPP. From the figure, it can be seen that adsorption amount of PC is reduced obviously with the increasing dosage of STPP. Without STPP, adsorption amount of PC is 0.72 mg/g; with the addition of STPP (0.2%), it is 0.52 mg/g, which is reduced by

Table 2
Chemical composition of STPP.

	Insoluble	Pb	Cl	As	SO_4^{2-}	Fe
wt/%	0.03%	0.01%	0.01%	0.002%	0.1%	0.03%

Table 1
Chemical composition of cement.

	Loss	SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	K_2O	Na_2O
wt/%	3.82	24.08	4.72	2.46	2.31	58.24	1.95	1.02	0.27