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# A polycarboxylate as a superplasticizer for montmorillonite clay in cement: Adsorption and tolerance studies

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**Abstract** A novel polycarboxylate superplasticizer (PCE) with a long polyoxyethylene (PEO) chain and a terminal carboxylic group was synthesized from a modified polyether (SAE-IPEG) to increase its performance in cement. The molecular structure of the PCE was characterized by infrared spectroscopy and <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy. The performance of synthesized PCE in cement was studied in the absence and the presence of montmorillonite (Mmt) clay. It was found that the PCE disperses in cement uniformly without aggregation, which is different significantly from the conventional PCEs. Adsorption measurements and X-ray diffraction analysis revealed that the synthesized PCE only interacted with Mmt *via* surface adsorption, whereas the conventional PCEs interact with the clay through the surface adsorption and the chemical intercalation. Such dramatic change could be ascribed to the introduction of an electronegative carboxylic acid group as a terminal group into the long polyoxyethylene chain of PCE, which reduced the adsorption and enhanced tolerance of PCE on Mmt.

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## 1. Introduction

As a new generation of high-performance water-reducer in cement, polycarboxylate superplasticizer (PCE) has attracted considerable interests in academia and industry, compared with naphthalene sulfonate-formaldehyde superplasticizer (NFS) (Yoshioka et al., 1997; Halim et al., 2017). The NFS is a linear polymer, while PCE is a comb-type polymer, which is usually prepared by grafting long side chain with a polyoxyethylene (PEO) group (Yamada et al., 2000; Rahman et al., 2017). The side chain on the PCE provides an effective

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barrier to the aggregation of cement particles that are suspended in water (Winnefeld et al., 2007; De'nan et al., 2017). Therefore, excellent dispersion performance of PCE was observed. Considering the environmental friendliness, high water reducing rate, long slump retention rate, and easy structural modification, PCE has gradually become an alternative to NFS as a concrete water-reducer (Habbaba et al., 2013; Alonso et al., 2007; Singh et al., 2012; Liu et al., 2012; Kong et al., 2016; Dalas et al., 2015).

Polycarboxylate superplasticizer also exhibited some limitations. A major concern is its poor tolerance to clay minerals in cement (Hassan and Ismail, 2017). The PCE cannot effectively prevent the clay minerals in concrete from forming aggregates (Ismail and Hanafiah, 2017). This is nontrivial as it will lead to a dramatic decrease of dispersion of clay minerals in concrete and its stability. For practical application, it is desirable for clay to disperse in concrete uniformly without forming aggregates in a certain period of time (Atarashi et al., 2004; Aziz and Hanafiah, 2017; Khan et al., 2017). The main clay minerals in concrete include montmorillonite (Mmt), illite and kaolin. The Mmt has a stratified structure consisting of silica tetrahedron and alumina octahedral in a 2:1 ratio (Norvell et al., 2007; Aslam et al., 2017). The adsorption of PCE on Mmt is approximately 100 times larger than that of Portland cement (Ng and Plank, 2012; Razali et al., 2017a). Strong affinity of PCE through side chain to Mmt enables an effective insertion of PCE into the interlayer of Mmt, thus inhibiting the performance of PCE in fresh concrete (Lei and Plank, 2014a,b; Razali et al., 2017b; Nordin et al., 2017). Some researcher reported that intercalation adsorption is the dominant mechanism for Mmt-PCE adsorption (Ng and Plank, 2012; Lei and Plank, 2014a,b). When the concrete aggregate contains clay minerals, the aggregates often cause the rapid loss of the fluidity of the concrete, therefore, the increased amount of PCE used to meet the requirements of concrete. Such a phenomenon is often referred to as poor clay tolerance of PCE (Roslan et al., 2017). Under such circumstance, the tolerance of PCE to clay minerals in cement needs to be improved to increase the fluidity of the cement.

A variety of functionalized PCEs have been reported and their performance in concrete was also studied. In other studies, a group researcher stated that synthesized two PCEs without a PEO long side chain (Lei and Plank, 2012; Lei and Plank, 2014a,b). The first type of PCE was synthesized using methacrylic acid and hydroxyalkyl methacrylate, while the other type of PCE was synthesized using maleic anhydride, maleic monoalkyl ester, 4-hydroxy-butyl-ethylene ether as materials. The dispersion capacity of two PCEs is less affected when Mmt content is 1%. XRD test shows that PCEs did not intercalate into Mmt, and only a small amount of PCEs are observed. The absence of a chain prevents the PCE from intercalating into Mmt. Other researchers also conducted numerous studies on novel PCE without PEO long side chain. Other researcher prepared amphiphilic polycarboxylic acid copolymer (APCs) using 3-(2-(methacryloyloxy) ethyl) (ZI) and dimethylammonio-propane-1-sulfonate (DMAPS) as amphiphilic monomers and found that that the APCs with the ZI group was more likely to be adsorbed on clay surface, but not penetrate into clay layer structure (Li et al., 2016). A scientist also prepared a PCE from a reaction of 2-(dimethylamino)ethylmethacrylate (DMAM), acrylic acid and itaconic

acid (Xing et al., 2016). They found the synthesized PCE had sound dispersion capacity in the presence of clay due to the weak adsorption of PCE into the inner layer of clay, however, some PCEs still adsorbed on the clay surface. Since intercalation adsorption can be avoided by removing the PEO long side chain in PCE, grafted  $\beta$ -cyclodextrin as an anti-clay group into PCE molecular structure under the condition of maintaining a PEO long side chain (Xu et al., 2015, 2016). An improved tolerance to clay was observed, which was ascribed to the reduced adsorption of PCE on the Mmt due to the bulky structure of  $\beta$ -cyclodextrin. These studies indicated that the performance of PCEs can be tuned by structural modification.

Recent studies showed that surface of the Mmt is electrically charged. Some researcher found that under the alkaline condition the surface and edge of a laminated structure of Mmt particle were negatively charged (Tombacz and Szekeres, 2004). During the course of a study between clay and a polymer, a researcher also found that the negatively charged polymers did not intercalate into the inter layers of clay (Theng, 1982). When Mmt interacts with surfactant, Sanchez-Martin found that the quantity of adsorbed non-ionic surfactant and cationic surfactant on Mmt was much larger than that of anionic surfactant (Martin et al., 2008). These studies indicated clearly that performance of PCEs could be tuned by charge plasticizers. To this end, we prepared a new type of PCE. We used succinic anhydride to esterify and modify the long-chain terminal group of isobutenyl polyoxyethylene ether (IPEG), making the long-chain terminal group negatively charged. Our results revealed that the prepared PCEs exhibited much better tolerance, low adsorption properties, and the resulting concrete is quite uniform.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Chemicals

Isobutenyl polyoxyethylene ether (IPEG,  $\geq 99\%$  purity, Wuhan Oxiranchem Co., Ltd., China, the degree of polymerization is about 48–52), succinic anhydride (SAE), acrylic acid (AA), mercaptopropionic acid, Vitamin C (both  $\geq 99\%$  purity, Aladdin Industrial Corporation, China), hydrogen peroxide (30% aqueous solution, Aladdin Industrial Corporation, China), and polyacrylic acid (PAA, Mw,  $\sim 2000$ , Aladdin Industrial Corporation, China) were used without further purification. All chemicals were used as received without further purification.

#### 2.1.2. Cement

The cement used in this study was an ordinary Portland cement (PO 42.5R, supplied by China United Cement Group Co., Ltd), and the chemical compositions are shown in Table 1. The average particle size ( $d_{50}$  value, determined by laser granulometry) was found at 11.6  $\mu\text{m}$ . Its density was 3.20  $\text{g}/\text{cm}^3$  (powdered Lee pycnometer method).

#### 2.1.3. Clay

The clay sample used in this study was a sodium Mmt supplied under the trade name of PGW by Nanocor (Chicago, America). This clay mineral is a naturally occurring sodium

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