**β-Cyclodextrin-based Zwitterionic Polymers as Clay-Tolerance Sacrificial Agents of Polycarboxylate Superplasticizers**

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**ABSTRACT**

β-Cyclodextrin (β-CD)-based zwitterionic polymer (β-CD-PDMAPS) was synthesized via activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP). As a clay-tolerance sacrificial agent, β-CD-PDMAPS combined with common polycarboxylate superplasticizer (CPC) can result in modified polycarboxylate superplasticizer (MPC). The dispersion and the dispersive retention of MPC in a cement system in the absence and presence of clay were investigated. The results indicated that MPC possesses excellent dispersing ability and can effectively inhibit the preferential adsorption of CPC onto the surface of clay. Compared to CPC, MPC displayed enhanced robustness toward clay. This can be attributed to the easy adsorption of the β-CD-PDMAPS onto clay and the steric hindrance derived from β-CD, which can inhibit CPC from incorporating into the lattice structure of the clay. This work provides new insight into the development of polycarboxylate superplasticizers with enhanced clay tolerance.1

**INTRODUCTION**

Polycarboxylate superplasticizer (PC) has been recognized as one of the most important concrete admixtures with outstanding advantages such as high water-reducing rate, long slump retention, tunable molecular structure, and enviromental friendliness [1]. Generally, the PC molecule is composed of the polycarboxylate main chain and poly(ethylene oxide) (PEO) side chains [2]. With rapid development

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of construction industry, the supply of high-quality gravel has been almost exhausted with increasing high-clay-content sand instead [3]. The efficiency of PC is limited by the clay minerals such as kaolinite, illite, and montmorillonite, which exhibit high affinity for PC [4]. The PEO side chains can easily insert into their interlayer structure, resulting in serious destruction in the dispersibility of the cement particles [5]. The compatibility between PC and clay still faces challenge. To avoid the negative effect of clay on the performance of PC, some strategies have been attempted, such as increasing the dosage of PC and optimizing of the PC molecular structure [6]. In contrast, the use of sacrificial agent can be considered as the effective and convenient approach to enhance clay tolerance [7]. Our group synthesized a clay inhibitor of β-CD-based poly(methyl acryloyloxyethyl trimethylammonium chloride) (DMC) exhibiting fine anti-clay effect and certain retarded properties when mixed with CPC [8]. Considering the corrosion of chloride ion to metal in concrete, alternative products are still highly desirable.

β-CD-based zwitterionic poly[3-[2-(methacryloyloxy)ethyl]dimethylammonio-propane-1-sulfonate] (β-CD-PDMAPS) was prepared via activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) in this work. β-CD-PDMAPS as a novel clay-tolerance sacrificial agent mixed with the CPC, resulting in a new-type MPC. The dispersion and the dispersive retention of the MPC in a cement system in the absence and presence of clay were investigated.

Experimental

Materials. β-Cyclodextrin (β-CD), 2-bromoisobutyryl bromide (BIBB), CuBr, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), acrylic acid (AA), 3-mercapto propionic acid (3-MPA), and vitamin C (Vc) were purchased from Aladdin Agent Co., Ltd in China. 3-[2-(methacryloyloxy)ethyl]dimethylammonio-propane-1-sulfonate (DMAPS) and isopentenol polyoxyvinyl ether (TPEG2400) were supplied by Yipintang and Jiangtai Co., Ltd in China, respectively.

Synthesis of β-CD-PDMAPS and CPC. A certain of β-CD was mixed with THF and triethylamine in a flask with magnetic stirring. 2-Bromoisobutyryl bromide was added dropwise to the β-CD solution over 2 h under a nitrogen atmosphere. After that, the reaction mixture was stirred at room temperature for 24 h. The final reaction mixture was precipitated in deionized water. The precipitate was collected by centrifugation and dried in a vacuum oven at 60 °C overnight. The macroinitiator β-CD-Br, DMAPS, Vc, and H2O were added to a flask, then CuBr/PMDETA was transferred. The polymerization was allowed to proceed under continuous stirring at room temperature for 10 h, resulting in a colorless transparent viscous liquid. Following the Ref. [8], the CPC product was obtained.

Cement paste test. The fluidity of cement paste was measured by the mini-slump test according to “Methods for Testing the Uniformity of Concrete Admixture” (GB/T 8077-2012). The water/cement (w/c) ratio (0.29), the dosage of CPC (0.13 wt% of cement mass), and the clay inhibitor (5, 10, 15, 20 wt% of CPC mass) were
RESULTS AND DISCUSSION

The steric effect of β-CD was strong enough to hinder the adsorption of PC on the sodium bentonite and has certain retarded properties. In this work, ARGET ATRP was used to polymerize DMAPS by β-CD-based macroinitiator, and a clay inhibitor β-CD-PDMAPS was obtained (Figure 1). The clay inhibitor can be mixed with CPC by a certain proportion. A modified cement paste fluidity test was designed by substituting different proportion of cement with sodium bentonite to evaluate the clay tolerance of the clay inhibitor.

Dispersion performance analysis. The effect of the β-CD-based clay inhibitor on the dispersion capacity of CPC was first tested in pure cement paste. The w/c ratio was determined to be 0.29, the dosage of CPC used in the paste was 0.13 wt% (to the cement weight). The effect of 5, 10, 15, 20 wt% (to the CPC weight) clay inhibitor on the dispersion capacity of CPC was studied. By comparing the fluidity of pure cement paste with CPC, the effect of the clay inhibitor on the dispersion capacity of CPC was analyzed. It can be seen that the initial fluidity of MPC is slightly higher than that of CPC (Figure 2A), indicating that the clay inhibitor had positive effect on the dispersion capacity of CPC.

Performance of clay tolerance. To evaluate the clay tolerance of the clay inhibitor based on β-CD, a certain of cement were substituted by an equal mass of sodium bentonite to prepare bentonite-containing paste. The fluidity of cement paste was tested by 1 wt% bentonite, and the clay resistance of as-prepared clay inhibitor based on β-CD was studied. As shown in Figure 2B, when 1 wt % sodium bentonite was added, the initial fluidity of the composite clay inhibitor was higher than that of CPC, while the fluidity of cement paste at 60 min was obviously higher than that of CPC, and the phenomenon of post release was also observed. The results show that the clay inhibitor has excellent anti-clay and retarding effect. The clay inhibitor is zwitterionic polymer, and the positively charged ammonium can be preferentially adsorbed on the clay surface. The macromolecular structure of β-CD can be acted as steric hindrance, and also hinder the adsorption of CPC when clay inhibitor is adsorbed onto bentonite, achieving the anti-clay effect. The increase of the clay inhibitor has not a significant impact on the dispersion capacity of bentonite-containing paste.
ARGET ATRP technique was employed to synthesize β-CD-PDMAPS as a clay inhibitor. The obtained MPC possesses excellent dispersing ability and can effectively inhibit the preferential adsorption of CPC onto the surface of clay. This can be attributed to the easy adsorption of the PDMAPS onto clay and the steric hindrance derived from β-CD, which can inhibit the CPC from incorporating into the lattice structure of the clay.

CONCLUSIONS

REFERENCES