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Synthesis, characterization and working mechanism of a novel polycarboxylate superplasticizer for concrete possessing reduced viscosity

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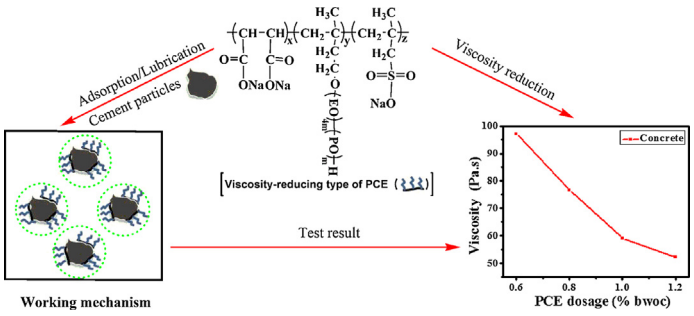
HIGHLIGHTS

- Synthesizes viscosity-reducing type of PCE based on innovative molecular design.
- Reduces viscosity and ensures superior workability and rheological performances.
- Calculates plastic viscosity via mesomechanics process model showing good correlation.
- Proposes working mechanism in viewpoints of lubrication and release of free water.
- Provides advanced viscosity-reducing applications in high-grade fresh concrete.

GRAPHICAL ABSTRACT



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ABSTRACT

To solve the problem of high viscosity for fresh concrete especially high-grade concrete, a novel viscosity-reducing type of polycarboxylate superplasticizer (PCE) was synthesized based on innovative design of molecular structure, and also was characterized to confirm the designed molecular structure. The rheological performances of cement paste and fresh concrete containing synthesized PCE were probed, which were analyzed by means of surface tension, adsorption behavior and zeta potential. The plastic viscosity showed a good correlation with T50 and V-funnel time according to mesomechanics process model. Moreover, the investigation of working mechanism interestingly showed that lowering molecular weight and side chain length and introducing hydrophobic groups can achieve improved dispersion capacity and viscosity-reduction effectiveness. The aim of this study is to provide a promising avenue to synthesize PCE with superior workability and viscosity-reducing performance in fresh concrete. This new type of PCE can be used as a viscosity-reducing agent in concrete engineering.

1. Introduction

In recent years, with the rapid development of the construction industry, modern buildings show the trends of high-rise, light weight and large span. Therefore, the high-grade concrete is

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gradually applied in some infrastructures due to its advantages of high strength, high integrity and light weight [1–3]. However, to reach high strength or ultra-high strength, the concrete should be made by using a large quantity of cementitious materials and employing low water-binder ratio, leading to high viscosity and poor flowability for fresh concrete. This problem causes great difficulties in practical construction especially in pumping construction for ultra-high concrete, resulting in the frequent occurrence of engineering accidents [4–8].

Polycarboxylate superplasticizer (PCE), an important type of concrete admixture, has been widely applied in various engineering projects, which greatly promotes the concrete technology and the building construction modernization. Consequently, there are greater demands on the performances of concrete by the developments of building structures towards large scale and high functionality. As one important component of concrete, PCE shows strong designability in molecular structure, and thus the high-performance PCE can be obtained via adjusting and optimizing the backbone length, side chain length and functional groups [9–12]. Consequently, the researchers focus on the architecture design of PCE macromolecule to specially solve some problems occurred in concrete science and engineering.

At present, there are two main techniques employed to reduce the viscosity of high-strength concrete, i.e., increasing the dosage of superplasticizer and optimizing the size distribution of grain. For the first technique, it can bring high construction cost, severe retardation, bleeding and segregation of fresh concrete, leading to some difficulties in building construction [13–16]. For the second technique, there are many studies on this, whereas it cannot thoroughly solve the practical problems [17–20] since good fluidity of fresh concrete is mainly contributed by strong adsorption and dispersive capacity of superplasticizer. Therefore, it has great significance to develop a viscosity-reducing type of superplasticizer.

With the continuous development of concrete technology in this field, researchers generally adopt a combination of conventional PCE and viscosity modifying admixture (VMA) [21–24] which essentially increases viscosity and thus thickens the mix to prevent segregation [25–28]. VMA, as an important component, have proved to be very effective in enhancing the cohesion (such as water retention capacity of paste [29–31]) and rheological stability of self-compacting concrete, underwater concrete [28,30,32–34] and cement grout used for repairs, injection, embedding of anchors and post-tensioning, and rock and oil-well grouting [35,36]. Recently, there has been a growing interest in the effects of VMA content [21,37,38] and type [34,39–41] on the properties of mortars and concretes. However, the negative effect of VMA was proved in many literatures [24,42–44], such as increases yield stress and plastic viscosity of cement-based grout [28,30,32,34]; only using conventional PCE will lead to severe segregation and bleeding though it may reduce the viscosity of concrete to some extent [45,46]. The question is why not design and synthesize a novel PCE having a similar effect in this regard? Why not develop a viscosity-reducing type of PCE from the viewpoints of molecular architecture and surface-interface chemistry to control the viscosity of concrete? There are few studies reported on these. Another significance of this study is giving a guideline in reducing the viscosity of concrete by specialized design and synthesis in molecular structure of PCE, instead of blindly adjusting composition of concrete. Compared with previous work, herein we synthesized a novel type of PCE possessing the function of reducing viscosity of concrete through molecular design, which has more attractive potentials in construction.

In this study, a viscosity-reducing type of PCE was synthesized by using isopentenyl polyethylene polypropylene glycol (IPEPPG), maleic anhydride (MA) and sodium methallyl sulfonate (SMAS) as monomers. To evaluate the effects of the structural parameters, the molecular weights of side chains and whole polymer were varied. The synthetic products were characterized by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR), Infrared Spectroscopy (IR) and Gel Permeation Chromatography (GPC), respectively. The dispersion capacities of PCEs to cement pastes and the rheological properties of fresh concretes containing PCEs with different architectures were probed; besides, the effects of structural parameters on the viscosity-reducing capacity and interfacial adsorption behavior of PCE were investigated through the measurements of surface tension, adsorption amount and zeta potential. Furthermore, the working mechanism of viscosity-reducing type of PCE in the concrete system was summarized, and the relationship between workability and viscosity for fresh concrete was investigated via mesomechanics model. From these data, we hoped to gain an insight into whether the novelly synthesized PCE according to the molecular design would perform more effectively in the reduction of concrete viscosity. This research provides not only a new direction for exploring novel viscosity-reducing type of PCE which can improve the workability and rheological properties of fresh concrete, but also a theoretical guidance for developing the working mechanism of PCE in the field of viscosity-reduction of concrete.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Maleic anhydride (MA), sodium methallyl sulfonate (SMAS), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH) and vitamin C (all ≥99% purity, purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), were used in the study without further purification. Isopentenyl polyethylene polypropylene glycol (IPEPPG, ethylene oxide (EO) unit/propylene oxide (PO) unit = 4:1) with the molecular weights of 800, 1500 and 2900 identified as $IPE_{12}PP_3G$, $IPE_{24}PP_6G$ and IPE_{48}-$PP_{12}G$ respectively, were received from Liaoning Kelong Fine Chemical Co., Ltd (Liaoning, China).

2.1.2. Component materials of concrete

Reference cement P.I.42.5, a type of cement specially used for examining the performances of concrete admixture, which quality was controlled according to the standard method GB 8076-2008 [47] described in the National Standards of China, was supplied by China Building Materials Research Institute (Beijing, China). Its chemical and mineral compositions determined respectively by X-ray Fluorescence (XRF) and X-ray diffraction (XRD) using Rietveld refinement method are illustrated in Table 1. The medium sand with a fineness modulus of 2.7 had a density of 2550 kg/m^3 and a bulk density of 1460 kg/m^3. The gravel with a continuous grading of 5–20 mm (wherein 40% of 5–10 mm and 60% of 10–20 mm; content of elongated and flaky particles ≤5%; voidage ≤40%; clay content ≤0.5%) had a density of 2630 kg/m^3 and a bulk density of 1540 kg/m^3. Tackifier (hydroxypropyl methyl cellulose MHPC500PF) as a role of viscosity modifying agent (VMA) (residue ≤1%) was commercially available from Shanghai Greenchem Trading Co., Ltd (Shanghai, China). Deionized water was used throughout the experiment.

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	22.91	4.29	2.89	66.23	1.93	0.34	0.71
Cement	Loss (%)	f-CaO(%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	
Reference cement	1.48	0.63	58.68	21.48	6.49	8.79	