

## Synthesis, characterization and performance of a polycarboxylate superplasticizer with amide structure



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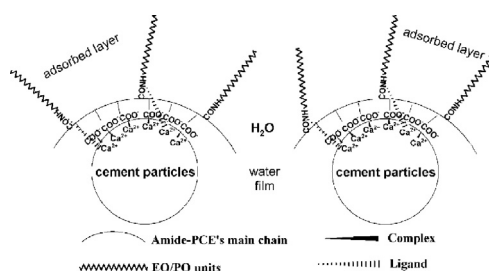
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### HIGHLIGHTS

- Amide-PCE was synthesized successfully and the optimal conditions were determined.
- The structure of amide-PCE and its sufficient amidation reaction were confirmed.
- Amide-PCE has better application performance than the conventional PCE in concrete.
- The dispersion mechanism of amide-PCE in cement–water system was illustrated.
- It can provide electrostatic repulsion, steric hindrance, complex and lubrication.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The amide-structural polycarboxylate superplasticizers (amide-PCEs) were synthesized by amidation reaction between polyacrylic acid (PAA) and amino-terminated methoxy polyethylene glycol (amino-PEG) under different conditions, and the effects of amide-PCE's synthesis on amidation rate and flow performance of cement paste were investigated. Fourier Transform Infrared Spectroscopy (FTIR), <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR), and molecular-weight measurements were used for structural characterization, and the results confirmed ideal amide structure and sufficient amidation reaction. Amide-PCE with the carboxyl–amino ratio of 4:1 exhibited the lowest surface tension, highest adsorption percentage, and the best paste fluidity results. Based on the above results, the dispersion and adsorption mechanisms of amide-PCE in cement–water system were discussed. The application performances in concrete showed that amide-PCE had similar slump to that of conventional PCE, but also had better air-entraining ability, bubble retention and concrete frost-resistance than those of conventional PCE. Depending on this amide structure and good performances, amide-PCE shows broad application prospects.

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## 1. Introduction

Superplasticizers are an important class of chemical admixture that can be added to concrete mixtures to improve workability of

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concrete by dispersing agglomerated hydrating cement particles present in the paste [1] and other applications [2–4]. Strength of concrete is inversely proportional to the amount of water added or water–cement ratio ( $w/c$ ); however, if the amount of water is too low, the concrete mixture can be unworkable and difficult to mix and place. Therefore, the main function of a superplasticizer is to enable a decrease in the  $w/c$  without losing fluidity of the cement pastes, which results in higher strength and better durability of concrete [5,6].

There are three generations of superplasticizers in concrete. The first generation is commonly manufactured from lignosulfonates and the second generation from sulfonated naphthalene formaldehyde or sulfonated melamine formaldehyde. In the 1980s, polycarboxylate superplasticizers (PCEs) were introduced as the third, new generation of concrete admixtures [7] and are still developing. Because of its comb-type structure with poly(ethylene glycol) (PEG) grafted side chains [8] and the associated steric interparticle repulsive forces [9], PCEs are effective at lower dosages, and provides improved slump retention [10,11] than polycondensates. Thus, nowadays PCEs have been introduced into the cement systems replacing admixtures based on melamine and naphthalene [12,13], and have attracted great research attention in recent years [14–16].

Generally speaking, PCEs have a great diversity of chemical structures and can mainly be classified as two categories. The one is polyester-type PCE, made from  $\omega$ -methoxy poly(ethylene glycol) methacrylate ester (MPEG-MA), either by aqueous free radical copolymerization [17] or by esterification/transesterification reaction [18–21]. The other is polyether-type PCE, including  $\alpha$ -allyl- $\omega$ -methoxy or  $\omega$ -hydroxy poly(ethylene glycol) (APEG) ether and maleic anhydride as key monomers via radical copolymerization either in bulk or in aqueous solution [22], isoprenyl oxy poly(ethylene glycol) macromonomers by copolymerization with acrylic acid [23], and  $\alpha$ -methallyl- $\omega$ -methoxy or  $\omega$ -hydroxy poly(ethylene glycol) ether as macromonomer [24]. However, the development of concrete technology needs more structure types of PCE with better performance to meet the requirements in different projects. Only changing material ratio, chain length, initiator concentration, or reaction conditions to achieve some performance improvements [5,17,25–27] is not enough.

Amide/imide type PCE firstly was reported by Jeknavorian in Grace [28,29] who obtained a copolymer formed by an acrylic polymer with ammonia or an alkoxyated amine had higher imidization degree and production cost. Hereafter, Vickers [30] synthesized a PCE with at least one ester linkage and one amide linkage, which had high water reduction and long shelf life. Peev [31] reported a PCE comprising a water-soluble alkanolamines modified acrylic copolymer had both good flowability and high early strength. Schober [32] described an acrylic polymer which comprised side chains connected to the backbone by ester, amide or imide linkages. Danzinger [33] provided a polycarboxylic acid-based cement dispersant containing a polyamide-polyamine in a skeleton of a polymer, which had improved water reducing ability and slump-flow retention but not in application due to its unavailable raw materials. Recently, PCE's increased application promotes the development of concrete technology, which in turn puts forward higher requirements to its performance. Hence, exploring new structural PCE with unique performance of concrete or cement paste cannot be ignored, but there have been few studies on this.

The conventional PCEs produced by radical co-polymerization are growing rapidly, whereas they have many shortcomings. For the different monomers' polymerization activities, it is difficult to control the copolymer's unit arrangement and molecular weight of backbone. A part of copolymers with low molecular weight can widen the molecular weight distribution and further weaken the final performance. To overcome these difficulties, an amide-PEG

was synthesized by grafting reaction to form amide linkages. It derives from the homopolymer with a constant molecular weight and a narrow molecular weight distribution, and normally results in a more statistically uniform distribution of PEGs attached onto the polyacrylic acid backbone. This grafting approach thus is beneficial to obtain a superior PCE-based dispersant which has broad application prospects.

In this study, polycarboxylate superplasticizers with amide structure (amide-PCEs) were synthesized by amidation reaction between polyacrylic acid (PAA) and amino-terminated methoxy polyethylene glycol (amino-PEG), and the optimal synthesis process was determined. Influences of amide-PCEs with different variable synthesis factors upon amidation rate and flow performance of cement paste were described by the investigations of catalyst dosage, water-carrying agent dosage, carboxyl–amino ratio, amidation reaction temperature, and amidation reaction time. In order to confirm its amide structure, amide-PCE was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and  $^1\text{H}$  Nuclear Magnetic Resonance ( $^1\text{H}$  NMR). The molecular characteristics including molecular weight and its distribution were measured by gel permeation chromatography (GPC). Also, the effects of amide structure and grafting density on the properties of amide-PCEs were examined and analyzed by assessing the paste fluidity, surface tension and adsorption of a series of amide-PCEs with different grafting densities. Both amide-PCE and conventional PCE's application performances in concrete including air content, slump and slump flow, and frost-resistance were measured. Additionally, the dispersion and adsorption mechanisms of amide-PCE in cement–water system were discussed.

## 2. Materials and measurements

### 2.1. Materials

Polyacrylic acid (PAA) with solid content of 49% and molecular weight of 5000 was supplied by BASF (China) Co., Ltd (Shanghai, China), and the amino-terminated methoxy polyethylene glycol (amino-PEG) with molecular weight of 2000 was from Clariant Chemicals (China) Ltd. (Shanghai, China). The conventional PCE was liquid with a solid content of 42%. Toluene, sodium hydroxide, concentrated sulfuric acid (98 wt%), and cyclohexane were of analytical grade and purchased from Beijing Chemical Works (Beijing, China). The *p*-toluene sulfonic acid and sulfamic acid were of analytical grade and from Tianjin Guangfu Fine Chemical Research Institute. Reference cement P. I. 42.5 and Liulihe cement P. O. 42.5 were supplied by China United Cement Qufu Co., Ltd (Qufu, China) and Beijing Liulihe Cement Co., Ltd (Beijing, China), respectively. The medium sand with a fineness module of 2.7 had a density of 2550 kg/m<sup>3</sup> and a bulk density of 1460 kg/m<sup>3</sup>, and the gravel with a continuous grading of 5–20 mm had a density of 2630 kg/m<sup>3</sup> and a bulk density of 1540 kg/m<sup>3</sup>. The chemical and mineral compositions of cements are illustrated in Table 1.

### 2.2. Synthesis of amide-PCE

The amino-PEG, PAA, and catalyst were added in sequence to a 500 mL four-neck round-bottom flask with a stirrer, a water separator with a condenser, a thermometer and an intelligent control temperature device by using the one-step process. The temperature was slowly raised to 80 °C by stirring and heating, and then the water-carrying agent was added to the flask to ensure the uttermost amidation reaction by continually removing the produced water from reaction system to water separator. The temperature was raised to 130–150 °C and maintained for several hours. After the reaction, the product was vacuumized to separate

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