Study on Synthesis and Properties of Highly Adaptable Polycarboxylate Superplasticizer

Lina Zhong1,*, Yunhui Fang1, Yuliang Ke1, Xiaofang Zhang1, ShaoHong Zhu1, Yuanqiang Guo1, Xiuxing Ma2

1 KZJ New Materials Group Co., Ltd. Xiamen 361101, China
2 Xiamen Academy of Building Research Group Co., Ltd., Xiamen 361004, China
* Corresponding author (Tel: 86-18959212113; E-mail: 514204325@qq.com)

Abstract. A highly adaptable polycarboxylate superplasticizer (PCE-2) was synthesized by free radical copolymerization in aqueous solution with isoprenol polyoxyethylene ether as macromonomer, acrylic acid and hydroxyethyl acrylate and 2-methacryloyloxyethyl phosphate as unsaturated monomers, mercaptopropionic acid as chain transfer agent, hydrogen peroxide - Bruggolite FF6/ferrous sulfate heptahydrate as redox initiator. The structure of the copolymer was characterized by IR and GPC. The adaptability of the copolymer to concrete was studied from four aspects, such as dosage, water consumption, temperature and clay content. The results show that adaptability of the PCE-2 is better than those of the commercially available Polycarboxylate Superplasticizer (PCE-1).

1. Introduction
Polycarboxylate Superplasticizer (PCE) has become the most widely used admixture in the world due to its high water-reducing rate, environmental friendliness and strong molecular designability [1]. However, with the increasingly fierce competition in the market of polycarboxylate superplasticizers, in order to reduce production costs and improve the competitive advantage of products, the water reduction rate of polycarboxylate superplasticizers on the market is increasing year by year, which leads to the increasingly prominent sensitivity of PCE. Especially in recent years, with the rapid growth of infrastructure construction and real estate development in China, and in the situation of natural sandstone resources are gradually scarce and the state constantly strengthens the situation of mineral resources and environmental protection, machine-made sandstone and sea sand and recycled aggregate and other inferior sandstone have been used in large quantities. The change of these concrete raw materials makes the requirement of PCE more and more stringent. Therefore, it is particularly important to develop highly adaptable polycarboxylate superplasticizer.

4-hydroxyl vinyl butyl polyoxyethylene ether (VPEG) is a new kind of macromonomer developed in recent years. It has been found that the PCE synthesized by VPEG has well dispersibility and dispersion retention, and is less sensitive than PCE synthesized by other macromonomers [3-6]. However, VPEG is a macromonomer obtained by ethoxylation of 4-hydroxybutyl vinyl ether, and its polymerization activity is high. The preparation of PCE by VPEG usually needs to be carried out at low temperature of about 15℃, which is particularly harsh for production equipment. In this paper, A highly adaptable polycarboxylate superplasticizer (PCE-2) was synthesized by free radical copolymerization in aqueous solution with isoprenol polyoxyethylene ether as macromonomer, acrylic acid and hydroxyethyl acrylate and 2-methacryloyloxyethyl phosphate as unsaturated monomers,
mercaptopropionic acid as chain transfer agent, hydrogen peroxide - Bruggolite FF6/ferrous sulfate heptahydrate as redox initiator. The adaptability of polycarboxylate superplasticizer was evaluated by studying the sensitivity of dosage, water consumption, temperature and clay content.

2. Experimental

2.1. Materials

2.1.1. raw materials for synthetic experimental
Isopentenol polyoxyethylene ether (TPEG, Mn=2400), Acrylic acid (AA), Hydroxyethyl acrylate (HEA), 2-Methacryloyloxyethyl phosphate (P-2M), 27.5wt% Hydrogen peroxide (H2O2), Bruggolite FF6 (industrial grade), Ferrous sulfate heptahydrate (Fe2+), Mercaptopropionic acid (3-MPA), 32wt% Alkali liquids (NaOH) were all industrial grade.

2.1.2. raw materials for performance testing
The cement is a type P·O 42.5 Portland cement, The chemical and physical properties of cement are given in Tables 1 and 2. The fly ash is a grade II fly ash, The fineness modulus Mx of river sand is 2.6~2.9, The particle size of G1 is 10-20 mm; The particle size of G2 is 20-40 mm, The clay is the soil sifted out of river sand by 0.08mm sieve, common polycarboxylate superplasticizer (PCE-1) is on sale from KZJ New Materials Group Co., Ltd.

| Parameter                      | Value |
|-------------------------------|-------|
| specific surface area (g/cm³) | 368   |
| Water content for standard consistence (%) | 28    |
| Initial setting time (min)     | 195   |
| Final setting time (min)       | 325   |
| 3d Flexural strength (MPa)     | 5.0   |
| 3d Compressive strength (MPa)  | 25.1  |

2.2. Synthesis of copolymer
The molar ratio of each component is η(AA): η(TPEG2400): η(HEA): η(P-2M): η(H2O2): η(FF6): η(Fe²⁺): η(3-MPA)=1:0.5:0.3:0.1:0.5:0.05:0.002:0.1. The TPEG-2400 polyether macromonomer and deionized water is placed in a 500 ml flask equipped with agitator and peristaltic pump feeding device. After the macromonomer is completely dissolved, 50% mixed aqueous solution A consisting of AA and HEA and P-2M are added at one time, adding appropriate liquid alkali to make the pH value of the solution 5.0-5.5, then adding 50% 3-MPA solution B and H2O2 and Fe²⁺. Continuing stirring for 1 min, adding residual solution A, residual solution B, and FF6 Solution C. Solution A and solution B were dripped for 30 minutes, solution C was dripped for 35 minutes. Keep warm for 1h, then a 30% aqueous solution of sodium hydroxide was added to adjust the pH to 6.0-7.0, thus obtaining a highly adaptable polycarboxylate superplasticizer (PCE-2).

2.3. Characterization

2.3.1. Concrete test
The concrete test is conducted in accordance with GB/T 8076-2008 "Concrete Admixture", GB/T 50080-2002 "Test Method for Performance of Ordinary Concrete Mixture" and GB/T 50081-2002 "Test Method for Mechanical Properties of Ordinary Concrete". The concrete mix ratio (kg/m³) is m₃(cement): m₃(fly ash): m₃(sand): m₃(G1): m₃(G2): m₃(water) = 260:80:790:630:420:170.
2.3.2. **infrared spectrum test**
The synthesized liquid sample was evenly smeared on potassium bromide tablets. After drying and removing water, the infrared spectra were determined by infrared spectroscopy.

2.3.3. **Gel permeation chromatography test**
The molecular weight and molecular weight distribution of PCE-2 were measured by GPC. Waters 1515 Isocratic HPLC pump / waters 2414 differential detector and Breeze software acquisition and analysis system were used in the experiment. The column consists of Ultrahydrage TM 250 and Ultrahydrage TM 500 in series. The mobile phase is 0.1mol/L NaNO₃ solution and the flow rate is 0.8mL/min.

2.3.4. **Sensitivity test**

2.3.4.1. **The dosage sensitivity test**
The experiment was carried out at 23°C±2°C. The PCE-1 and PCE-2 samples were diluted to 10% solid content. The dosage sensitivity of the superplasticizer is characterized by the superplasticizer dosage width y, \( y = \frac{y_1}{y_0} \). The initial dosage point \( y_0 \) was specified when the concrete extensibility reached 400 mm ±10 mm, and the final dosage point \( y_1 \) was specified when the concrete extensibility reached 550 mm ±10 mm. The higher the superplasticizer dosage width y, the less sensitive the admixture is to the dosage.

2.3.4.2. **The water consumption sensitivity test**
The experiment was carried out at 23°C±2°C. \( y_0 \) was used as the reference dosage to test the initial extensibility of concrete, then the water consumption increased by 15 kg/m³ to measure the extensibility of concrete with other conditions unchanged, the smaller the difference value (D-value) between the extensibility of concrete before and after water addition, the less sensitive the admixture is to water consumption.

2.3.4.3. **The temperature sensitivity test**
\( y_1 \) was used as the reference dosage. Keeping the mix ratio of concrete and the dosage of admixture unchanged, concrete extensibility tests were carried out at the conditions of 38°C±2°C, 23°C±2°C, and 3°C±2°C. The smaller the difference of concrete extensibility, the less sensitive the admixture was to temperature.

2.3.4.4. **The clay content sensitivity test**
The experiment was carried out at 23°C±2°C. \( y_1 \) was used as the reference dosage to test the initial extensibility of concrete, then 6% sand was replaced by clay to to measure the extensibility of concrete with other conditions unchanged, the smaller the difference between the extensibility of concrete before and after sand was replaced by clay, the less sensitive the admixture was to clay content.

3. **Experimental results and discussion**

3.1. **infrared spectrum test results**
The infrared spectra of PCE-2 are shown in Fig1.
3.2. Gel permeation chromatography test results

The gel permeation chromatography test results of PCE-2 are shown in Table 3.

| Sample | $M_n$ | $M_w$ | $M_p$ | PDI ($M_w/M_n$) | $M_p$ | Conversion rate/% |
|--------|-------|-------|-------|----------------|-------|------------------|
| PCE-2  | 27377 | 56208 | 42314 | 2.05           | 2347  | 87.76            |

As shown in Table 3, the $M_n$ of PCE-2 was 27377, the $M_w$ of PCE-2 was 56208, the PDI of PCE-2 was 2.05, and the monomer conversion rate was 87.76%, indicating that PCE-2 can meet the application requirements.

3.3. The dosage sensitivity test results

The dosage of PCE-1 and PCE-2 for concrete with extensibility of 400 mm ±10 mm and 550 mm ±10 mm was tested respectively at 23°C±2°C. The test results are shown in Table 4.

| Sample | dosage % | concrete extensibility /mm | remarks |
|--------|----------|-----------------------------|---------|
| PCE-1  | 1.57     | 400                         | y0      |
| PCE-2  | 3.78     | 390                         |         |
| PCE-1  | 2.20     | 555                         | y1      |
| PCE-2  | 7.55     | 550                         |         |
As shown in Table 4, the dosage width of PCE-1 which is $2.20/1.57=1.40$ is greater than the dosage width of PCE-2 which is $7.55/3.78=2.00$, indicating that PCE-2 has better dosage sensitivity than PCE-1.

3.4. The water consumption sensitivity test results

The concrete extensibility of PCE-1 and PCE-2 were tested before and after water addition. The test results are shown in Table 5.

| Sample | dosage (%) | Initial concrete extensibility /mm | Concrete extensibility when the water consumption increased by 15 kg/m³ /mm | D-value /mm |
|--------|------------|-----------------------------------|-------------------------------------------------|-------------|
| PCE-1  | 1.57       | 400                               | 545                                             | 145         |
| PCE-2  | 3.78       | 390                               | 505                                             | 115         |

As shown in Table 5, the D-value of PCE-1 is greater than the D-value of PCE-2, indicating that PCE-2 has better water consumption sensitivity than PCE-1.

3.5. The temperature sensitivity test results

The concrete extensibility tests of PCE-1 and PCE-2 were carried out at the conditions of $38^\circ C\pm 2^\circ C$, $23^\circ C\pm 2^\circ C$, and $3^\circ C\pm 2^\circ C$. The test results are shown in Table 6.

| Temperature | Sample | dosage (%) | Concrete extensibility /mm |
|-------------|--------|------------|----------------------------|
| $3^\circ C\pm 2^\circ C$ | PCE-1  | 2.20       | 520                        |
|              | PCE-2  | 7.55       | 545                        |
| $23^\circ C\pm 2^\circ C$ | PCE-1  | 2.20       | 555                        |
|              | PCE-2  | 7.55       | 550                        |
| $38^\circ C\pm 2^\circ C$ | PCE-1  | 2.20       | 400                        |
|              | PCE-2  | 7.55       | 460                        |

As shown in Table 6, the concrete extensibility of PCE-2 from large to small is $(38^\circ C\pm 2^\circ C)=(23^\circ C\pm 2^\circ C)>(3^\circ C\pm 2^\circ C)$, the concrete extensibility of PCE-1 from large to small is $(23^\circ C\pm 2^\circ C)>(3^\circ C\pm 2^\circ C)>(38^\circ C\pm 2^\circ C)$. The concrete extensibility of PCE-2 and PCE-1 is the same at $23^\circ C\pm 2^\circ C$, the concrete extensibility of PCE-1 and PCE-2 decreases when the temperature increase from $23^\circ C\pm 2^\circ C$ to $38^\circ C\pm 2^\circ C$, the D-value of PCE-2 is 95mm, the D-value of PCE-1 is 155mm, indicating that PCE-2 has better high temperature sensitivity than PCE-1. When the temperature decrease from $23^\circ C\pm 2^\circ C$ to $3^\circ C\pm 2^\circ C$, the D-value of PCE-2 is 5mm, the D-value of PCE-1 is 35mm, indicating that PCE-2 has better low temperature sensitivity than PCE-1.

3.6. The clay content sensitivity test results

The concrete extensibility of PCE-1 and PCE-2 were tested before and after sand was replaced by clay. The test results are shown in Table 7.

| Sample | dosage (%) | Initial concrete extensibility /mm | Concrete extensibility when 6% sand was replaced by clay /mm | D-value /mm |
|--------|------------|-----------------------------------|-------------------------------------------------|-------------|
| PCE-1  | 2.20       | 555                               | 415                                             | 135         |
| PCE-2  | 7.55       | 550                               | 560                                             | 10          |

As shown in Table 7, the D-value of PCE-1 is greater than the D-value of PCE-2, indicating that PCE-2 has better clay content sensitivity than PCE-1.

4. Conclusions

(1) A highly adaptable polycarboxylate superplasticizer (PCE-2) was successfully synthesized using isoprenol polyoxyethylene ether as macromonomer at room temperature. The conversion rate of
polymer is 87%.

(2) The Sensitivity test results show that PCE-2 has better dosage sensitivity, water consumption sensitivity, temperature sensitivity, clay content sensitivity than PCE-1, indicating that the adaptability of PCE-2 to concrete is better than that of PCE-1.

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