Synthesis of Early Strength Polycarboxylate Superplasticizer for Precast Concrete and Study on its Early-strength Mechanism

ChuanDeng Wu¹, GeLi Li¹, YunHui Fang¹, ZhanHua Chen¹, GuangXing Lai¹ and Po-Hsiang Chuang¹

¹KZJ New Materials Group Co., Ltd. Xiamen 361101, Fujian, China
E-mail: cdforjob@foxmail.com

Abstract. In this paper, an early-strength polycarboxylate superplasticizer ZQ-PC for precast concrete was prepared by introducing an alcohol amine small monomer DAC into a traditional polycarboxylate superplasticizer. The prepared sample ZQ-PC, the commercially available sample SL-1, and the blank sample were selected for comparison test. The peak time and peak height of the cement hydration heat added to the cement mortar of the three groups of samples and the scanning electron microscope observation microscopic images after 3 days of curing in the concrete samples were tested. The results show that the addition of ZQ-PC can significantly accelerate the hydration time of the cement and accelerate the formation of C-S-H gel in concrete.

1. Introduction

With the rapid development of social economy, precast concrete has been favored by all walks of life because of its advantages of improving quality, improving efficiency, shortening construction period, improving labor and saving resources [1]. In the traditional prefabricated component production process, in order to better utilize its high efficiency and short-term characteristics, it is usually improved by steam curing in the concrete curing process. But this method is energy intensive and costly. At the same time, in order to meet the production line and construction performance, the initial 1h slump loss of precast concrete can not be large. In order to solve this technical problem, we decided to develop a pre-cast concrete early-type polycarboxylate superplasticizer. In the field of early-strength polycarboxylate water reducer, Lai Guangxing, Lin Yanmei, Chen Hao and others have done more research on the early strength and early strength mechanism of early strength polycarboxylate superplasticizer [2-6].

In this paper, an early-strength polycarboxylate superplasticizer was prepared by introducing an alcohol amine small monomer DAC into a traditional polycarboxylate water reducer. Isobutyl polyoxyethylene ether was selected as the macromonomer and acrylic acid, unsaturated monomer and DAC were subjected to free radical polymerization in a complex high-efficiency initiation system. The SEM and cement hydration heat meter were used to study the early strength effect of the concrete mixed with the water reducing agent from the microscopic point of view. Experimental.

1.1. Raw materials

Synthetic raw materials: macromonomer (HPEG, molecular weight 6000), acrylic acid (AA), ammonium persulfate, thioglycolic acid, alcohol amine small monomer DAC, early strong functional
monomer P1, all industrial level.

Performance test raw materials: cement (C1): China Resources P.O42.5R cement; fly ash (F): Hongshan F class II fly ash; mineral powder (K): Sangang S95 grade ore; sand (S): using a fineness modulus of 2.6 to 2.9, Mud content less than 1% of desalinated sand; stone (G1): using a nominal particle size of 10 to 20 mm graded gravel; stone (G2): using a nominal particle size of 20 ~ 40mm grade gravel; stone (G3): use the nominal particle size 5 ~ 20mm grading counterattack broken stone; water (W): tap water. Meet the requirements of the standard "JGJ63-2006 Concrete Water Standard"; admixture (A): 1.S11A: a brand of ordinary polycarboxylic acid mother liquor commercially available, containing 49% solids, colorless transparent liquid. 2.SL-1: A brand of early-strength polycarboxylic acid mother liquor, which has a solid content of 48% and a pale yellow transparent liquid.

1.2. Synthesis process
In a four-necked flask equipped with a mechanical stirring device and a temperature control device, HPEG-6000, acrylic acid (AA), ammonium persulfate, alcohol amine small monomer DAC and water, which have been weighed according to the design requirements, wear loaded into the flask. After stirring for 100 min in 25℃ water bath, the solution A (components of acrylic acid and water), solution B (components of reducing agent P1 and water) and solution C (thioglycolic acid and water) were added dropwise to the flask. After the completion of the dropwise addition, 33% sodium hydroxide was added thereto to adjust the pH of the product to 6-7, and a pre-strong polycarboxylic acid water reducing agent having a solid content of 49% was obtained.

1.3. Performance test method
1.3.1 Determination of homogeneity of product admixture: The test is carried out in accordance with the provisions of GB/T8077-2012 "Test method for homogeneity of concrete admixtures".

1.3.2 Mechanical properties of concrete: Tested in accordance with GB/T50081-2002 "Test methods for mechanical properties of ordinary concrete".

1.3.3 Hydration heat test: The hydration heat test uses the eight-channel cement hydration heat meter of Wuhan Botaisi Technology Co., Ltd. to determine the cement hydration heat release curve. The test was carried out in accordance with the provisions of GB/T12959-2008 "Method for determination of cement hydration heat".

1.3.4 SEM analysis of cement hydration products: Several pieces of concrete pieces with an age of 3 days were selected. After soaking in absolute ethanol for 30 minutes, it was taken out and dried in a constant temperature drying oven at 55 ℃. Then, the dried sample was placed in an ion sputtering apparatus, and the pressure was set to 2 MPa, and the ion current was 6 to 8 mA. The sample was sputter-treated for 120 s. Next, the SEM image of the sample was observed by EM-20 scanning electron microscope produced by COXEM, Korea.

2. Results and discussion
2.1. Synthesis of Early Strength Polycarboxylate Superplasticizer
The synthesis of an early-strength polycarboxylate superplasticizer was carried out using a macromonomer HPEG-6000 having a side chain polymerization degree of 80 and a molecular weight of about 6000 and a DAC. Orthogonal experiment was carried out with the amount of macromonomer, acrylic acid, DAC and chain transfer agent as variables. The effects of different variables on the slump of concrete of early strength polycarboxylate superplasticizer and the compressive strength of concrete were studied. Table is shown in Table 1, test results and analysis are shown in Table 2.
Table 1 Orthogonal experimental design

| Item       | HPEG-5000 (g) | AA (g) | DAC (g) | Mercaptoacetic acid (g) |
|------------|---------------|--------|---------|-------------------------|
| Level 1    | 175           | 13     | 1.46    | 0.65                    |
| Level 2    | 200           | 12     | 1.96    | 0.75                    |
| Level 3    | 225           | 11     | 2.46    | 0.85                    |

Table 2 Test results

| Test number | HPEG-5000 (g) | AA (g) | DAC (g) | Mercaptoacetic acid (g) | Cement paste fluidity (mm) | 1d compressive strength (MPa) |
|-------------|---------------|--------|---------|-------------------------|---------------------------|------------------------------|
| ZQ-1        | 175.00        | 13     | 1.46    | 0.65                    | 212                       | 27.9                        |
| ZQ-2        | 175.00        | 12     | 1.96    | 0.75                    | 240                       | 30.1                        |
| ZQ-3        | 175.00        | 11     | 2.46    | 0.75                    | 170                       | 26.7                        |
| ZQ-4        | 200.00        | 13     | 1.96    | 0.85                    | 251                       | 30.4                        |
| ZQ-5        | 200.00        | 12     | 2.46    | 0.65                    | 179                       | 26.2                        |
| ZQ-6        | 200.00        | 11     | 1.46    | 0.75                    | 180                       | 26.3                        |
| ZQ-7        | 225.00        | 13     | 2.46    | 0.75                    | 180                       | 27.1                        |
| ZQ-8        | 225.00        | 12     | 1.46    | 0.85                    | 160                       | 30.5                        |
| ZQ-9        | 225.00        | 11     | 1.96    | 0.65                    | 168                       | 28.8                        |

According to the results of orthogonal experiment in Table 2, we can see that: (1) The influence of the above four factors on the properties of early-strength polycarboxylate superplasticizer for 1d concrete compressive strength, From large to small in order is as follows: AA > HPEG-6000 > DAC > thioglycolic acid; The factors affecting the flow of concrete slurry, From large to small in order is as follows: DAC > AA > HPEG-6000 > thioglycolic acid; Through means of range analysis, AA and HPEG-6000 The preferred dosage values are all at the level 1 position. But DAC and thioglycolic acid at level 2. Therefore, the synthesis of early-strength polycarboxylate superplasticizer agent has better early strength performance and mass ratio of process conditions. To: HPEG-5000: AA: DAC: thioglycolic acid = 175.00: 13: 1.96: 0.75.

Based on the molecular structure design and research of the above polycarboxylate superplasticizer, we determined the optimum process conditions for the early-strength polycarboxylate superplasticizer: the amount of HPEG macromonomer with a molecular weight of 6000 in the side chain is 175.00g, the amount of acrylic acid was 13 g, the amount of ammonium persulfate was 2.0 g, the amount of thioglycolic acid was 0.75 g, and the amount of early strong functional monomer DAC was 1.96 g. The sample number synthesized by this process is ZQ-PC, which has the best working performance and 1d compressive strength. When the single dose is 1.7kg, the initial slump loss is 170mm, and the 1d compressive strength is 24.7MPa.

2.2. Analysis of hydration mechanism of early strength

Hydration heat is the study of cement hydration by characterizing the thermal effects (heat release, heat release rate, etc.) of cement mineral dissolution and hydration product formation during cement hydration. During the hydration process of cement, in the early stage of induction, a large amount of heat is released due to the large amount of dissolution of cement minerals; In the process of cement hydration, in the early stage of induction, a large amount of heat is released due to the large amount of dissolution of cement minerals; after entering the hydration induction period, the rate of hydration heat release is rapidly reduced; in the accelerated period of hydration, the rate of hydration is accelerated and The large amount of hydration products generated, the rate of heat release increased significantly; during the hydration deceleration period, the hydration heat release rate gradually decreased; after the
stable period, the heat release rate was lower and more stable. From the corresponding relationship, the cement hydration heat release rate corresponds to the cement hydration reaction rate, and the hydration heat release corresponds to the cement hydration degree.

In this experiment, the hydration heat release of the synthetic early-strength polycarboxylate superplasticizer ZQ-PC and the commercially available early-strength polycarboxylate superplasticizer SL-1 were tested by cement hydration heat meter. Blank samples made with common carboxylic acid superplasticizer agents were compared. The hydration heat test results of the cement before and after the incorporation of different superplasticizers are shown in Figure 1, and the dosage is 0.1%.

It can be seen from Figure 1 that SL-1 and ZQ-PC early-strength polycarboxylate superplasticizers accelerate the hydration behavior of cement, and the hydration heat peak position was ahead of time, and the main exothermic peak height is compared with the blank sample have rise. Compared with SL-1, the hydration heat release peak of ZQ-PC early-strength polycarboxylate superplasticizer was ahead of time, and the height of the main exothermic peak increased more. It can be seen that the early-strength polycarboxylate superplasticizer ZQ-PC accelerates the early hydration of the benchmark cement, promotes the hydration of C3A, and accelerates the formation of AFt. Therefore, this is also the main reason why the early strength properties of ZQ-PC early-strength polycarboxylate superplasticizer incorporated into concrete are better than SL-1 early strength polycarboxylate superplasticizer.

![Figure 1 Curve of hydration heat release rate of cement system with different early strength polycarboxylate superplasticizer](image)

2.3. **Microscopic manifestation of early strength effect of early strength polycarboxylate superplasticizer**

Adsorption and dispersion affect the hydration behavior of cement, which in turn affects the morphology of cement hydration products, the microstructure and mechanical properties of concrete. For the reason that study the effect of early strength polycarboxylate superplasticizer on the morphologies of hydration products is of great significance for adjusting the macroscopic properties of concrete. Concrete samples without the addition of early-strength polycarboxylate superplasticizer and concrete samples with ordinary water-reducing agents S11A and ZQ-PC were prepared, cured under natural conditions for 3 days, and their hydration was observed by scanning electron microscopy. The morphology of the product is shown in Figure 2 (a, b, c).

It can be seen from Figure 2 (a, b, c) that when the reference concrete is hydrated for 3 days, the structure is looser and the pores are more, and more short columnar ettringite AFt and reticulated C-S-H gel appear. This indicates that the hydration product on the surface of the cement particles has formed. However, no obvious characteristic hydration products were observed, which may be due to the lower degree of hydration of cement. The concrete with ZQ-PC and the comparative S11A was added, and the fibrous, reticulated C-S-H gel and the needle prismatic-shaped Aft appeared in the hydration for 3 days. At the same time, the shape of the product after the 3 days hydration of the
concrete added with ZQ-PC is shown in Figure 2(c). This shows that the addition of ZQ-PC and S11A can promote the hydration of cement, accelerate the hydration of cement, and the early strength of ZQ-PC is better than that of S11A.

3. Conclusion
From the discussion above, we may safely draw the conclusion above:

(1) The introduction of alcohol-amine small monomer DAC can improve the early strength of polycarboxylate superplasticizer and have good early strength effect.

(2) Under the same conditions, the early-strength polycarboxylate superplasticizer ZQ-PC prepared in this paper was earlier than the commercially available early-strength polycarboxylate superplasticizer, and the cement hydration peak time was earlier. Promote better performance.

(3) The addition of ZQ-PC can major accelerate the hydration time of cement and accelerate the formation and improvement of C-S-H gel in concrete.

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