Preparation and application of low molecular weight polyether polycarboxylate superplasticizer

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Abstract. In this paper, a low molecular weight polycarboxylate superplasticizer was designed and synthesized by using low molecular weight polyether macromonomer with molecular weight of 800 as the side chain of polycarboxylate superplasticizer; The ratio of oxidant and reductant in inorganic salt initiator system is 2:1, and that in organic water solvent initiator system is 4:1. The amount of initiator in the two systems accounts for 5% and 2% of the total amount of polyether macromonomer, respectively; GPC and Fourier transform infrared spectroscopy tests showed that the number average molecular weight of the water reducer was about 24000, the conversion rate of polyether macromonomer was more than 90%, and the molecular structure of the polymerization product met the design requirements. The influence of the polymer on the fluidity and bleeding rate of manufactured sand concrete is also discussed.

1. Introduction

Polycarboxylate superplasticizer, as the third generation of concrete superplasticizer, has a unique comb structure and steric effect. Compared with the first and second generation of superplasticizers, it improves the performance of concrete mixture more significantly. In recent years, it has been widely used at home and abroad. Polycarboxylic acid water reducing agent is polymerized based on organic polymer materials. It has strong designability of molecular structure and large space for performance adjustment. There are many studies on its performance and molecular structure in China. Zhou Keli, Liu Jin, Li Zhen and others believe that the new polycarboxylic acid water reducer with short side group and low molecular weight has good dispersion, good fluidity retention of cement paste and no bleeding segregation [1]. He Yan, Kong Yaning, Wang Xiaofu and others found that the ratio of acid to ether, the molar ratio of chain transfer agent to polyether have a great influence on the molecular weight of polycarboxylic acid water reducer, and the molecular conformation curls with the increase of polyether molecular weight [3]. Therefore, the molecular weight and conformation can be designed by adjusting the ratio of acid to ether and the molar ratio of chain transfer agent to polyether. Wu yingzhe and Huang Furen pointed out that the relative molecular weight increase of polycarboxylate water reducer affects the fluidity of cement paste and the slump of concrete [2].

At present, when domestic polycarboxylic acid water reducing agent encounters some poor sand and gravel materials, the fluidity of concrete will become poor and easy to bleed. For example, when the fineness modulus is greater than 3.0, the concrete will leak stone, have poor fluidity and serious bleeding; In view of the above problems, it is difficult to solve the water reducing agent produced by conventional materials and processes. In this paper, organic and inorganic redox systems are used as polymerization initiators, polyether macromonomer with molecular weight of 800 is used for room temperature polymerization, and a polyether water reducing agent with number average molecular weight 24000 and more than 90% conversion rate of polyether macromonomer is synthesized.
weight of 24000 is obtained. The water reducing agent in this paper has good adaptability in coarse machine-made sand and low bleeding rate of mixed concrete. The water reducing agent has the advantages of simple production operation, no special equipment, no pollution in production, and is convenient for market promotion and application. At the same time, the water reducing agent solves the problem of the decline of concrete construction performance caused by the deterioration of the quality of sand and gravel materials.

2. Test

2.1. Raw material
Raw materials for raw material test synthesis are shown in Table 1 below. Raw materials for concrete test are as follows: Cement: conch P.O 42.5; Fly ash: Datang Shenglong class II fly ash; Sand: machine-made sand, fineness modulus MX = 3.2; Stone: Double graded basalt (small stone 5 ~ 16mm, large stone 5 ~ 31.5mm); Additive pce0: polycarboxylic acid water reducer is synthesized in this test, with solid content of 50% and water reduction rate of 32%; Admixture pce1: commercially available polycarboxylic acid water reducer, with solid content of 49.8% and water reduction rate of 32%.

Table 1. Chemical raw materials

| Name                                | Essential information                                           |
|-------------------------------------|-----------------------------------------------------------------|
| Isopentenyl polyoxyethylene ether   | Industrial products, Produced in Guangdong, molecular weight 800 |
| Methacrylic acid                    | Analytical pure, Produced by Sinopharm group                   |
| Acrylic acid                        | Analytical pure, Produced by Sinopharm group                   |
| Potassium hypophosphite             | Analytical pure, Produced by Sinopharm group                   |
| Sodium bisulfite                    | Analytical pure, Produced by Sinopharm group                   |
| Hydrogen peroxide                   | Analytical pure, Produced by Sinopharm group                   |
| Organic reducing agent (f)          | Industrial products, Clariant Chemical (Huizhou) Ltd.          |

2.2. Synthetic test method
In this experiment, the amount of fixed modified isopentenyl polyoxyethylene ether is m, and the amount of other raw materials is calculated according to the mass ratio of m, including 13% m of acrylic acid, 3% m of methacrylic acid, 0.4% m of reducing agent F, 1.7% m of sodium bisulfite, 1.6% m of hydrogen peroxide and 3.3% m of potassium hypophosphite. The admixture preparation operation in the synthesis stage of this test is as follows:

(1) Prepare liquid A and liquid B. Liquid A is composed of acrylic acid, methacrylic acid and some deionized water; Liquid B consists of reducing agent F, sodium bisulfite and deionized water;
(2) Add a certain amount of modified isopentenyl polyoxyethylene ether macromonomer, hydrogen peroxide, potassium hypophosphite and some deionized water to the four mouth flask equipped with thermometer and stirrer, and stir to the state of aqueous solution;
(3) Add liquid A and B dropwise at the same time. The dropping of liquid A is completed in 3H and the dropping of liquid B is completed in 3.5H;
(4) Hold for half an hour, add sodium hydroxide and adjust the pH value to about 5 ~ 7;
(5) Make up water until the solid content is 50% to obtain polycarboxylic acid water reducer mother liquor pce0.

2.3. Test methods
The test method is as follows:

(1) Gel permeation chromatography (GPC) was characterized by Waters1515 Isocratic HPLP pump/Waters2414 differential detector, and the molecular weight and conversion rate of the sample PCE0 and commercial sample PCE1 were obtained by gel chromatography;
(2) The synthetic samples were analyzed by PE spectrum 100 infrared chromatograph (FT-IR) produced by American PE company. The solution is coated on the KBr wafer to form a thin liquid
film, dried under the infrared lamp for determination, and its main molecular structure is analyzed to judge whether the sample meets the expected goal of molecular design;

(3) The fluidity of cement paste shall be tested in accordance with GB / T 8077-2008 test method for homogeneity of concrete admixtures. It mainly tests the performance of synthetic water reducing agent pce0 and commercial water reducing agent pce1 in the fluidity test of cement paste at the initial and 1H and 2H, and the comparison of the state of cement paste;

(4) The concrete test shall be carried out in accordance with the relevant provisions of GB 8076-2008 concrete admixtures. It mainly tests the difference of fluidity, bleeding rate and other performance indexes between synthetic water reducing agent pce0 and commercial water reducing agent pce1 in mixing C30 concrete. See Table 2 concrete raw materials and mix proportion for concrete mix proportion.

| Material variety | Cement | Fly ash | Machine-made sand (Mx=3.2) | Crushed stone (5~16mm) | Crushed stone (5~31.5mm) | Tap water |
|------------------|--------|---------|-----------------------------|------------------------|--------------------------|-----------|
| mix proportion (kg/m3) | 280 | 80 | 870 | 300 | 680 | 155 |

3. Test results and discussion

3.1. Gel chromatographic test results
In this experiment, the PCE0 and commercial samples PCE1 were tested by gel permeation chromatography (GPC). The test results were shown in Figure 1 Gel chromatogram, and the data analysis was shown in Table 3 GPC test results.
### Table 3. Concrete raw materials and mix ratio

| Sample | Mn    | Mw    | MP    | Mz    | Polydispersity | Total area | Retention time (min) | Conversion rate /% |
|--------|-------|-------|-------|-------|----------------|------------|----------------------|------------------|
| PCE0   | 24663 | 65906 | 37215 | 178264| 2.672272       | 1820880    | 90.35                | 17.729           |
| PCE1   | 32579 | 83800 | 54382 | 204474| 2.572222       | 1909249    | 80.67                | 17.058           |

According to the data in Figure 1 and table 3, the number average molecular weight of polycarboxylic acid water reducer sample pce0 in this test is more than 24000, the weight average molecular weight is more than 65000, and the viscosity average molecular weight is more than 37000. According to the calculated area, the conversion rate is about 90%; The number average molecular weight of the commercial sample pce1 is more than 32000, the weight average molecular weight is more than 83000, and the viscosity average molecular weight is more than 54000. The calculated area shows that the conversion rate is about 80%; In this experiment, the modified isopentenyl polyoxyethylene ether monomer with molecular weight of 800 was selected, and its weight average, number average and viscosity average molecular weight were lower than those of conventional polycarboxylic acid water reducer; The polycarboxylic acid water reducer pce0 polymerized in the organic and inorganic double initiator system has higher polymerization conversion than the conventional polycarboxylic acid water reducer on the market; The polymerization conversion rate of this test is about 10% higher than that of conventional products, which makes this test product have higher economic performance price ratio, improve the utilization rate of raw materials and be more environmentally friendly; The number average molecular weight of the test product is more than 8000 lower than that of the conventional product, which provides more space for the performance improvement and functional particularity of the product.

### 3.2. Fourier infrared spectrum test results

The mother liquor pce0 was tested by Fourier infrared spectrometer, and the obtained infrared spectrum is shown in Fig. 2.

![Infrared spectrogram](image)

According to the infrared spectrum analysis in Figure 2, 2869.91cm\(^{-1}\) is the stretching vibration peak of saturated carbon-C-H, 1725.71cm\(^{-1}\) is the stretching vibration peak of - C = O in carboxyl functional group, 1579.52cm\(^{-1}\) is the C = C skeleton vibration peak, 1454.64cm\(^{-1}\) is the bending absorption peak of saturated carbon-C-H, 1350.08cm\(^{-1}\) is the in-plane bending vibration absorption peak of saturated carbon-C-H, and 1250.26cm\(^{-1}\) is the stretching vibration peak of carbon
oxygen-C-O in alcohol ether, 1107.61 cm⁻¹ is the characteristic absorption peak of ether bond-O - and 847.43 cm⁻¹ is the trans vibration peak of alkyne. The infrared spectrum of pce0 and the above analysis show that the mother liquor pce0 reaches the expected functional group structure, and there is no unreacted C = C unsaturated double bond.

3.3. Fourier infrared spectrum test results
The cement paste test results of pce0 and pce1 in this test are shown in Table 4 cement paste test results below.

| Water reducing agent model | Dosage of water reducing agent (%) | Fluidity of cement paste (mm) | State                      |
|----------------------------|-----------------------------------|------------------------------|----------------------------|
|                            |                                   | 0h  | 1h  | 2h  |                          |                            |
| PCE0                       | 0.2                               | 220 | 240 | 230 | The homogeneity is good after standing |
| PCE1                       | 0.2                               | 225 | 240 | 200 | Slight bleeding at the edge after standing |

It can be seen from the test data of cement paste fluidity in Table 4 that under the same dosage of pce0 and pce1, the initial paste fluidity and the paste fluidity after 1h are close, but the pce1 paste fluidity obviously loses faster after 2h, indicating that the water reducer pce0 synthesized in this test has better slump retention performance than pce1; Through the static state of cement slurry mixed with two water reducing agents, it can be seen that pce1 has slightly poor water locking performance, while pce0 has good water locking performance. Therefore, it can be inferred that pce0 water reducing agent has better uniformity in concrete.

3.4. Concrete application experiment
In the experiment, the low molecular weight polyether polycarboxylic acid water reducer pce0 synthesized in this paper and the commercial water reducer pce1 are tested for concrete performance under the same slump. The results are shown in Table 5 concrete test results.

| Water reducing agent model | Dosage of water reducing agent (%) | Expansion / Slump (mm) 0h | Gas content (A/%) 1h | Strength (MPa) 7d | Bleeding rate ratio (B/%) 28d |
|----------------------------|-----------------------------------|---------------------------|---------------------|------------------|--------------------------|
|                            |                                   |                           |                     |                  |                          |
| PCE0                       | 0.15                              | 590/230                   | 570/230             | 37.5             | 44.6                     | 1.0                      |
| PCE1                       | 0.15                              | 590/220                   | 560/230             | 34.0             | 42.8                     | 4.5                      |

It can be seen from the experimental data of concrete in Table 5 that the water reduction rate of low molecular weight polyether water reducer pce0 synthesized in this test is equivalent to that of commercial water reducer pce1. Under the same slump, the fluidity of concrete is close, and the slump loss and fluidity loss in 1H are equivalent; Compared with pce1, the air content of pce0 mixed concrete is slightly higher, so the concrete slurry is fuller; The 7d and 28d strength of concrete, pce0 mixed concrete is significantly higher than pce1; Finally, the bleeding rate of pce0 mixed concrete is much lower than that of pce1 mixed concrete, which effectively solves the problem of easy bleeding of coarse machine-made sand concrete. According to the results of gel permeation chromatography (Fig. 1), the polycarboxylate superplasticizer synthesized by polyether macromonomer with 800 molecular weight is shorter. The average molecular weight of the superplasticizer is lower because of its short side chain structure. Therefore, the steric hindrance effect of the superplasticizer is not obvious, thus reducing the sensitivity of the superplasticizer. At the same time, due to the reduction of
the molecular weight of the side chain, the overall molecular weight of the water reducer is reduced, which is more conducive to the rapid adsorption of polycarboxylic acid water reducer in the cement slurry, the concrete has good slurry starting effect, the bleeding rate of the mixed coarse machine-made sand concrete is lower than that of the conventional water reducer, and the adaptability is better.

4. Conclusion
In conclusion, the following conclusions can be drawn:

(1) Due to the short side chain, the average molecular weight of polycarboxylic acid water reducer synthesized from low molecular weight polyether macromonomer is lower than that of conventional polycarboxylic acid water reducer, and the number average molecular weight is only more than 24000; Under the double initiator system of organic aqueous solution and inorganic salt, the conversion of polymerization is 10% higher than that of conventional water reducer, and the polymerization efficiency is high;

(2) Through the Fourier infrared spectrum test, it can be known that the molecular main structure and functional groups of the low molecular weight polyether water reducer pce0 in this test are in line with the molecular structure of ether polycarboxylic acid water reducer, and the reaction of main monomers such as acrylic acid and methacrylic acid in the product is complete, which meets the design goal;

(3) Due to its low average molecular weight, low molecular weight polyether water reducer has more flexible and efficient adsorption on cement slurry, and has good slurry starting effect in coarse mechanism concrete. On the premise of maintaining the workability of concrete such as high fluidity and low slump loss, compared with conventional water reducer, concrete strength is higher and bleeding rate is lower.

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