Study on Synthesis and Properties of Vinyl Polyoxyethylene Ether Type Polycarboxylate Superplasticizer

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Abstract. Vinyl polyoxyethylene ether type polycarboxylate superplasticizer PCE-6C is prepared by copolymerization of vinyl polyoxyethylene ether and acrylic acid. The initiation system is a hydrogen peroxide-sodium formaldehyde sulfoxylate hydrate redox initiation system. The chain transfer agent is mercaptopropionic acid. The test results show that the monomer conversion rate of the synthesized PCE-6C is high and the dosage sensitivity of PCE-6C is significantly better than that of the conventional ester type polycarboxylate superplasticizer and the conventional ether type polycarboxylate superplasticizer, and the water consumption sensitivity and temperature sensitivity of PCE-6C is slightly better than that of the conventional ester type polycarboxylate superplasticizer and the conventional ether type polycarboxylate superplasticizer.

1. Introduction
Polycarboxylate superplasticizer has become the mainstream concrete superplasticizer product due to its good design, high water reduction rate and environmental protection [1-2]. Through the selection and design of monomers in the polymerization process, technicians have been able to synthesize polycarboxylate superplasticizer suitable for different applications, such as early strength type, viscosity reduction type, high water reducing type, high slump retention type, mud resistant type [3-10]. However, these functional polycarboxylate superplasticizers are mainly realized by using different types of small comonomers. Since the advent of HPEG, the macromonomers used have not been updated for a long time. In this paper, a new polycarboxylate superplasticizer PCE-6C was prepared by using a new type of polyether macromonomer vinyl polyoxyethylene ether macromonomer in recent years, and its monomer conversion, dosage sensitivity, water consumption sensitivity and temperature sensitivity were studied.

2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials
Vinyl polyoxyethylene ether (industrial grade), Acrylic acid (industrial grade), Hydrogen peroxide (industrial grade), Sodium formaldehyde sulfoxylate hydrate (industrial grade), Ferrous sulfate (industrial grade), Mercaptopropionic acid (industrial grade), Sodium hydroxide (30% aqueous solution, industrial grade).
2.1.2. Main performance test raw materials for experiment
Cement(C, P.O 42.5 Cement), Fly ash(F, Level II), Sand(S, Mx=2.4-2.8), Gravel(G, grain size of 5-31.5mm), Polycarboxylate superplasticizer(PCE-1, conventional ester type polycarboxylate superplasticizer, self made), Polycarboxylate superplasticizer(PCE-2, conventional ether type polycarboxylate superplasticizer, self made).

2.2. Preparation of PCE-6C
Add measured water, vinyl polyoxyethylene ether and Hydrogen peroxide into a four-mouth bottle. Control the reaction temperature to 10-15℃. Add ferrous sulfate after all macromonomers are dissolved. After 10 minutes, a mixture of acrylic acid and mercaptopropionic acid is added dropwise. Aqueous solution of sodium formaldehyde sulfoxylate hydrate is also added dropwise. Control all materials to complete dropping in 1 hour. Keep warm for 0.5 hour, then a 30% aqueous solution of sodium hydroxide was added to adjust the pH to 6.0-7.0, thus obtaining a vinyl polyoxyethylene ether type polycarboxylate superplasticizer PCE-6C.

2.3. Performance test method

2.3.1. Concrete test
Concrete tests shall be carried out in accordance with GB/T50080-2016 Standard of Test Methods for Performance of Ordinary Concrete Mixtures.

2.3.2. Sensitivity test
The sensitivity evaluation was carried out according to the Technical Specification for the Sensitivity Evaluation of Polycarboxylate Superplasticizer compiled by KZJ New Materials Group Co., LTD. Specific test the dosage sensitivity (represented by $R_C$), the water consumption sensitivity (represented by Wr) and the temperature sensitivity (represented by Wt) [11]. The concrete mix ratio is shown in Table 1:

| W (kg/m³) | C (kg/m³) | S (kg/m³) | G (kg/m³) | F (kg/m³) |
|-----------|-----------|-----------|-----------|-----------|
| 170       | 260       | 790       | 1050      | 80        |

2.3.3. Gel permeation chromatography test
American Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector and Breeze software acquisition and analysis system were used. Chromatographic columns are separated by UltrahydragelTM250 and UltrahydragelTM500 in series. The mobile phase was 0.1mol/L sodium nitrate aqueous solution (containing 0.05% sodium azide). The mobile phase was degassed by vacuum of 0.22 m microporous membrane and then by ultrasonic degassed. The flow rate of mobile phase was 0.8mL/min. Injection volume 200 μL. The temperature of the column box is 40℃. The internal temperature of the differential detector is 40℃.

3. Experimental results and discussion

3.1. Gel permeation chromatography test results
PCE-1, PCE-2 and PCE-6C were tested by gel permeation chromatography. The polymer content in gel permeation chromatogram reflects the monomer conversion of the sample. The gel permeation chromatograms of PCE-1, PCE-2 and PCE-6C are shown in Figure1- Figure3.
In Fig.1, at the time of 17.718 min, the peak of the polymer was observed. The peak at the time of 21.401 min was the unreacted monomer. The peak of the solvent was at 25.992 min. In Fig.2, at the...
time of 17.096 min, the peak of the polymer was observed. The peak at the time of 21.348 min was the unreacted monomer. In Fig. 3, at the time of 17.592 min, the peak of the polymer was observed, and there was no obvious peak of unreacted monomer in the gel permeation chromatogram. The polymer content of PCE-1, PCE-2 and PCE-6C can be calculated by integrating the peaks of gel permeation chromatogram. The results are shown in Table 2.

Table 2. Polymer content test results

| Sample | Polymer content % |
|--------|------------------|
| PCE-1  | 82.62            |
| PCE-2  | 89.63            |
| PCE-6C | 100.00           |

As shown in Table 2, the polymer content of PCE-1 is 86.62%, the polymer content of PCE-2 is 89.63%, and the polymer content of PCE-6C is 100%, indicating that PCE-6C has higher monomer conversion than PCE-1 and PCE-2.

3.2. The dosage sensitivity test results

At the same time, PCE-1, PCE-2, and PCE-6C were tested for the dosage sensitivity. The test results are shown in Table 3:

Table 3. The dosage sensitivity test results

| Sample | $R_{C1}/\%$ | Concrete extensibility at $R_{C1}/$mm | $R_{C2}/\%$ | Concrete extensibility at $R_{C2}/$mm | $R_{C}$ |
|--------|-------------|--------------------------------------|-------------|--------------------------------------|---------|
| PCE-1  | 0.41        | 410                                  | 0.55        | 550                                  | 1.34    |
| PCE-2  | 0.37        | 400                                  | 0.44        | 540                                  | 1.20    |
| PCE-6C | 0.34        | 400                                  | 0.51        | 550                                  | 1.50    |

As shown in Table 3, the $R_{C1}$ of PCE-1, PCE-2, and PCE-6C are PCE-1, PCE-2, and PCE-6C from large to small, the $R_{C2}$ of PCE-1, PCE-2, and PCE-6C are PCE-1, PCE-6C, and PCE-2 from large to small, indicating that there is a certain one sidedness to evaluate the dispersion effect of the sample only at one dosage point. The $R_{C}$ of PCE-1, PCE-2, and PCE-6C are PCE-6C, PCE-1, and PCE-1 from large to small, indicating that the dosage sensitivity PCE-6C is the best, followed by PCE-1 and PCE-2 worst.

3.3. The water consumption sensitivity test results

At the same time, PCE-1, PCE-2, and PCE-6C were tested for the water consumption sensitivity. The test results are shown in Table 4:

Table 4. The water consumption sensitivity test results

| Sample | Dosage/$\%$ | Initial concrete extensibility /mm | The water consumption is 170 kg/m$^3$ | The water consumption is 180 kg/m$^3$ | W_r/mm |
|--------|-------------|-----------------------------------|--------------------------------------|--------------------------------------|--------|
| PCE-1  | 0.41        | 410                               | 525                                  | 115                                  |
| PCE-2  | 0.37        | 400                               | 525                                  | 125                                  |
| PCE-6C | 0.34        | 400                               | 500                                  | 100                                  |
As shown in Table 4, Wr of PCE-1, PCE-2, and PCE-6C are PCE-2, PCE-1, and PCE-6C from large to small, indicating that the water consumption sensitivity PCE-6C is the best, followed by PCE-1 and PCE-2 worst. However, the difference in Wr among the three samples is not very large, indicating that the water consumption sensitivity of these three samples is not very different.

3.4. The temperature sensitivity test results

At the same time, PCE-1, PCE-2, and PCE-6C were tested for the temperature sensitivity. The test results are shown in Table 5:

| Sample    | Dosage/% | Initial concrete extensibility /mm | Wt/mm |
|-----------|----------|-----------------------------------|-------|
|           |          | The temperature is 20±3°C | The temperature is 5±3°C |
| PCE-1     | 0.55     | 550                               | 590   | 40    |
| PCE-2     | 0.44     | 540                               | 585   | 45    |
| PCE-6C    | 0.51     | 550                               | 585   | 35    |

As shown in Table 5, Wt of PCE-1, PCE-2, and PCE-6C are PCE-2, PCE-1, and PCE-6C from large to small, indicating that the temperature sensitivity PCE-6C is the best, followed by PCE-1 and PCE-2 worst. However, the difference in Wt between the three samples is not very large, indicating that the temperature sensitivity of these three samples is not very different.

4. Conclusions

(1) A vinyl polyoxyethylene ether type polycarboxylate superplasticizer PCE-6C was synthesized in the experiment, which has higher monomer conversion than the self-made conventional ester type polycarboxylate superplasticizer PCE-1 and conventional ether type polycarboxylate superplasticizer PCE-2.

(2) The dosage sensitivity test results show that the $R_C$ of PCE-6C is the largest compared with PCE-1 and PCE-2, indicating that PCE-6C has better dosage sensitivity than PCE-1 and PCE-2.

(3) The water consumption sensitivity test results showed that the Wr of PCE-6C was slightly lower than that of PCE-1 and PCE-2, indicating that the water consumption sensitivity of PCE-6C was slightly better than that of PCE-1 and PCE-2.

(4) The temperature sensitivity test results showed that the Wt of PCE-6C was slightly lower than that of PCE-1 and PCE-2, indicating that the temperature sensitivity of PCE-6C was slightly better than that of PCE-1 and PCE-2.

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