Study on Synthesis and Performance of Low-bleeding Polycarboxylate Superplasticizer

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Abstract—A low-bleeding polycarboxylate superplasticizer was synthesized by using 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG) as the macromonomer and unsaturated polyhydroxy compound (BD) as the functional monomer. The synthesis conditions were optimized by single factor method. The structure of the polymer was characterized by infrared spectroscopy (FTIR) and gel permeation chromatography (GPC), and the properties of the synthesized samples were examined using paste, mortar and concrete. The results showed that when the BD content was 2.0%, the polycarboxylate superplasticizer PCE-HR had better comprehensive properties. Compared with the standard polycarboxylate superplasticizer PCE-S, PCE-HR had excellent performance in water retention, slump protection and reinforcement.

1. INTRODUCTION

Compared with the previous water reducing agent, polycarboxylate superplasticizer has many advantages such as good dispersibility, low dosage, molecular structure design and production, energy saving and environmental protection[13], therefore, the use amount of polycarboxylate superplasticizer is increasing. However, in practical engineering applications, the polycarboxylate superplasticizer has a problem of sensitive content, that is, the concrete has poor fluidity when the content is slightly lower, and the bleeding is severe when the content is slightly higher, especially at low temperature, and it is particularly obvious in the low rubber mix ratio concrete, and the phenomenon of severe water bleeding often occurs. Although the method of compounding thickeners can improve the bleeding problem of concrete, most of the thickeners such as cellulose, warm wheel rubber and xanthan gum still have some problems, for example, the compatibility with polycarboxylic acid water reducer, and thickeners will increase the viscosity of concrete, affect the fluidity, and most will affect the concrete setting time[4].

Therefore, in order to solve the bleeding problem of concrete, this paper selects 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG) as the macromonomer and unsaturated polyhydroxy compound as the functional monomer to synthesize a low-bleeding polycarboxylate superplasticizer. Among them, VPEG is used as a macromonomer because it has higher polymerization activity than APEG, TPEG, and HPEG. Comb polymers with more uniform side chain distribution can be obtained, which reduces the sensitivity of polycarboxylate superplasticizer[5], and the introduction of unsaturated polyhydroxy compounds with hydroxyl groups can improve the water retention performance of polycarboxylate superplasticizer.
2. EXPERIMENT

2.1. Materials
4-hydroxybutyl vinyl polyoxyethylene ether (VPEG, molecular weight 3000), acrylic acid (AA), unsaturated polyhydroxy compound (BD), mercaptoethanol (ME), 27.5% hydrogen peroxide (H2O2), ferrous sulfate heptahydrate (FeSO4.7H2O), reducing agent (FF6) and 30% sodium hydroxide (NaOH) are all industrial grade.

Cement (C, Feilu brand, P.O 52.5R); Sand(S, river sand with fineness modulus of 2.6-2.9 and mud content less than 1%); Gravel(G, grain size of 5-20mm); Fly ash (F, Level II), Slag powder (K, S95); Standard polycarboxylate superplasticizer (PCE-S, 50% solid content, commercially available); Low bleeding polycarboxylate superplasticizer (PCE-HR, 50% solid content, homemade).

2.2. Copolymerization
Put the metered VPEG macromonomer and water into a four-necked flask equipped with a stirrer, temperature control device and peristaltic pump feeding device, start the stirrer to stir, and adjust the initial temperature of the reaction to 5-20°C with an ice water bath. Add hydrogen peroxide, ferrous sulfate heptahydrate, and unsaturated polyhydroxy compounds, continue stirring for 10 minutes, and then start adding the reducing agent FF6 aqueous solution, mercaptoethanol aqueous solution, and acrylic acid aqueous solution separately. After the dropwise addition, keep the temperature for 1~2 h, and add liquid alkali to adjust the pH to 6-7, a low-bleeding polycarboxylate superplasticizer with a solid content of 50% is obtained.

2.3. Performance test method

2.3.1 Cement paste fluidity test: Cement pastes were prepared at a water cement ratio of 0.29 by adding the tap water with the defined amount of polycarboxylate superplasticizer dosages (0.20% by cement mass).

2.3.2 Mortar bleeding rate test: The mortar mix ratio is cement: fly ash: river sand: water = 220: 100: 780: 150. By adjusting the dosage of polycarboxylate superplasticizer, the mortar is initially 240 ± 10mm, and then put in the constant temperature and humidity standard curing box. Record the time of adding water, use this as the starting point of the time, and suck the amount of water exuded with a plastic dropper every 15 minutes until the mortar stops bleeding. Mortar bleeding rate = bleeding amount / water consumption × 100%.

2.3.3 FTIR measurement: Perkin Elmer Spectrum 100 Fourier transform infrared spectrometer is used to perform the test by using the thin film method.

2.3.4 GPC analysis: Molecular weight was performed by gel permeation chromatography (GPC) using UltraHydrogel Liner Column and UltraHydrogel 120 Column made by Waters.

2.3.5 Hydration heat determination: The hydration heat determination of cement slurry mixed with polycarboxylate superplasticizer was conducted in accordance with GB/T 12959-2008 “Determination Method for Cement Hydration Heat”.

2.3.6 Concrete test: Referred to GB/T 50080-2016 “Standard for Performance Test Methods of General Concrete Mixtures” and GB/T 50081-2019 “Standard for Test Methods of Physical and Mechanical Properties of Concrete” respectively.
3. RESULTS AND DISCUSSION

3.1. Paste fluidity test
Control the amount of VPEG (Mn = 3000), acrylic acid, initiator, chain transfer agent and the reaction conditions remain unchanged. By introducing 0 to 2.0% of BD (accounting for the mass of VPEG of the macromonomer), the influence of different BD amount on the dispersion properties of the polycarboxylate superplasticizers were investigated. The dosage of polycarboxylate superplasticizer in the paste test was 0.25%.

![Paste fluidity test graph](image1)

Figure 1. The result of paste fluidity test

It can be seen from figure 1 that, the number average molecular weight Mn of PCE-HR is 18106, the weight average molecular weight Mw is 34115, the peak molecular weight Mp is 28029, and the dispersion coefficient Mw / Mn is 1.88, there is not much difference with PCE-S, but the conversion rate is high, reaching 93.03%.

3.2. Mortar bleeding rate test
Through the mortar test, the water retention performance of the polycarboxylate superplasticizer can be simply tested. In this paper, by adjusting the dosage of polycarboxylate superplasticizer, the initial fluidity of the mortar is 240 ± 10mm, and then the mortar is placed in a plastic bowl and placed in a constant temperature and humidity standard curing box to test its bleeding rate and investigated the effects of different BD amount on the water retention performance of polycarboxylic acid water reducer.

![Mortar bleeding rate test graph](image2)

Figure 2. The result of mortar bleeding rate test
It can be seen from figure 2 that as the amount of BD increases, the bleeding rate of the mortar decreases. This is because as the amount of BD increases, the number of hydroxyl groups on the molecular chain of the polycarboxylate superplasticizer also increases, and hydrogen bonds are formed between the hydroxyl groups or between the hydroxyl groups and the water molecules. At the same time, similar micro-crosslinked structures are formed due to the formation of hydrogen bonds, increase the viscosity of the paste, reduce the exudation of free water, thereby improving water retention. Based on the comprehensive water reduction, water retention performance and cost-effectiveness advantages, 2.0% is selected as the optimal amount of BD, and the modified PCE is marked as PCE-HR.

3.3. FTIR measurement results

The infrared spectrum of the prepared low-bleeding polycarboxylate superplasticizer PCE-HR is shown in figure 3.

![Figure 3. The infrared spectrum of PCE-HR](image)

As shown in Figure 3: 3448 cm⁻¹ (O-H; N-H); 2870 cm⁻¹ (C–H); 1580 cm⁻¹, 1722 cm⁻¹ (C=O); 1106 cm⁻¹ (C–O–C); 1454 cm⁻¹ (–CH2–); 948 cm⁻¹ (C-O) and 846 cm⁻¹ (C-C). It can be seen that the prepared low-bleeding polycarboxylate superplasticizer PCE-HR contains various functional groups such as hydroxyl groups, carbonyl groups, ether groups, and alkyl groups in the molecule, which is basically consistent with the designed structure.

3.4. GPC test results

PCE-HR and PCE-S were subjected to gel permeation chromatography (GPC) test. The molecular weight data are shown in table 1.

| Sample  | Mn  | Mw  | Mp  | Mw/Mn | Conversion rate (%) |
|---------|-----|-----|-----|-------|---------------------|
| PCE-HR  | 18106 | 34115 | 28029 | 1.88  | 93.03               |
| PCE-S   | 16200 | 32375 | 26121 | 2.00  | 90.47               |

It can be seen from table 1 that, the number average molecular weight Mn of PCE-HR is 18106, the weight average molecular weight Mw is 34115, the peak molecular weight Mp is 28029, and the dispersion coefficient Mw / Mn is 1.88, there is not much difference with PCE-S, but the conversion rate is high, reaching 93.03%.
3.5. Concrete test results
In order to verify the improvement effect of PCE-HR on the bleeding of concrete, PCE-HR and PCE-S were subjected to a concrete comparison test (the polycarboxylate superplasticizers were diluted to 8% solid content) in a low temperature environment of 10 °C. C30 concrete test mix ratio (kg / m3) is m (cement): m (fly ash): m (river sand): m (large stone): m (water) = 220: 100: 780: 1060: 170. By adjusting the dosage of polycarboxylate superplasticizer, the initial expansion of concrete is in the range of 500 ± 20mm. The test results are shown in Table 2.

| Sample | dosage/% | Concrete slump /mm | Concrete expansion /mm | Bleeding rate % | Compressive strength /MPa |
|--------|----------|---------------------|------------------------|----------------|--------------------------|
|        |          | 0h 1h 0h 1h         |                        |                | 7d 28d                   |
| PCE-HR | 1.6      | 220 185 510 420     | 1.2                    | 16.8           | 33.7                     |
| PCE-S  | 1.5      | 205 150 500 360     | 3.8                    | 15.3           | 31.4                     |

It can be seen from table 2 that the PCE-HR content will be slightly higher than that of PCE-S when the initial expansion of the concrete is similar. From the initial state of fresh concrete, PCE-HR concrete has better workability. By testing the normal pressure bleeding rate of concrete with different polycarboxylate superplasticizers, the results show that the normal pressure bleeding rate of concrete with PCE-S is 3.8%, while the normal pressure bleeding rate of concrete with PCE-HR is significantly lower, only 1.2%, indicating that PCE-HR has a better water bleeding improvement effect and has significant water retention performance. From the expansion degree after 1h and the compressive strength of 7d and 28d, PCE-HR also has good slump retention and strengthening properties.

4. CONCLUSION
(1) In this study, a low bleeding polycarboxylate superplasticizer was synthesized by using 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG) as the macromonomer and unsaturated polyhydroxy compound (BD) as the functional monomer.
(2) The paste and mortar test results showed that the paste flowability and the mortar bleeding rate of the modified PCE both decreased with the increase of the amount of BD. When the BD content was 2.0%, the obtained polycarboxylate superplasticizer (PCE-HR) had better comprehensive performance.
(3) Infrared spectrum showed that PCE-HR contains various functional groups such as carboxyl, ether, and hydroxyl groups, which was basically consistent with the designed structure.
(4) The results of gel permeation chromatography showed that the molecular weight of PCE-HR was not significantly different from that of standard polycarboxylate superplasticizer PCE-S, but the conversion rate was high.
(5) The C30 concrete test results showed that PCE-HR was significantly better than PCE-S in water retention, slump retention and strengthening properties.

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