Synthesis and performance study of a highly dispersed HPEG-type polycarboxylate superplasticizer

Zeyu Lin
KZJ NEW MATERIALS CO., LTD, Xiamen 3631010, China
linzeyu350628@qq.com

Abstract—HPEG has long been widely used as an alternative to TPEG. In this study, a new high-performance HPEG-type polycarboxylate superplasticizer PCE-A was synthesized by using H₂O₂ and sodium hypophosphite/Vc redox initiation system to provide free radicals under aqueous polymerization conditions with HPEG and acrylic acid as the main raw materials. The results showed that the best performance of the synthetic polycarboxylate superplasticizer was achieved when the acid to ether ratio was 4.50, Vc was 0.25%, H₂O₂ was 0.80% and sodium hypophosphite was 1.7%, which could effectively reduce the amount of admixture without affecting the working performance of concrete, and the concrete strength was higher.

1. Introduction
With the continuous development of science and technology, people's requirements for the performance of concrete are also increasing, so the types of concrete applications continue to increase [1-3]. As the third generation of polycarboxylate superplasticizer, polycarboxylate superplasticizer is the most widely used polycarboxylate superplasticizer in the market due to its low admixture, high water reduction rate, good enhancement effect, strong molecular adjustability, and no formaldehyde used in the synthesis process [4].

At present, the polyether macromonomers used in the production process of polycarboxylate superplasticizer mainly include MPEG, APEG, TPEG and HPEG, among which TPEG and HPEG occupy most of the market [5]. In this study, a highly dispersed HPEG-type polycarboxylate superplasticizer was synthesized using HPEG and acrylic acid as the copolymer monomer, hydrogen peroxide and Vc as the initiating system and sodium hypophosphite as the chain transfer agent. The effects of different synthesis factors on the dispersion performance of polycarboxylate superplasticizer were investigated, and its application performance was compared with that of similar polycarboxylate superplasticizer with better performance in the market.

2. Experiment parts
2.1. Raw materials
Methyl allyl polyethylene glycol ether (HPEG, Mn=2400), Acrylic acid (AA), Hydrogen peroxide solution (H₂O₂), Sodium hypophosphite, Vc, Sodium hydroxide solution (NaOH), 30 wt%.

2.2. Synthesis of polycarboxylate superplasticizer (PCE)
Add HPEG, sodium hypophosphite and water to the four flasks with accurate weighing and start stirring. After the HPEG is completely dissolved in the four flasks, turn on the peristaltic constant flow...
pump and add acrylic acid solution, H2O2 solution and Vc material solution drop by drop for 2~2.5h. After the drop, keep warm for 1.0~1.5 h. After the reaction is finished, adjust the pH value to neutral with NaOH to finally produce the polycarboxylate superplasticizer PCE-A with 50% solid content.

2.3. Performance test methods

2.3.1. Gel Permeation Chromatography (GPC)
The samples were examined by gel permeation chromatography (GPC, Waters 1515/2414, Waters, USA) using 0.10 mol/L aqueous sodium nitrate as the mobile phase.

2.3.2. fluidity of cement paste
According to GB/T 8077-2012 "concrete admixture homogeneity test method", the amount of water reducing agent is 0.18% of its solid content.

2.3.3. Concrete Performance Testing
According to GB 8076-2008 "Concrete Admixtures", PCE was tested for compressive strength ratio and slump of concrete. The concrete mix ratio (kg/m³) used to evaluate the workability and strength of the concrete in this paper is: m (cement):m (sand):m (stone):m (water) = 360:830:1000:175.

3. Results and discussion

3.1. Orthogonal experimental design and analysis
A 3-level 4-factor (L934) orthogonal experiment was designed with four factors: acid to ether ratio (A), mass percentage of Vc (B), mass percentage of H2O2 (C) and mass percentage of sodium hypophosphite (D). The results of the horizontal factor table and orthogonal test are shown in Tables 1 and 2.

| Sample | A/wt% | B/ wt% | C/ wt% | D/ wt% | Fluidity of cement slurry/mm |
|--------|-------|--------|--------|--------|----------------------------|
| 1#     | 3.50  | 0.10   | 0.70   | 1.60   | 170.00                     |
| 2#     | 4.00  | 0.20   | 0.80   | 1.75   | 180.00                     |
| 3#     | 4.50  | 0.30   | 0.90   | 1.90   | 155.00                     |
| 4#     | 4.00  | 0.10   | 0.80   | 1.90   | 185.00                     |
| 5#     | 4.00  | 0.20   | 0.90   | 1.60   | 185.00                     |
| 6#     | 4.00  | 0.30   | 0.70   | 1.75   | 185.00                     |
| 7#     | 4.50  | 0.10   | 0.90   | 1.75   | 200.00                     |
| 8#     | 4.50  | 0.20   | 0.70   | 1.90   | 200.00                     |
| 9#     | 4.50  | 0.30   | 0.80   | 1.60   | 195.00                     |
| k1j    | 168.33| 185.00 | 185.00 | 183.33 | 183.33                     |
| k2j    | 185.00| 188.33 | 186.67 | 188.33 | 188.33                     |
| k3j    | 198.33| 178.33 | 180.00 | 180.00 | 180.00                     |
| R      | 30.00 | 10.00  | 6.67   | 8.33   | -                          |

Table.1 The orthogonal experiment design factor

Table.2 Results and analysis of the orthogonal experiment
Table 2 shows the results of the PCE orthogonal test, from the table, it can be seen that when the orthogonal test is carried out, the R value can reflect the influence of each factor, where A to D are 30.00, 10.00, 6.67 and 8.33 respectively, and the order of influence on PCE is \( A > B > D > C \). Through the orthogonality, it can be seen that the best synthesis process is \( A_3B_2C_2D_2 \), that is, the acid to ether ratio is 4.50, B is 0.20%, C is 0.80% and D is 1.75%.

3.2. effect of acid ether ratio on properties of PCE
According to the results of the orthogonal test, the best process was selected and the rest of the conditions were kept constant to investigate the effect of acid to ether ratio on the performance of polycarboxylate superplasticizer, the experimental results are shown in Figure 1.

As can be seen from Figure 1, when the acid to ether ratio is less than 4.5, the fluidity of cement paste increases with the increase of the acid to ether ratio; when the acid to ether ratio is 4.5, the fluidity of cement paste increases with the increase of the acid to ether ratio reaches its peak. This is due to the fact that as the acid to ether ratio increases, the effective adsorption amount increases, and its adsorption on the surface of cement particles provides electrostatic repulsion to disperse the cement particles, thus making the dispersion performance of polycarboxylate superplasticizer improve; when the acid to ether ratio is too large, the number of monomers on the main chain is relatively reduced, which cannot provide sufficient electrostatic repulsion to reduce the spatial site resistance effect, thus leading to the reduction of fluidity of cement paste.

3.3. Effect of Vc on the initial paste fluidity of PCE
The best process was selected and the rest of the conditions were kept constant to investigate the effect of Vc dosage on the performance of polycarboxylate superplasticizer, the experimental results are shown in Figure 2.

As can be seen from Figure 2, the fluidity of paste increases with the increase of Vc dosage. This is due to the fact that as the Vc dosage increases, the number of monomers on the main chain increases, thus leading to the increase of fluidity of paste.
As can be seen from Figure 2, with the increase of Vc dosage, the fluidity of cement paste first increases and then decreases. May be due to, with the increase of Vc dosage, the system due to H₂O₂ will Vc oxidation, the release of free radicals more, the reaction activity is higher, so the synthetic polycarboxylate superplasticizer dispersion performance is better; when the amount of Vc is greater than 0.25%, H₂O₂ gradually consumed, its release of carboxyl groups gradually reduced, so the synthetic polycarboxylate superplasticizer dispersion performance gradually reduced. Therefore, the best amount of Vc is 0.25% of the mass of large monomer.

3.4. Effect of sodium hypophosphite on the initial paste fluidity of PCE

The best process was selected and the rest of the conditions were kept constant to investigate the effect of sodium hypophosphite dosage on the performance of polycarboxylate superplasticizer, the experimental results are shown in Figure 3.

![Fig. 3 Effect of sodium hypophosphite on the initial paste fluidity of PCE](image)

From Fig. 3, it can be seen that with the increase of sodium hypophosphite dosage, the initial flow of fluidity of cement paste showed first increase and then decrease. The main reason may be that, at the beginning, as the dosage of sodium hypophosphite increases, the length of the main chain shortens, the proportion of long side chains increases, its spatial dispersion effect is enhanced and the initial dispersibility increases; however, when the dosage of sodium hypophosphite exceeds 1.7%, the main chain is too short, the speed of adsorption of cement slows down and the initial dispersibility decreases. Therefore, the optimum amount of sodium hypophosphite is 1.7% of the mass of the macromonomer.

3.5. GPC

The polycarboxylic acid water reducing agent (PCE-A) synthesised by the optimum process was subjected to GPC tests with a commercially available comparable product (PCE-S) with better performance. Table 3 shows the gel permeation chromatography data for PCE-S and PCE-A.

| Sample | Mn   | MW   | MP    | MW/Mn | Conversion rate/% |
|--------|------|------|-------|-------|-------------------|
| PCE-S  | 31730| 72368| 43147 | 2.280730 | 86.61             |
| PCE-A  | 24220| 45010| 38773 | 1.858391 | 90.79             |

The data show that compared with PCE-S, PCE-A has lower number average molecular mass, heavier average molecular mass and peak molecular mass, more concentrated molecular distribution and higher conversion rate, which is conducive to obtaining water reducing agent products with excellent dispersibility.
3.6. **Concrete application performance**

The polycarboxylate superplasticizer (PCE-A) synthesised by the optimum process was tested against a commercially available product with better performance (PCE-S) for concrete and the test results are shown in Table 4.

| Sample  | Dosage/% | (Slump/Slump expansion) /mm | Compressive strength/MPa |
|---------|----------|----------------------------|--------------------------|
|         |          | 0 h       | 1 h       | 3 d       | 7 d       | 28 d      |
| PCE-S   | 1.63     | 215/585   | 205/380   | 26.7      | 36        | 43.3      |
| PCE-A   | 1.42     | 220/590   | 200/400   | 27.6      | 36.4      | 46        |

The results show that the PCE-A synthesised in this study can achieve the same working performance with reduced admixture and its concrete has a higher compressive strength, indicating the superior performance of PCE-A.

4. **Conclusions**

(1) A polycarboxylic acid high performance water reducing agent PCE-A was synthesised by free-radical polymerisation of the macromonomer HPEG at room temperature under the following conditions: acid to ether ratio of 4.50, Vc of 0.25%, H2O2 of 0.80% and sodium hypophosphite of 1.7%.

(2) The polycarboxylate superplasticizer reducing agent prepared under the best process conditions compared with similar commercially available products, to achieve the same work performance, the amount of admixture can be reduced by 13%, and the concrete strength is higher, has a broad application prospects.

(3) The adsorption mechanism of polycarboxylate superplasticizer reducing agents and their effect on cement hydration have not been systematically investigated and tested in this paper. Further research and optimisation will be carried out in future trials.

**References**

[1] Xiaobin Qian, Shilin Zhao, Xiaobing Zhang, Xiaobin Huang. Research on properties and acting mechanisms of concrete superplasticizers [J]. Journal of Nanjing Tech University (Natural Science Edition), 2002(02): 61-64.

[2] J. Plank et al. Chemical admixtures — Chemistry, applications and their impact on concrete microstructure and durability [J]. Cement and Concrete Research, 2015, 78: 81-99.

[3] Zhenping Sun. Six Urgent Problems in the Further Study on Polycarboxylate Based Plasticizers [J]. Journal of Building Materials, 2020, 23(01): 128-129.

[4] Shanshan Qian et al. Synthesis, characterization and working mechanism of a novel polycarboxylate superplasticizer for concrete possessing reduced viscosity [J]. Construction and Building Materials, 2018, 169: 452-461.

[5] Yexiang Wang, Wenjuan Wang. Research Progress of Naphthalene Series Highly Efficient Water Reducing Agent [J]. Chemical Enterprise Management, 2018(04): 199-200.