Synthesis of the VPEG Polycarboxylate Superplasticizer with Controllable Activity and Its Properties

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Abstract. This paper focuses on the synthesis of a kind of VPEG polycarboxylate superplasticizer with controllable activity with 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG), acrylic acid (AA) and fumaric acid (FMA) as the main raw materials. Through the experimental results, it can be found that the optimum process conditions are as follows: the water-reducing admixture has ideal fluidity and workability in concrete, with the temperature of 20℃, the reaction system concentration of 40%, the mass ratio of acid to ether of 9.2%, and the initiator and the chain-transfer agent respectively accounting 0.3% and 0.09% of the total mass.

1.Introduction

With the advancement of admixtures and concrete industries, buildings such as skyscrapers, grand bridges and long tunnels are frequently constructed, which call for the concrete with high performance and high strength. But in the process of mixing construction, the concrete with high performance and high strength often encounter problems such as partial viscosity, poor flow performance, excessive slump loss, amplification, segregation, and poor sensitivity [1]. These problems are all related to the poor gradation of sand and gravel, large mud content, and poor-quality admixtures. The effect of polycarboxylate superplasticizer on the performance of concrete cannot be ignored. Because of its mature production technology, relatively simple production process, economic applicability, diversified and controllable molecular structure, and the concrete with the advantages of high-water reduction rate under the condition of low parameters, polycarboxylate superplasticizer has become one of the indispensable admixtures in the market.

Polycarboxylate superplasticizer is mainly prepared by the reaction of polyether macromonomer with the acrylic acid containing hydrophilic group in unsaturated double bonds and its derivatives. It has superior water-reduction rate, long slump protection, good dispersion to cement [2], and obvious improvement on the concrete workability and compressive strength. Its molecular structure mainly contains carboxyl, hydroxyl, amino, sulfonic acid and other functional groups[3].

Due to the poor gradation of sand and gravel materials, large mud content and the introduction of inferior admixtures, and unqualified site operation of polycarboxylate superplasticizer, it is necessary to modify it, so as to ensure its performance can meet requirements of site operation. As a kind of vinyl-terminated polyether macromonomer with high reactivity, VPEG is mainly prepared by
ethoxylation with 4-hydroxybutyl vinyl ether as the starting agent \[4\]. In order to solve the quality problems caused by the difficulty of concrete construction and poor workability, in this paper, 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG), acrylic acid (AA) and fumaric acid (FMA) are used to do reaction experiment, so as to overcome difficulties in concrete construction and solve the problems of poor workability \[5\].

2. Experiment

2.1. Raw Materials and Equipment

The details of raw materials used in this experiment are shown in Table 1:

| Raw materials                                      | Specifications                | Factory                                      |
|----------------------------------------------------|-------------------------------|----------------------------------------------|
| 4-hydroxybutyl vinyl polyoxyethylene ether VPEG    | Molecular weight: 3000        | Lin'an Technology chemical Co., Ltd.         |
| Acrylic acid AA                                     | Main content: \(\geq 99.5\%\) | Fujian Binhai Chemical Industry Co., Ltd.    |
| Mumaric acid FMA                                    | Main content: \(\geq 99.0\%\) | China Bluestar Harbin Petrochemical Co., Ltd.|
| Methylallyl sulfonate TGA                          | Main content: \(\geq 99.0\%\) | Jinan Blueprints Chemical Co., Ltd.          |
| Hydrogen peroxide solution \(\text{H}_2\text{O}_2\) | Main content: \(\geq 27.5\%\) | Guiyang Nanming Hongfeng Chemical Co., Ltd.  |
| Ascorbic acid Vc                                    | Main content: \(\geq 99.5\%\) | Sichuan Lingde Chemical Co., Ltd.            |
| Sodium hydroxide NaOH                              | Solid content: \(\geq 30\%\)  | Guiyang Nanming Hongfeng Chemical Co., Ltd.  |
| Cement C                                           | Water of standard consistency: \(26.2\%\) | Guizhou Hongshi Cement Co., Ltd.             |
| Mechanism of green sand                             | Fineness modulus: \(2.6-3.4\) | Zhongjiao Road and Bridge North China Engineering Co., Ltd. |
| Gravel G1                                          | Particle size: 5-10mm         | Zhongjiao Road and Bridge North China Engineering Co., Ltd. |
| Gravel G2                                          | Particle size: 10-20mm        | Zhongjiao Road and Bridge North China Engineering Co., Ltd. |
| Water W                                            | Water supply                  | Made by oneself                             |
| Common polycarboxylic acid water reducer PC        | Solid content: \(40\%\)      | KZJ New Materials Group Guizhou Co., Ltd.    |

The details of the main instruments used in this experiment are shown in Table 2:
| Laboratory apparatus | Type             | Main technical parameters            |
|----------------------|------------------|--------------------------------------|
| Water bath           | DFY-5L/30℃       | Capacity: 5000ml                     |
| Electric mixer       | JJ-1             | Rotary speed: 3000r/min              |
| Peristaltic pump     | BT100-01         | Rotary speed: 0.1 ~ 100 rpm          |
| Cement mixer         | NJ-160B          | Automatic control of program time: 255±3s |
| Single horizontal shaft test mixer | HJW-60 | Quota mixing quantity: 60L |
| Digital pressure testing machine | DYE-2000 | Maximum load: 2000KN |
| Gel permeation chromatograph | 2414 | Moving phase: 0.1mol/L NaNO3 liquor |
| Infrared spectrometer | FTIR-850         | KBr The chip daub                    |

### 2.2. Synthesis Method

First, weigh a certain amount of VPEG and FMA into a four-port flask with a stirrer. Then add appropriate amount of W, turn on the stirrer, set the temperature (-10 ~ 30℃), and drop the solutions of A, B and C. The three solutions are respectively composed of H2O2 and W, AA and W, and TGA, Vc and W. When the dropping reaction of A for 2h, the dropping reaction of B and C for 2h and constant temperature reaction for 1h, then adding 2% NaOH and stirring for 5 min, a light yellow and transparent functional controllable polycarboxylate superplasticizer (PEFA) with the solid content of 40% can be obtained.

### 2.3. Performance Test Methods

1. Fluidity of cement paste: the water cement ratio is 0.29, and the solid content of admixture is 0.23% by using Hong Shi P.O42.5 cement according to GB/T 8077-2012 Test Method for Homogeneity of Concrete Admixtures.

2. Concrete performance test: according to GB 8076-2008 Concrete Admixtures, C50 concrete performance test is carried out, the admixture contains solid is 15% and content is 1.3%. The concrete mix can be shown in Table 3:

| Strength grade | C | S | G1 | G2 | W | Amixture |
|---------------|---|---|----|----|---|----------|
| C50           | 497 | 790 | 200 | 804 | 159 | 5.96     |

### 3. Results and Analysis

#### 3.1. The Effect of Mass ratio of Acid to Ether on the Fluidity of PEFA Cement Paste

When the reaction temperature is 20℃ and the concentration of reaction system is 50% (the mass ratio of H2O2, VC, 30% NaOH, TGA and total mass is 0.3%, 0.09%, 2.5% and 0.12%, respectively, and the mass ratio of acid to ether is 8.6%, 8.8%, 9.0%, 9.2%, 9.4%, 9.6%, respectively), the test results of the influence of mass ratio of acid to ether on the fluidity of PEFA cement paste are shown in Figure 1:
Figure 1 effect of mass ratio of acid to ether on fluidity of PEFA cement paste

It can be seen from Figure 1 that with the increase of mass ratio of acid to ether, the initial fluidity of water purification slurry increases first and then decreases. When the mass ratio of acid to ether is 9.4%, the initial fluidity of cement paste reaches the peak, which is 242mm. After 2 hours of loss, the fluidity of cement paste is 202, which is larger. When the mass ratio of acid to ether is 9.2%, the distance between the two broken lines is the shortest. It can be seen that when the mass ratio of acid to ether is 9.2%, the initial cement paste of PEFA is larger and the loss is smaller.

3.2. The Effect of Temperature on the Fluidity of PEFA Cement Paste

When the concentration of reaction system is 50%, the mass ratio of acid to ether is 9.2%, and other conditions remain unchanged, PEFA is synthesized at -10℃, 0℃, 10℃, 20℃ and 30℃, respectively. The test result of the influence of different temperature conditions on the fluidity of cement paste is shown in Figure 2:

Figure 2 effect of temperature on fluidity of PEFA cement paste

It can be seen from Figure 2 that when the reaction temperature is -10℃, the maximum fluidity of PEFA initial cement paste is 232mm; when the reaction temperature is 30℃, the minimum fluidity of PEFA initial cement paste is 184mm. The trend of initial cement paste fluidity can be seen, In the temperature range of -10 ~ 30℃, the initial fluidity of PEFA cement paste decreases with the increase of reaction temperature, while the fluidity of PEFA increases with the increase of reaction temperature. When the temperature is 20℃, the distance between the two fluidity broken lines is the shortest. It can be seen that under the temperature condition, the initial fluidity of cement paste and the fluidity of 2-hour cement paste are optimal.

3.3. The Effect of the Concentration of Reaction System on the Fluidity of PEFA Cement Paste

When the reaction temperature is 20℃, the mass ratio of acid to ether is 9.2%, other conditions remain unchanged. The influence of reaction system concentration of 35%, 40%, 45%, 50%, 55% on the fluidity of cement paste is investigated. The test results are shown in Figure 3.
It can be seen from Figure 3 that with the increase of reaction system concentration may cause initial fluidity fluctuation of PEFA. When the concentration of reaction system is 45%, the initial fluidity of PEFA reaches its peak of 240mm. Meanwhile, the fluidity of 2h cement paste decreases with the increase of reaction system concentration. When the concentration of the reaction system is around 40%, the two broken lines intersect, which indicates that the 2h difference of fluidity of cement paste is the smallest, and the fluidity loss is the lowest. It indicates that the process conditions are optimal under the concentration of the reaction system when the concentration of reaction system is 40%.

3.4. Effect of Dropping Time on Fluidity of PEFA Cement Paste
When the reaction temperature is 20℃, the concentration of reaction system is 40%, the mass ratio of acid to ether is 9.2%, and other conditions remain unchanged, the test results of the influence of dropping time 1.0h, 1.5h, 2.0h, 2.5h, 3.0h on the fluidity of cement paste is shown in Figure 4.

It can be seen from Figure 4 that with the prolongation of dropping time, the initial fluidity of cement paste gradually decreases, the inflection point appears at 2.5h, and the fluidity of cement paste slightly increases, while the fluidity of 2h cement paste increases at first and then decreases with the extension of dropping time. When the dropping time is 2.5h, the difference of fluidity is the smallest and the distance between the two broken lines is the shortest. When the dropping time is 2.5h, the process data is the best.

3.5. Concrete Performance Test
According to the above optimal conditions, when the final reaction temperature is 20℃, the concentration of reaction system is 40%, the reaction dropping time is 2.5h, the mass ratio of acid to ether is 9.2%, the mass ratio of H₂O₂, Vc, 30% NaOH solution and TGA to is 0.3%, 0.09%, 2.5% and
0.12%, the workability of the prepared PEFA and PES can be compared. The two superplasticizers can be diluted to a solution with 15% solid content, and C50 concrete test can be conducted according to Table 3. When the mixing time of concrete mixer is set to 2 min, the observation results of concrete out of machine state are shown in Figure 5:

(a) drawing of concrete with PES   (b) drawing of concrete with PEFA

Figure 5 comparison of the states of concrete out of machine between PES and PEFA

It can be seen from Figure 5 that the concrete mixed with common polycarboxylate water reducer (PES) has poor concrete fluidity, less paste and thicker concrete, and the stone exposed to the concrete surface is serious; the concrete with newly synthesized polycarboxylate water reducer (PEFA) has better fluidity, more slurry and better encapsulation of stone. From the view of concrete state, the fluidity, cohesiveness and wrapping property of concrete are obviously better after adding the newly synthesized polycarboxylate water reducer (PEFA), which can solve the problems of difficult construction and poor workability of concrete.

The slump, expansion, setting time, air content and compressive strength of the above concrete are tested. The experimental results can be shown in Table 4:

| Sample number | Slump/ Expansion (mm/mm) | Concrete air (%) | Rewinding time (s) | Setting time (h) | Compressive strength (MPa) |
|---------------|---------------------------|------------------|-------------------|-----------------|---------------------------|
|               | Initial 2h |                  |                   | Initial set     | Final set     | 3d  | 7d  | 28d |
| PES           | 215/565    | 185/475          | 2.6               | 5.4             | 7.0  | 9.0  | 36.4 | 51.0 | 58.2 |
| PEFA          | 230/585    | 215/520          | 2.4               | 3.6             | 7.0  | 9.0  | 36.9 | 51.6 | 59.5 |

It can be seen from the test results in Table 4 that the initial slump and expansion of PES concrete with 15% solid content are 215mm and 565mm respectively; the slump loss and expansion loss of concrete are 30mm and 90mm respectively after 2h. Compared with the concrete with 15% solid PEFA admixture, the initial slump and expansion of concrete with 15% solid PEFA admixture are 15mm larger and 20mm larger; after 2h of concrete loss, the loss of slump and expansion is smaller, the slump loss is 15mm, and the expansion loss is 60mm. The differences of air content and setting time of concrete between the two are small, but the compressive strength of concrete with 15% solid PEFA in 3d, 7d and 28d is slightly higher. It can be seen from the concrete performance test that the new additive prepared by water reducing and slump retaining polycarboxylate mother liquor (SC) can greatly improve the fluidity, cohesiveness, wrapping property of concrete, and the working performance of concrete to a certain extent, which has high use value.

3.6. GPC Analysis
The results of GPC test of PEFA are shown in Table 5.

| Sample number | Mn   | Mw   | Mp   | Mw/Mn | Conversion rate % |
|---------------|------|------|------|-------|------------------|
| PES           | 26715| 52362| 37526| 1.96   | 91.53            |
According to the GPC data test in Table 5, the weight average molecular weight of PES is relatively large, which is 52,362 with its polydispersity coefficient of 1.96. The average molecular weight of PEFA is 43,725, with its polydispersity coefficient of 1.72, a relatively narrow molecular weight distribution and a relatively large conversion rate.

3.7. The Analysis on Infrared Spectrum

The functional controllable polycarboxylate superplasticizer (PEFA) can be analyzed in terms of infrared spectrum, the result of which can be shown in Figure 6.

![Figure 6 infrared spectrum of functional controllable polycarboxylate superplasticizer (PEFA)](image)

As shown in Figure 6, 3,402 cm\(^{-1}\) is the stretching vibration absorption peak of hydroxyl (-OH), 2,874 cm\(^{-1}\) is the stretching vibration absorption peak of alkyl (-C-H), 1,466 cm\(^{-1}\) and 1,344 cm\(^{-1}\) are the in-plane bending vibration absorption peaks of alkyl (-C-H), 1,723 cm\(^{-1}\) is the stretching vibration absorption peak of alkyl (-C=CO-O-), and 1,112 cm\(^{-1}\) is the stretching vibration absorption peak of ether bond (-C-O-C). It can be inferred that the structural formula is shown in Figure 7.

![Figure 7 structure diagram of functional controllable polycarboxylate superplasticizer](image)

Polimerization degree: a, b, c and d

4. Conclusion

(1) Through screening the influence conditions of mass ratio of acid to ether, dropping time, reaction system concentration and dropping time on the fluidity of PEFA cement paste, it can be seen that, when the mass ratio of acid to ether is 9.2%, the reaction temperature is 20°C, the concentration of reaction system is 40%, the reaction time is 2.5h, the mass ratio of H\(_2\)O\(_2\), Vc, 30% NaOH, TGA and total mass is 0.3%, 0.09%, 2.5%, 0.12% respectively, the process level of the functional controllable VPEG polycarboxylate superplasticizer can reach its peak. When the dosage of PEFA is 0.23%, the initial fluidity of cement paste is larger, and the fluidity loss of 2h cement paste is the minimum.
(2) The results show that the fluidity, cohesiveness and encapsulation of concrete with PEFA are better than those with PES. The concrete fluidity is 20 mm larger than that of PES. The concrete cohesiveness and encapsulation of concrete show that there are no exposed stones on the surface of concrete, and the slurry is more abundant. The construction performance of concrete can be effectively improved by adding functional controllable polycarboxylate superplasticizer (PEFA).

(3) According to the GPC data, when the polydispersity coefficient of the synthesized PEFA is 1.72 and the molecular weight distribution is narrower. The results of infrared spectrum show that the molecular structure of the product has carboxyl, ester, polyoxyethylene, which is consistent with the molecular structure of the designed water-reducing admixture.

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