Process design and optimization of VPEG-PCEs

Youzhe Shao, Guangxing Lai, Yunhui Fang and Yuanqiang Guo
KZJ New Materials Group Co., Ltd., Xiamen, Fujian, 361101, China
E-mail: 157198689@qq.com

Abstract. The VPEG type polycarboxylate superplasticizer (PCE-A) was synthesized by using 4-hydroxybutylvinyl polyoxyethylene ether (VPEG) as macromonomer, hydrogen peroxide ($H_2O_2$) reducing agent (sodium formaldehyde sulfoxylate) as redox system, and thioglycolic acid as the chain transfer agent. The effects of synthesis temperature, acid-ether ratio and reaction time on the dispersion properties of polycarboxylate superplasticizer were investigated experimentally, and the results showed that the optimal preparation process of PCE-A is n(AA):n(VPEG)-4000=4.4:1, hydrogen peroxide, formaldehyde sodium hydrogen sulfite and thioglycolic acid respectively account for the total mass of VPEG monomer 0.75%, 0.2%, and 0.4%, the optimum synthesis temperature, dripping time, and constant temperature reaction time were 14 ℃, 60 min, and 60 min, respectively. The concrete results showed that the dispersibility and slump retention performance of PCE-A were better than the commercially available VPEG type polycarboxylate superplasticizer PCE-W01, PCE-W02 and PCE-W03.

1. Introduction

4-hydroxybutyl vinyl polyoxyethylene ether (VPEG), a new macromonomer to synthesize polycarboxylate water reducing agent, exhibits superior polymerization activity compared with allyl alcohol polyoxyethylene ether (APEG), prenyl alcohol polyoxyethylene ether (TPEG), methacrylic polyoxyethylene ether (HPEG)\cite{1-4}. Munich University of Technology in Germany studied the sensitivity of VPEG type PCE to clay components, and some related researches also have been done by domestic researchers, for example Zeng Jun investigated the synthesis technology of the VPEG type PCE and the result showed that the water-reducing agent has excellent concrete work performance\cite{5}. Lai Huazhen et al. used VPEG to prepare a PCE which is insensitive to the dosage, cement raw materials and temperature\cite{6}. At present, there are more and more manufacturers in China launch VPEG type PCE, indicating that VPEG monomer and its PCE have gradually revealed its excellent features, with broad development prospects and huge market space.

In this paper, we came up with a new type of Carboxylic acid water reducing agent PCE-A, which used hydrogen peroxide/reducing agent to form a redox initiation system to initiate polymerization, 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG) as macromonomer and thioglycolic acid as the chain transfer agent. Through the single factor adjustment of PCE-A process, the effects of synthesis temperature, acid-ether ratio, injection time and constant temperature on the performance of VPEG-type PCE were discussed. This study has certain guiding significance for the development of VPEG-type polycarboxylate superplasticizer.

2. Experimental

2.1. Materials
The raw materials used in the synthesis of this experiment include: 4-hydroxybutyl vinyl ethoxylate (VPEG, domestic, molecular weight 4000), acrylic acid (AA), hydrogen peroxide, thioglycolic acid, 32% sodium hydroxide, formaldehyde sulfuric acid Sodium hydrogen is commercially available in industrial grade.

2.2. Synthesis
Hydrogen peroxide (H$_2$O$_2$), water, acrylic acid (AA) and VPEG monomer were placed to the four-necked flask equipped with a stirrer. With setting the temperature of the water bath to between 4-30℃, keep stirring until the temperature of the four-necked flask solution reaches the set temperature. Then through the peristaltic pump feeding device, the solution A,B,C were fed dropwise as follows. The solution A (the mass ratio of AA to VPEG is 5%) was prepared by acrylic acid, sodium hydroxide and water. The solution B was prepared by reducing agent sodium formaldehyde sulfoxylate and water, and the solution C was prepared from thioglycolic acid and water. After the dropwise addition, it need to be kept at a constant temperature for 45 minutes, and the pH was adjusted to 6-7 by adding base liquid. Therefore, we can obtain a VPEG type polycarboxylate superplasticizer with solid content of 40%.

2.3. Performance test method

2.3.1. Cement paste fluidity test. According to GB/T 8077-2012 "Methods for testing uniformity of concrete admixture", the amount of cement was kept at 300 g and the water-cement ratio was 0.29.

2.3.2. Concrete performance test. The concrete performance was tested according to GB/T 50081-2002 "Standard for testmethod of mechanical Properties on ordinary concrete" and GB/T50080-2016 "Standard for test method of performance on ordinary fresh concrete".

2.3.3. GPC analysis. Molecular weight was performed by gel permeation chromatography (GPC) using Ultrahydrogel Liner Column and Ultrahydrogel 120 Column made by Waters. The elution solvent used was 0.1 M of NaNO$_3$ aqueous solution.

3. Experimental results and discussion

3.1. Effect of synthesis temperature on performance of PCE
The total molar mass ratio of AA to VPEG was maintained at 4.8:1, and the mass of hydrogen peroxide, sodium formaldehyde sulfoxylate and thioglycolic acid were 0.75%, 0.2% and 0.4%, respectively, of the total mass of the VPEG monomer. Testing the performance of the polycarboxylate superplasticizer synthesized at a temperatures of 4 ℃ to 30 ℃, the results is shown in figure 1.

Figure 1. Performance of water reducing agent at different synthesis temperatures
As can be seen from figure 1, when the temperature is lowered by 2 °C under high temperature, the cement paste fluidity is increased by about 9 mm. The fluidity of the cement paste increases with the decrease of the synthesis temperature, but when the temperature is too low, the increase rate of fluidity of the cement paste is significantly reduced. In addition, the performance of the polycarboxylate superplasticizer synthesized at low temperature is significantly better than the high temperature condition, because VPEG macromonomer is unstable at high temperature, easy to decompose, resulting in long side chain in the PCE structure shortening and the steric hindrance of the PCE structure becomes smaller. However, when the temperature is too low, the chain initiation rate is affected, resulting in a slower polymerization rate. Considering both cost and effect, it is preferred to select a polymerization temperature of 14 °C to 16 °C.

3.2. Effect of acid ether ratio on performance of PCE

The synthesis temperature was kept at 14 °C, the mass of hydrogen peroxide, sodium formaldehyde sulfoxylate and thioglycolic acid were 0.75%, 0.2% and 0.4%, respectively, of the total mass of the VPEG monomer. Adjust the molar mass ratio of AA to VPEG to 5.2, 4.8, 4.4, 4.0, 3.6, 3.2, 2.8, respectively and the effect of different molar mass ratios on the performance of cement paste was studied. The results are shown in figure 2.

![Figure 2. Performance of water reducing agent with different acid-ether ratio](image)

It can be seen from figure 2 that as the ratio of acid to ether increases, the pulp fluidity of the synthesized PCE increased first and then decreased slightly. When the ratio of acid to ether is 4.4, the fluidity of the cement paste reaches a maximum of 238 mm. This is because when the ratio of acid ether is too low, the carboxylic acid in the PCE structure is low, and the effective adsorption amount is small, resulting in a small initial fluidity of the cement paste. As the ratio of acid to ether increases, the effective adsorption amount of PCE increases, and the macroscopic performance shows an increase in the fluidity of the cement paste. However, when the ratio of acid ether is too large, the fluidity of the cement paste will decrease. This is because the ratio of acid ether is too large, resulting in a decrease in the density of the long side chain, a decrease in steric hindrance, and a macroscopic decrease in the fluidity of the cement paste. According to the performance of the cement paste under the same dosage, the optimum acid-ether ratio is 4.4:1.

3.3. Effect of reaction time on performance of PCE

The synthesis temperature was kept at 14 °C, the mass of hydrogen peroxide, sodium formaldehyde sulfoxylate and thioglycolic acid were 0.75%, 0.2% and 0.4%, respectively, of the total mass of the VPEG monomer, and the total molar mass ratio of AA and VPEG was 4.4 :1. By changing the injection time, constant temperature reaction time, and performing gel chromatography test on the synthesized water reducing agent samples 1~9, the monomer conversion was measured as shown in table 1.
Table 1. Effect of injection time and constant temperature on monomer conversion rate

| Serial number | Injection time (min) | Constant temperature time (min) | Total reaction time (min) | Conversion rate (%) |
|---------------|----------------------|---------------------------------|--------------------------|---------------------|
| 1             | 30                   | 30                              | 60                       | 69.94               |
| 2             | 30                   | 45                              | 75                       | 75.72               |
| 3             | 30                   | 60                              | 90                       | 76.47               |
| 4             | 60                   | 30                              | 90                       | 79.05               |
| 5             | 60                   | 45                              | 105                      | 83.26               |
| 6             | 60                   | 60                              | 120                      | 85.01               |
| 7             | 90                   | 30                              | 120                      | 84.06               |
| 8             | 90                   | 45                              | 135                      | 85.08               |
| 9             | 90                   | 60                              | 150                      | 85.12               |

The effects of different injection time and constant temperature reaction time on the performance of cement paste were tested, and the results are shown in Figure 3.

![Figure 3. Effect of different drop Time and constant temperature reaction Time on the performances of cement paste](image)

It can be seen from Figure 3 that the fluidity of the water-reducing agent samples with the serial numbers of 1, 2, 3, 7, 8, and 9 is significantly lower than that of the samples with the serial numbers of 4, 5, and 6 under the same dosage. This is because when the injection time is 30 minutes, the dripping speed is too fast, and the total reaction time is short, resulting in low conversion of monomers and low fluidity of cement paste. When the injection time is 90 min, the total reaction time is long and the monomer conversion rate is large. However, due to the monomer dropping rate is too slow during the injection stage, the side chain density of the polymer is low, which can not produce enough steric hindrance effect. The macroscopic performance of the polymer is that the fluidity of the cement paste is low. When the injection time is 60 min, the suitable dripping speed ensures a large side chain density in the polycarboxylate superplasticizer structure, and sufficient reaction time makes the monomer conversion rate higher. Comparing the samples 4, 5, and 6, it can be found that the order of the monomer conversion rate and the cement paste fluidity of the three samples are all: sample 6 > sample 5 > sample 4. In summary, when the injection time and the constant temperature reaction time are both 60 min and the total reaction time is 120 min, the performance of the water reducing agent is best, and the water reducing agent synthesized by the process is named PCE-A.
3.4. Concrete performance test
Keep the experimental conditions unchanged, as shown in table 2 for concrete materials and mix ratios. The PCE-A synthesized under the optimal process conditions was compared with the commercially available VPEG-type polycarboxylate superplasticizer PCE-W01, PCE-W02 and PCE-W03 under the equal-folding solid content (The solid content of both PCE-A and PCE-W03 is 40%, the solid content of both PCE-W01 and PCE-W02 is 50%), and the experimental results are shown in figure 4 to figure 6.

| Material variety | C  | S1  | G1  | G2  | W  |
|------------------|----|-----|-----|-----|----|
| Model            | P.O42.5(R) | Medium sand (Mx=2.8) | Gravel (20-40mm) | Gravel (10-20mm) | Tap water |
| Dosage /kg·m$^{-3}$ | 380 | 175 | 310 | 730 | 175 |

![Figure 4. Comparison of compressive strength](image)
![Figure 5. Comparison of slump flow](image)
![Figure 6. Comparison of slump](image)

It can be seen from figure 4 that under the same experimental conditions, the 3d and 7d compressive strength of PCE-A are higher than the commercially available VPEG type polycarboxylate superplasticizer PCE-W01, PCE-W02 and PCE-W03. As can be seen from figure 5, the initial expansion and 60min expansion of PCE-A are 535 mm and 390 mm, respectively, which are larger than the other three commercially available samples. It shows that its initial dispersion is better. As can be seen from figure 6, the slumps of PCE-A, PCE-W01, PCE-W02 and PCE-W03 were reduced by 25 mm, 25 mm, 35 mm and 30 min, respectively, from 0 to 60 min. It shows that the slump retention of PCE-A and PCE-W01 is better among the four samples, but the initial slump and the 60
min slump of PCE-A are the largest. Therefore, the overall performance of PCE-A is superior to the commercially available VPEG-type polycarboxylate superplasticizer PCE-W01, PCE-W02 and PCE-W03.

4. Conclusion
The effects of synthesis temperature, acid-ether ratio and reaction time on the dispersion properties of polycarboxylate superplasticizer PCE-A were investigated. This study demonstrates that the optimum acid-ether ratio for synthetic PCE-A is n(AA): n(VPEG-4000) = 4.4:1. The ratio of hydrogen peroxide, reducing agent sodium formaldehyde sulfoxylate and thioglycolic acid to total mass of VPEG monomer were 0.75%, 0.2% and 0.4%, respectively. The optimum synthesis temperature, injection time and constant temperature reaction time were 14 ℃, 60 min, and 60 min, respectively.

Under the same experiment and equal-folding conditions, the overall performance of PCE-A is better than that of commercially available VPEG type polycarboxylate superplasticizer PCE-W01, PCE-W02 and PCE-W03 by comparing the initial dispersion and the slump retention of concrete.

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