Study on the Preparation and Performance of Hexa-carbon Polycarboxylate Superplasticizer with High Workability

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ABSTRACT: In this paper, 4-hydroxybutylvinyl polyoxyethylene ether (VPEG), methacrylic acid (MA) and methylene phosphate (MEPA) are used as main raw materials to synthesize a hexa-carbon polycarboxylate superplasticizer with high workability under the action of an initiator. The test results show that the superplasticizer has high water-reducing rate and good slump-retention, and its workability is greatly increased, which can be used in practical concrete projects that have high requirements.

1. Introduction
With the increasing construction of national infrastructure, the application of concrete and concrete admixtures is getting more and more common. On one hand, many highways, high speed railways and high-rise buildings are being constructed. On the other hand, sand and gravel materials are being exhausted. Many concrete enterprises use sand and gravel materials with poor quality for survival and development. Moreover, enterprises that manufacture concrete admixtures are facing challenges of making high quality products, and providing good technologies and services brought by high requirements of the workability of concrete in construction sites.

Among concrete admixtures, polycarboxylate superplasticizer is the most important one and used the most frequently, which has become an essential component of concrete [1]. To a great extent, the quality of polycarboxylate superplasticizer determines the scope of the application of concrete admixtures.

The workability of concrete mixed with traditional C4 and C5 polycarboxylate superplasticizer is poor [2]. Generally speaking, its performance can be improved by mixing proper amount of air entraining agent, water-retaining agent or viscosity modifier, but it will greatly increase both the cost of production and the complexity of the additive formulas. Moreover, the use of other additives will cause the change of the quality of concrete. Especially when the polycarboxylate superplasticizer and air entraining agents are combined, it will be difficult to eliminate the harmful air bubbles which act on concrete, and this will easily affect the surface of concrete honeycomb as well as the quality of concrete.

In recent years, some scholars have synthesized polycarboxylate superplasticizer with VPEG, which can make up for the deficiency of traditional C4 and C5 superplasticizer by using the special performance of C6 polyether. VPEG is a kind of vinyl-terminated polyether macromonomer with high
reactivity\cite{3}, but its performance in different kinds of synthetic superplasticizer shows poor adaptability, such as unsatisfactory workability of concrete and rapid slump loss. KZJ Guizhou company once tried to use isobutenol polyoxyethylene ether (HPEG), acrylic acid, and polypropylene glycol 400 diacrylate to synthesize polycarboxylate superplasticizer \cite{4}. They used the properties of polypropylene glycol 400 diacrylate to change the workability of concrete, and made some progress. However, the cost of polypropylene glycol 400 diacrylate is high. And when the additive produced by this kind of superplasticizer is used in the mix ratio of low rubber concrete, the workability of concrete is mediocre. For the better development of concrete market, it is quite urgent to research and develop the polycarboxylate superplasticizer with good adaptability and workability.

2. Experiment

2.1. Experimental Raw Materials and Equipment
Details of the raw materials used in this experiment are shown in Table 1:

| Table 1 Experimental Raw Materials |
|-----------------------------------|
| Raw materials | Specifications | Factory |
|----------------|----------------|---------|
| **Synthetic raw materials**      |                |         |
| 4-hydroxybutyl vinyl polyoxyethylene ether VPEG | Molecular weight: 4000 | Fushun Haoyuan Chemical Co.,Ltd. |
| Isobutenol polyoxyethylene ether HPEG | Molecular weight: 2400 | Guangdong Aoke Chemical Co.,Ltd. |
| Isopentenol polyoxyethylene ether TPEG | Molecular weight: 2400 | Guangdong Aoke Chemical Co.,Ltd. |
| Methacrylic acid MA | Main content: ≥99.5% | Fujian Binhai Chemical Co.,Ltd. |
| Methylene phosphate MEPA | Main content: ≥99.0% | Nanjing Qili New Material Co.,Ltd. |
| Thioglycolic acid TGA | Main content: ≥99.0% | Nanjing Qili New Material Co.,Ltd. |
| Hydrogen peroxide Solution H₂O₂ | Main Content: ≥27.5 % | Guiyang Nanming Hongfeng Chemical Co.,Ltd. |
| Ascorbic acid Vc | Main content: ≥99.5% | Sichuan Lingde Chemical Co.,Ltd. |
| Sodium hydroxide solution NaOH | Solid content: 30% | Guiyang Nanming Hongfeng Chemical Co.,Ltd. |
| **Performance test raw materials** | | |
| Cement C | Water of standard consistency: 26.2% | Guizhou Hongshi Cement Co.,Ltd. |
| Machine-made sand S | Fineness modulus: 2.5-3.5 | Beijing Municipal Construction Group Co.,Ltd. |
| Gravel G | Particle: 8-32mm | Beijing Municipal Construction Group Co.,Ltd. |
| Water | Tap water | Made by oneself |
Concrete admixtures

| W            | HWR          | Made by oneself |
|--------------|--------------|-----------------|
| Concrete admixtures A | HWR          | Made by oneself |

Details of the main instruments used in the experiments are shown in Table 2:

### Table 2 Major Instruments

| laboratory apparatus | Type      | Main technical parameters                      |
|----------------------|-----------|-------------------------------------------------|
| Electric mixer       | JJ-1      | Rotary speed: 3000 r/min                         |
| Water bath           | DFY-5L/30℃| Capacity: 5000 ml                               |
| Peristaltic pump     | BT100-01  | Rotary speed: 0.1 ~ 100 rpm                      |
| Single horizontal shaft test mixer | HJW-60 | Quota mixing quantity: 60L                      |
| Cement paste mixer   | NJ-160B   | Automatic control of program time: 255 ± 3s      |
| Digital pressure testing machine | DYE-2000 | Maximum load: 2000 KN                          |
| Gel permeation chromatograph | 2414 | Mobile phase: 0.1 mol/L NaNO₃ liquor           |
| Infrared spectrometer | FTIR-850  | KBr tablet                                      |

2.2. Process of the Synthesis

C4 polycarboxylate superplasticizer: The well-weighed HPEG is poured into a four-port flask with a stirrer, and a proper amount of W is also added. The stirrer is opened and the temperature is set at 25 °C. After the HPEG polyether dissolves, MEPA should be added and then stirred for 3 minutes. At the same time, three solutions should also be added, which are: A: H₂O₂+W, B: MA+W, and C: TGA+Vc+W. After solution A has been reacting for 2 hours, solution B and C for 2 hours and 30 minutes, as well as the one-hour reaction at constant temperature, 30% NaOH solution should be added neutralize the solution. And then a light yellow transparent C4 polycarboxylate superplasticizer with 40% solid content is made and it’s marked with PC-4.

C5 polycarboxylate superplasticizer: The well-weighed TPEG is poured into a four-port flask with a stirrer, and a proper amount of W is also added. The stirrer is opened and the temperature is set at 25 °C. After the TPEG polyether dissolves, MEPA should be added and then stirred for 3 minutes. At the same time, three solutions should also be added, which are: A: H₂O₂+W, B: MA+W, and C: TGA+Vc+W. After solution A has been reacting for 2 hours, solution B and C for 2 hours and 30 minutes, as well as the one-hour reaction at constant temperature, 30% NaOH solution should be added neutralize the solution. And then a light yellow transparent C5 polycarboxylate superplasticizer with 40% solid content is made and it’s marked with PC-5.

C6 polycarboxylate superplasticizer: The well-weighed VPEG is poured into a four-port flask with a stirrer, and a proper amount of W is also added. The stirrer is opened and the temperature is set at 5 °C. After the VPEG polyether dissolves, MEPA should be added and then stirred for 3 minutes. At the same time, three solutions should also be added, which are: A: H₂O₂+W, B: MA+W, and C: TGA+Vc+W. After solution A has been reacting for 2 hours, solution B and C for 2 hours and 30 minutes, as well as the one-hour reaction at constant temperature, 30% NaOH solution should be added neutralize the solution. And then a light yellow transparent C6 polycarboxylate superplasticizer with 40% solid content is made and it’s marked with PC-6.
2.3. Methods of Performance Tests

(1) Fluidity of cement paste: According to “GB/T 8077-2012 Test Method for Uniformity of Concrete Admixtures”, Hongshi P. O42.5 cement with 0.29 water-cement ratio is used and the solid content of an admixture should be 0.20%.

(2) Concrete performance test: According to “GB 8076-2008 Concrete Admixture”, the performance test of C50 concrete is conducted. The solid content of an admixture should be 13% and the amount added should be 1.8%. The proportion of the concrete mix is shown as Table 3.

| Table 3 Concrete Mixture Ratio kg/m³ |
|-------------------------------------|
| Strength grade | C | S | G | W | A |
| C50            | 500 | 795 | 104 | 160 | 9 |

3. Results and Analyses

3.1. Effects of Different Polycarboxylate Superplasticizers on Fluidity of Cement Paste

Compared with C4 monomer HPEG and C5 monomer TPEG, the activity of C6 monomer VPEG is higher. It is reacted at a low temperature of 5°C, and C4 monomer HPEG and C5 monomer TPEG are reacted at room temperature at 25°C. Compare the fluidity of the cement paste with the same dosage of PC-4, PC-5 and PC-6, and observe the dispersion performance and fluidity retention of the cement paste by the C4, C5 and C6 polycarboxylate superplasticizer performance, and the results are shown in Table 4.

| Table 4 Test Results of Fluidity of Cement Paste |
|-----------------------------------------------|
| Concrete admixtures | Admixture dosage /g | Fluidity of cement paste /mm |
|                   |                   | Initial | 2h     |
| PC-4              | 0.6              | 204     | 155    |
| PC-5              | 0.6              | 215     | 211    |
| PC-6              | 0.6              | 210     | 205    |

According to the results shown in Table 4, when they’re added at the same dosage, the initial fluidity of the cement paste with PC-4 polycarboxylate superplasticizer is 204mm, the dispersibility of the one with PC-5 polycarboxylate superplasticizer shows the best performance and its fluidity is 215mm, and the performance of the fluidity of the one with PC-6 polycarboxylate superplasticizer is between the other two. As for the fluidity maintenance of cement paste, PC-5 polycarboxylate superplasticizer shows the best performance with the 4mm loss of fluidity within 2 hours while the performance of PC-6 polycarboxylate superplasticizer is similar to that of PC-5 and the detailed number is 5mm loss of fluidity within 2 hours. Moreover, the initial fluidity of the cement paste with PC-4 polycarboxylate superplasticizer as well as its fluidity maintenance shows the poorest performance. Based on the result of the experiment, the dispersibility and fluidity maintenance of the cement paste with PC-5 and PC-6 polycarboxylate superplasticizers are similar.

3.2. Performance Tests of Concrete

In order to compare the performance of C4, C5 and C6 polycarboxylate superplasticizers more accurately, and well observe the state of concrete when leaving the machine, the same dosage of mother liquor of three kinds of superplasticizers is diluted to admixtures with 13% solid content. And then the experiment of C50 concrete with 1.8% above admixtures respectively is carried out. The experimental results are shown in Table 5 and the concrete state is shown as Fig. 1.

| Table 5 Performance Test of Concrete |
|--------------------------------------|
| Concrete admixtures | Slump/ Expansion (mm/mm) | Air content (%) | Emptying time (s) | Setting time (h) | Compressive strength (MPa) |
|                      | Initial | 2h   | Initia | Final | 3d | 7d | 28d |
| PC-4                 | 220/550 | 180/480 | 2.4  | 6.0  | 7.5 | 10.0 | 35.0 | 50.0 | 57.5 |
| PC-5                 | 225/580 | 210/530 | 2.6  | 4.5  | 7.5 | 10.0 | 36.5 | 52.0 | 58.5 |
The experimental results in Table 5 show that the initial slump and expansion of the concrete with PC-4 polycarboxylate superplasticizer are 220mm and 550mm, and the loss of the two parameters within 2 hours is relatively big. The initial slump and expansion of the concrete with PC-5 polycarboxylate-type superplasticizer are 225mm and 580mm, and the losses of the two parameters within 2 hours are 15mm and 50mm respectively. Compared with the concrete with PC-5 polycarboxylate superplasticizer, the initial slump of the one with PC-6 is 5mm larger while the expansion 10mm smaller. As can be seen from the test of air content in concrete, the concrete with C5 polycarboxylate superplasticizer has an obvious air-entraining effect while the one with C6 polycarboxylate-type superplasticizer has a low air-entraining effect. The pouring time of C50 concrete mixed with PC-6 admixture is 2.5s, which is obviously shorter than that with C4 and C5 superplasticizers. The setting time and compressive strength of the concrete with the above three superplasticizers are similar. From the test of concrete performance, it is obvious that the concrete with the admixture made up of PC-6 superplasticizer boasts good fluidity and slump retention, and low air content and viscosity, which means it’s more suitable for the pouring of concrete.

| PC-6 | 230/570 | 220/510 | 2.0 | 2.5 | 7.5 | 10.0 | 35.5 | 53.0 | 59.0 |

Fig. 1 Discharging States of the Concrete with Different Polycarboxylate Superplasticizers

As can be seen in Fig. 1, small stones in the concrete mixed with PC-4 superplasticizer can be seen clearly and there’s less slurry on its surface; Less stones can be seen in the concrete mixed with PC-5 superplasticizer and there’s less slurry on its surface; However, the concrete mixed with PC-6 superplasticizer has less exposed stones and more slurry on its surface. The stones are well wrapped in the concrete paste, and its fluidity is good with a shorter time of slump and pouring time. Seen from the contrast of the states of the concrete, the concrete mixed with PC-6 superplasticizer has better workability and can be used in practical projects.

3.3. GPC Analysis

GPC analysis will be conducted on the well-prepared PC-6 superplasticizer, and the molecular weight distribution of it can been seen in Fig.2. The results are shown in Table 6.
According to the GPC data analysis in Table 6, the average molecular weight of the C6 polycarboxylate-type superplasticizer is 25,185, and its distribution is relatively wide with the polydispersity coefficient 2.18 and the conversion rate 90.54%.

| Concrete admixtures | Mn    | Mw    | Mp    | Mw/Mn | Conversion rate % |
|---------------------|-------|-------|-------|-------|-------------------|
| PC-6                | 25185 | 54933 | 38526 | 2.18  | 90.54             |

3.4. Infrared Spectral Analysis

FT-IR analysis is conducted on the well-prepared PC-6 superplasticizer and the data is shown in Fig.3.

As can be seen from Fig. 3, the corresponding relationship between the absorption peak and functional group is shown as follows: 2,760cm⁻¹ and 965 cm⁻¹ are the stretching vibration absorption peaks of -CH₃ and -CH₂; 3,540 cm⁻¹ is the stretching vibration absorption peak of -OH, and 1,760 cm⁻¹ is the characteristic absorption peak of ester and carboxyl C=O; 1,310cm⁻¹ is the characteristic absorption peak of P=O⁵, and 1,055 cm⁻¹ is the stretching vibration absorption peak of ether bond C-O-C. It shows phosphate methylene acid has been successfully involved in the reaction. Moreover, the absorption peaks of each functional group show the structural formula of hexa-carbon polycarboxylate superplasticizer with high workability, which is shown as Fig.4.

![Fig. 4 Structure Diagram of Hexa-carbon Polycarboxylate Superplasticizer](image)

Polymerization degree: a, b, c and d

Fig. 4 Structure Diagram of Hexa-carbon Polycarboxylate Superplasticizer

4. Conclusion

(1) In this paper, 4000 molecular weight 4-hydroxybutylvinyl polyoxyethylene ether (VPEG), methacrylic acid (MA) and methylene phosphate (MEPA) are used as main raw materials to synthesize a hexa-carbon polycarboxylate superplasticizer. The dispersibility and fluidity maintenance of its cement paste boast good performance. When it’s added in concrete, the workability of the concrete is better than the one with C4 and C5 superplasticizers.
(2) The average molecular weight of the hexa-carbon polycarboxylate superplasticizer is 25,185, the molecular weight distribution index is 2.18, and the conversion rate 90.54%.

(3) The molecular structure of the hexa-carbon polycarboxylate superplasticizer is carboxyl group, phosphate ester group, polyoxyethylene group and so on, which accords with the designed molecular structure.

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