Study on Preparation and Performance of Carbon Hexapolycarboxylic Acid Comprehensive Mother Liquor

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Abstract: With ethylene polyethylene glycol ether (EPEG), acrylic acid (AA), hydroxyethyl acrylate (HEA), and sodium gluconate (SG) as the main raw materials, we synthesized the carbon hexapolycarboxylic acid comprehensive mother liquor with the use of initiator. And the test result shows that the carboxylic acid mother liquor concrete has better fluidity, better slump loss resistant property and lower concrete viscosity when the mother liquor has a reaction temperature of 10°C, a reaction system concentration of 40%, and when the hydroxyethyl propylene takes 0.89% of the total mass.

1. Preface

With the constant development in the architectural material industry in recent years, construction companies pay more and more attention to the concrete with high performance, high strength, high slump loss resistant and low viscosity. The slump loss resistant property and viscosity of concrete are among the most important problems that the construction companies are trying to solve. Sand with poor gradation and high powder content accelerates the slump and divergence loss of the concrete, and under the conditions of high temperature, dryness, and long-distance transportation, the viscosity of the concrete is too high and the slump loss resistant property becomes worse, which makes it hard for the on-site construction. Nowadays there are still some shortcomings by the common polycarboxylate superplasticizer, such as poor general adaptability to concrete, sticky concrete after loss and poor slump loss resistant property.

The polycarboxylate superplasticizer on the market these days is mainly obtained from copolymerizing isoamylene polyoxyethylene ether TPEG, acrylic acid and hydroxyethyl acrylate under the conditions of redox reactions. Plank. J synthesizes polycarboxylate superplasticizer with monomers such as MPEG and AA with different side chain lengths and demonstrates the complexation between anion and calcium ion in the polycarboxylate superplasticizer by measuring the anion charge density of the main polymer chain in the cement pore liquid [1]. Jiang Zhuojun synthesizes polycarboxylate superplasticizer with polyether macromonomers like MPEG, APEG, TPEG, HPEG and VPEG. The result shows that the polycarboxylate superplasticizer synthesized with mixing APEG and VPEG has better construction performance in C60 concrete [2]. In conclusion, Carbon Hexapolycarboxylic Acid has good performance in concrete,When it's constructed on site, the constructor will add water and other admixtures to the concrete to ensure the performance, which thus results in low strength of the concrete and segregation and bleeding.
In order to solve the problems of poor concrete fluidity and slump loss resistant property caused by sand and gravel quality fluctuations and high ambient temperature, we use ethylene polyethylene glycol ether (EPEG), acrylic acid (AA), hydroxyethyl acrylate (HEA) and sodium gluconate (SG) as the main raw materials to prepare carbon hexapolycarboxylic acid mother liquor in this article. We take advantage of the high reactivity of EPEG, and the polycarboxylate superplasticizer prepared with it has better cohesiveness and water retention in concrete [3]. The sodium gluconate increases the retarding effect of concrete and appropriately increases [4] and adjusts the reaction rate of the concrete at the later stage. Thus, we can better control the molecular weight of the mother liquor and solve the problems of poor concrete fluidity and slump loss resistant property caused by sand and gravel quality fluctuations and high ambient temperature.

2. Experiment

2.1. Experimental materials and instrument equipment

Table 1 shows the detailed information of the raw materials used in this experiment:

| Experimental materials | Specifications | Vendors |
|------------------------|----------------|---------|
| Ethylene polyethylene glycol ether EPEG | molecular weight: 2400 | Liaoning Kelong Fine Chemical Co., Ltd. |
| Acrylic acid AA | main content ≥ 99.5% | Fujian Binhai Chemical Co., Ltd. |
| Hydroxyethyl acrylate HEA | total esters content: ≥ 96.5% | Shanghai Haohua Chemical Co., Ltd. |
| Thioglycollic acid TGA | main content: ≥99.0% | Nanjing Xialian Chemical Co., Ltd. |
| Sodium gluconate SG | main content: ≥98.0% | Guiyang Nanming Hongfeng Chemical 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 | Specifications | Vendors |
|-------------------------------|----------------|---------|
| Cement C | water requirement of normal consistency: 26.2% | Guizhou Red Lion Cement Co., Ltd. |
| Machine-made yellow sand S | fineness modulus: 2.6-3.4 | Zhongjiao Road & Bridge North China Engineering Co., Ltd. |
| Gravel G | grain size: 10-35mm | Zhongjiao Road & Bridge North China Engineering Co., Ltd. |
| Water W | tap water | Made by ourselves |
| Commercially available comprehensive mother liquor PX-R | solid content: 40% | Some company in Guizhou |

Table 2 shows the detailed information of the main instruments used in this experiment:
| Table 2 Main instruments |  |
|--------------------------|--------------------------|
| **Experimental instruments** | **Model** | **Main technical parameters** |
| Low temperature constant temperature bath | DFY-5L/30°C | Volume: 5000ml |
| Electric mixer | JJ-1 | RPM: 3000r/min |
| peristaltic pump | BT100-01 | RPM: 0.1~100 rpm |
| cement paste mixer | NJ-160B | Time of the automatic control program: 255±3s |
| Single-shaft experimental mixer | HJW-60 | Mixing capacity: 60L |
| Digital pressure testing machine | DYE-2000 | Maximum load: 2000KN |
| Gel Permeation Chromatograph | Model 2414 | Mobile phase: 0.1mol/LNaNO₃ solution |
| Fourier Transform Infrared Spectroscopy FTIR | FTIR-850 | KBr chip coating |

2.2. Synthesis method
Weigh a certain amount of EPEG (200g), SG (5g) and W (246g), pour into a four-necked flask with a mixer, turn on the mixer, set the temperature to 10°C, and add solution A, B and C dropwise. Solution A is composed of H₂O₂ (0.85g) and W (30g), solution B is composed of AA (17.5g), HEA (3g) and W (30g) and solution C is composed of TGA (0.23g), Vc (0.75 g) and W (30g). Drop solution A and react for 2 hours, drop solution B and C, react for 2 hours 10 minutes, and then after 1 hour constant temperature reaction to get a colorless and transparent carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T ) with 40% solid content.

2.3. Performance test methods
(1) Cement paste fluidity: Tested in accordance with GB/T 8077-2012 "Test Methods for Homogeneity of Concrete Admixtures", using Red Lion P.O42.5 cement, with water cement ratio of 0.29, and admixture equivalent solid content of 0.15%.

(2) Concrete performance test: C50 concrete performance test carried out according to GB 8076-2008 "Concrete Admixtures". The admixture solid content is 15% and the admixture equivalent solid content is 0.18%. The concrete mix proportion is shown in Table 3.

3. Results and analysis
3.1. Cement paste fluidity test
Carry out cement paste fluidity test to the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T) and the commercially available comprehensive mother liquor (PX-R). The admixture equivalent solid content is both 0.15%, and the result is shown in Table 4.
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We can see from Table 4 that the initial fluidity of the cement paste with PX-R is 216mm, the fluidity at 2h is reduced to 162mm, and the fluidity loss of the cement paste in 2h is 54mm; the initial fluidity of the cement paste with PE-T is 228mm, the fluidity at 2h is 206mm, and the fluidity loss of the cement paste in 2h is 12mm. So the fluidity loss of PE-T cement paste is smaller and the initial fluidity is better.

3.2. concrete performance test
Add water and dilute the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T) and the commercially available comprehensive mother liquor (PX-R) to a 15% solution and carry out the C50 concrete test according to the mix proportion in Table 3. The test result is shown in Table 5.

| Admixtur  | Alump/divergence mm | Air content (%) | Rewinding time (s) | Setting time (h:min) | Compressive strength (MPa) |
|-----------|---------------------|-----------------|-------------------|---------------------|-----------------------------|
|           | initial 2h          |                 |                   | initia l             | final 3d 7d 28d             |
| PX-R      | 215/535 190/465     | 3.2             | 6.4               | 6:15 9:25             | 35.4 47.6 58.5              |
| PE-T      | 230/575 210/530     | 2.6             | 5.1               | 6:55 10:05             | 36.3 48.9 61.2              |

The test result in Table 5 shows that the initial divergence of PX-R concrete is 535mm and the 2h divergence difference is 70mm. The initial divergence of PE-T concrete is 575mm, the 2h divergence difference is 45mm, and the air content of PE-T concrete is lower than that of PX-R concrete and the concrete rewinding time is relatively shorter by 1.3s. The setting time of PE-T concrete is relatively prolonged by 45 minutes. Compared with PX-R, the 3d, 7d and 28d strength of PE-T is relatively increased with 1.1MPa, 1.3MPa and 1.7MPa.

3.3. GPC analysis
Carry out GPC test on the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T), and the result shows in Table 6.

Fig. 1 GPC integral curve of carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T)

| Sample    | Number-average molecular weight Mn | Seight-average molecular weight Mw | Peak molecular weight Mp | Polymersity coefficient Mw/Mn | Conversion rate % |
|-----------|-----------------------------------|-----------------------------------|-------------------------|-----------------------------|------------------|
| PE-T      | 27183                             | 52597                             | 40326                   | 1.93                        | 93.62            |
We can see from the GPC test data in Figure 1 and Table 6 that the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T) reaches a peak at 17 min. The peak molecular weight $M_p$ is 40326, the weight average molecular weight $M_w$ is 52597, and the polydispersity coefficient is 1.93. A smaller peak appears at 22.5 min, the peak molecular weight $M_p$ is 2354, and the molecular weight distribution is narrow. The ratio of the integral area of the two peaks tells that the reaction conversion rate is high, and that is up to 93.62%.

3.4. Infrared spectroscopy analysis

Carry out infrared spectroscopy analysis to the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T), and Figure 2 shows the result.

Fig. 2. Infrared spectroscopy of the carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T)

As shown in Figure 2, 3420 cm$^{-1}$ is the stretching vibration absorption peak of hydroxyl (-OH), 2884 cm$^{-1}$ is the stretching vibration absorption peak of alkyl (-CH), 1720 cm$^{-1}$ and 1359 cm$^{-1}$ are the in-plane bending vibration absorption peaks of alkyl (-CH), 1720 cm$^{-1}$ is the stretching vibration absorption peak of the carbonyl (-C=CO-O), and 1112 cm$^{-1}$ is the stretching vibration absorption peak of the ether bond (-C-O-C). It can be speculated that the structural formula is as shown in Figure 3.

Fig. 3. Structure diagram of carbon hexapolycarboxylic acid comprehensive mother liquor (PE-T)

$$\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \quad \text{C} \\
\text{C=O} & \quad \text{C=O} \\
\text{O} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{OH} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{H} & \quad \text{H} \\

da, \ b, \ c, \ d \text{ are all polymerization degree}
\end{align*}$$
4. Conclusions

(1) The newly developed carbon hexapolyacrylic acid comprehensive mother liquor has a small molecular weight, a narrow distribution and a higher conversion rate. And infrared spectroscopy shows that its molecular structure contains hydroxyl, carbonyl and ether bonds etc..

(2) The newly developed carbon hexapolyacrylic acid comprehensive mother liquor has better cement paste dispersion and fluidity than other admixtures on the market.

(3) The newly developed carbon hexapolyacrylic acid comprehensive mother liquor concrete has low viscosity, good fluidity and slump loss resistant property, and can effectively improve the 3d, 7d and 28d compressive strength of the concrete.

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