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Study on Synthesis and Properties of Low Sensitive Type Polycarboxylate Superplasticizer

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Abstract. Low sensitive type polycarboxylate superplasticizer P-DM is composed of methoxy polyethylene glycol methacrylate, 3-methyl-3-butene-1-ol polyoxyethylene ether, acrylic acid, ester type small monomers A, sulfonic acid type small monomer B, amide type small monomer C, phosphoric acid type small monomer D and silane type small monomer E. The initiator system is hydrogen peroxide-sodium formaldehydesulfoxylate dihydrate redox initiation system. The chain transfer agent is mercaptoethanol. The test results show that the monomer conversion rate of the synthesized P-DM is high and the dosage sensitivity of P-DM is significantly better than that of the conventional ether type polycarboxylate superplasticizer and the conventional ester type polycarboxylate superplasticizer, and the water consumption sensitivity and temperature sensitivity of P-DM is slightly better than that of the conventional ether type polycarboxylate superplasticizer and the conventional ester type polycarboxylate superplasticizer.

1. Introduction

Polycarboxylate superplasticizer has developed into the current mainstream concrete superplasticizer product because of its good designability, high water reduction rate, and environmental protection[1,2]. However, in recent years, with the increasing popularity of polycarboxylate superplasticizer, the problem that polycarboxylate superplasticizer are more sensitive than second-generation superplasticizer has become increasingly prominent. At the same time, with the rapid development of the national economy, China's real estate market and infrastructure construction have also developed at a rapid pace. A large number of project constructions have consumed a huge amount of cement and sandstone, which has exacerbated the tight supply of sand and gravel resources. In many parts of the country, the natural sand and gravel resources are becoming increasingly scarce, and the supply of sand and gravel materials is in short supply, resulting in a limited variety of aggregates and gradations in the concrete raw materials. At the same time, the cement production of China is large, the number of production enterprises is large, and the sources of materials are wide and there are great differences in the chemical compositions of different cement minerals. In addition, the quality of mineral admixtures varies, leading to a decline in cement quality. These factors cause the quality of concrete raw materials to fluctuate. The fluctuation of raw material quality will also increase the fluctuation of concrete flow performance, so it is particularly important to develop a low sensitive type polycarboxylate superplasticizer[3].

2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials

Methoxy polyethylene glycol methacrylate (self made), 3-Methyl-3-butene-1-ol polyoxyethylene ether (industrial grade), Acrylic acid (industrial grade), Ester type small monomer A (industrial grade), sulfonic acid type small monomer B (industrial grade), amide type small monomer C (industrial grade), phosphoric acid type small monomer D (industrial grade), silane type small monomer E (industrial grade), Hydrogen peroxide (industrial grade), Sodium formaldehydesulfoxylate dihydrate (industrial grade), 2-Hydroxy-1-ethanethiol (industrial grade), Sodium hydroxide (30% aqueous solution, industrial grade).

2.1.2. Main performance test raw materials for experiment

Cement (C,P.O 42.5 Cement), Sand (S,Mx=2.4-2.8), Gravel (G,grain size of 5-31.5mm), Fly ash (F, Level II), Polycarboxylate superplasticizer (PC1, Commercial ester type polycarboxylate superplasticizer), Polycarboxylate superplasticizer (PC2, Commercial ether type polycarboxylate superplasticizer).

2.2. Copolymerization

Add measured water, Methoxy polyethylene glycol methacrylate, 3-Methyl-3-butene-1-ol polyoxyethylene ether, and Hydrogen peroxide into a four-mouth bottle. Raise the temperature to the reaction temperature. After all macromonomers are dissolved, a mixture of AA, ester small monomer A, sulfonic acid small monomer B, amide small monomer C, phosphoric acid small monomer D and silane small monomer E is added dropwise. Aqueous solution of SFS and aqueous solution of MCE is added dropwise also. Control all materials to complete dropping in a certain period of time. Keep warm for a while,then a 30% aqueous solution of sodium hydroxide was added to adjust the pH to 6.0-7.0, thus obtaining a low sensitive type polycarboxylate superplasticizer P-DM.

2.3. Performance test method

2.3.1. Concrete test

The concrete test is conducted in accordance with GB/T50080-2016 "Standard Test Methods for Performance of Common Concrete Mixtures".

2.3.2. Sensitivity test

Sensitivity test was performed with reference to "Technical Regulations for Sensitivity Evaluation of Polycarboxylate Superplasticizer" compiled by KZJ New Materials Group Co., Ltd. The concrete mix ratio is shown in Table 1:

Table 1. Concrete mix ratio

W（kg/m^3）	C（kg/m^3）	S（kg/m^3）	G（kg/m^3）	F（kg/m^3）
170	260	790	1050	80

2.3.2.1. The dosage sensitivity test

The dosage sensitivity of the superplasticizer is characterized by the superplasticizer dosage width,which is named R_C. The larger the R_C, the better the dosage sensitivity of the superplasticizer is. The test method of R_C is: When the test environment temperature is 20±3°C,under the same conditions as other test conditions, the amount of superplasticizer was adjusted to test the initial concrete extensibility. When the initial concrete extensibility is (400±10)mm, the superplasticizer amount is R_{C1}. Gradually increase the amount of superplasticizer, so that the initial concrete extensibility gradually increased. When the initial concrete extensibility is (550±10)mm, the superplasticizer amount is R_{C2}， R_C is calculated as follows:

$$R_C = \frac{R_{C2}}{R_{C1}}$$

R_C–the superplasticizer dosage width.
R_{C1}–the superplasticizer dosage,when the initial concrete extensibility is (400±10)mm, %.
R_{C2}–the superplasticizer dosage,when the initial concrete extensibility is (550±10)mm, %.

2.3.2.2. The water consumption sensitivity test
The water consumption sensitivity is characterized by the difference in the degree of the concrete extensibility, which is named Wr. The smaller the Wr, the better the water consumption sensitivity of the superplasticizer. The test method of Wr is: superplasticizer dosage is R_{C1}, other test conditions remain unchanged, the water consumption increased by 10k kg/m3. The absolute value of the difference in concrete extensibility before and after the increase in water consumption was calculated as Wr.

2.3.2.3. The temperature sensitivity test
The temperature sensitivity is characterized by the difference in the degree of the concrete extensibility, which is named Wt. The smaller the Wr, the better the temperature sensitivity of the superplasticizer. The test method of Wt is: Superplasticizer dosage is R_{C2}, other test conditions remain unchanged, adjust the test environment temperature to 5±3°C. The absolute value of the difference in concrete extensibility before and after the test environment temperature changes was calculated as Wr.

2.3.3. Gel chromatography test
Use US Waters 1515 Isocratic HPLP pump/Waters 2414 refractive index detector and Breeze software acquisition and analysis system. The column consisted of UltrahydragelTM250 and UltrahydragelTM500 in series. The mobile phase consisted of a 0.1 mol/L aqueous solution of sodium nitrate (containing 0.05% sodium azide), which was degassed in advance through a 0.22 μm microporous membrane and then degassed by ultrasound. The flow rate was 0.8 mL/min. The injection volume is 200 Ml, the oven temperature is 40°C, the refractive index detector temperature is 40°C.

3. Experimental design ideas

Polycarboxylate superplasticizers are generally prepared by the copolymerization of unsaturated carboxylic acids and unsaturated macromonomers. Polycarboxylate superplasticizers are generally classified as ester type polycarboxylate superplasticizer and ether type polycarboxylate superplasticizer depending on the type of unsaturated macromonomer. Due to the difference in the molecular structure of these two types of polycarboxylate superplasticizers, their performance is also different. Generally, the ether type polycarboxylate superplasticizer has a higher water reducing rate than the ester type polycarboxylate superplasticizer, but the ester type polycarboxylate superplasticizer has better concrete workability[4]. In the early days of the application of polycarboxylate superplasticizer, the research mainly focused on how to increase its water reduction rate. In recent years, due to the increasing complexity of concrete materials and engineering applications, concrete manufacturers' requirements for polycarboxylate superplasticizer have gradually evolved from high water reduction rate to functional type. The realization of different functional polycarboxylate superplasticizer is mainly through the use of functional small monomers or macromonomers, such as the introduction of slump retention-type small monomers, to improve the polycarboxylate superplasticizer's slump retention properties[5]. The introduction of phosphoric acid type small monomer and silane type small monomer enables the polycarboxylate superplasticizer to be preferentially adsorbed on the cement in a high sulfate content environment, thereby achieving a sulfate-resistant function[6]. The amide type small monomer was introduced to realize the synthesis of the early strong type polycarboxylic water reducer[7]. The polycarboxylate superplasticizers have different structure due to the different structure of the different macromonomers and small monomers they used,and the performances are also different when they used in concrete, but there are also relatively suitable conditions for each. So, when synthesizing a polycarboxylate superplasticizer using a plurality of different structures of small monomers and macromonomers simultaneously, the resulting product will have different structures to adapt to the use under different conditions, thus the sensitivity exhibiting is also relatively low. This article is just based on this theory for the synthesis of low sensitive type polycarboxylate superplasticizer. Ester type macromonomer and ether type macromonomer and acrylic acid, ester type small monomer A, sulfonic acid type small monomer B, amide type small monomer C, phosphoric acid type small monomer D, silane type small monomer E were selected as copolymerized monomer to synthesize a low sensitive type polycarboxylate superplasticizer P-DM.

4. Experimental results and discussion

4.1. Gel chromatography test results

The synthesized P-DM was tested by gel chromatography. The measured polymer content in the spectrum reflects the monomer conversion of P-DM. The gel chromatogram of P-DM is shown in Figure1.

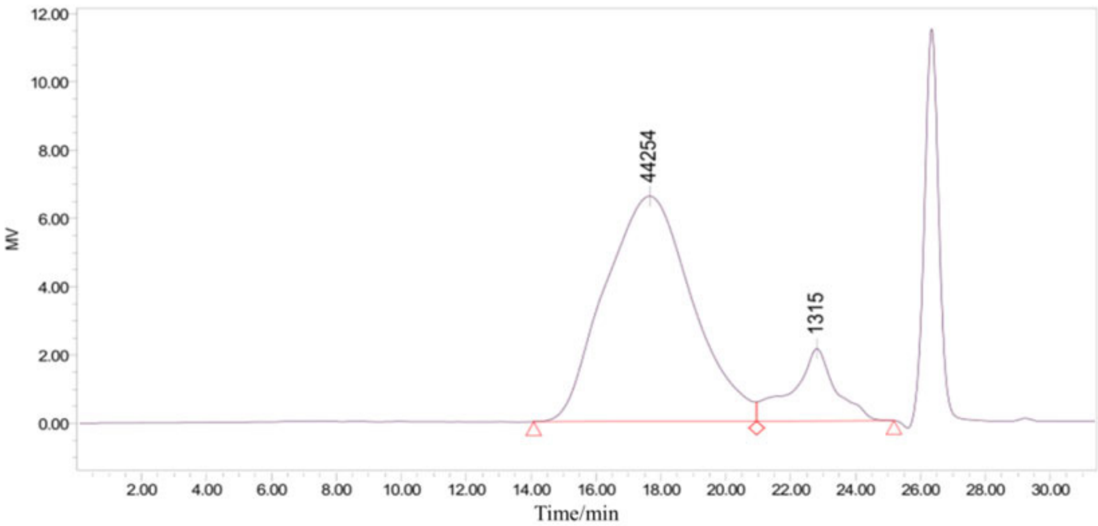

Figure1. Chromatogram of P-DM gel.

In Fig.1, at the time of 17.721 min, the peak of the polymer was observed. The peak at the time of 22.853 min was the unreacted monomer. The peak of the solvent was at 26.492min. The measured P-DM gel chromatographic peaks were integrated and the calculated polymer content was as high as 90.13%, indicating that P-DM has a high monomer conversion rate and can meet the application requirements.

4.2. The dosage sensitivity test results

At the same time, PC1, PC2, and P-DM were tested for the dosage sensitivity. The test results are shown in Table 2:

Table 2. The dosage sensitivity test results

Sample	R_{C1}/%	concrete extensibility at R_{C1}/mm	R_{C2}/%	concrete extensibility at R_{C2}/mm	R_C

PC1	1.60	410	2.20	540	1.38
PC2	1.35	400	1.66	550	1.23
P-DM	1.70	410	2.75	540	1.62

As shown in Table 2, both R_{C1} and R_{C2} of P-DM were higher than those of PC1 and PC2, indicating that P-DM had smaller water reduction rate than PC1 and PC2. However, the R_C of P-DM is significantly greater than that of PC1 and PC2, indicating that P-DM has better dosage sensitivity than PC1 and PC2.

4.3. The water consumption sensitivity test results

At the same time, PC1, PC2, and P-DM were tested for the water consumption sensitivity. The test results are shown in Table 3:

Table 3. The water consumption sensitivity test results

Sample	Dosage/%	Initial concrete extensibility /mm		Wr/mm
		The water consumption is 170 kg/m3	The water consumption is 160 kg/m3	
PC1	1.60	410	525	115
PC2	1.35	400	525	125
P-DM	1.70	410	515	105

As shown in Table 3, Wr of PC1, PC2, and P-DM are PC2, PC1, and P-DM from large to small, indicating that the water consumption sensitivity P-DM is the best, followed by PC1 and PC2 worst. However, the difference in Wr among the three samples is not very large, indicating that the water consumption sensitivity of these three samples is not very different.

4.4. The temperature sensitivity test results

At the same time, PC1, PC2, and P-DM were tested for the temperature sensitivity. The test results are shown in Table 4:

Table 4. The temperature sensitivity test results

Sample	Dosage/%	Initial concrete extensibility /mm		Wt/mm
		The temperature is 20±3℃	The temperature is 5±3℃	
PC1	2.20%	540	580	40
PC2	1.66%	550	595	45
P-DM	2.75%	540	570	30

As shown in Table 3, Wt of PC1, PC2, and P-DM are PC2, PC1, and P-DM from large to small, indicating that the temperature sensitivity P-DM is the best, followed by PC1 and PC2 worst. However, the difference in Wt between the three samples is not very large, indicating that the temperature sensitivity of these three samples is not very different.

5. Conclusions

A low sensitive type polycarboxylate superplasticizer P-DM was synthesized experimentally. The content of polymer of the product obtained by this synthesis method was as high as 90.13%, indicating that P-DM had a high monomer conversion rate and could meet the application requirements.

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The dosage sensitivity test results show that the R_C of P-DM is the largest compared with PC1 and PC2, indicating that P-DM has better dosage sensitivity than PC1 and PC2.

The water consumption sensitivity test results showed that the Wr of P-DM was slightly lower than that of PC1 and PC2, indicating that the water consumption sensitivity of P-DM was slightly better than that of PC1 and PC2.

The temperature sensitivity test results showed that the Wt of P-DM was slightly lower than that of PC1 and PC2, indicating that the temperature sensitivity of P-DM was slightly better than that of PC1 and PC2.

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