Study on Preparation and properties of low sensitive polycarboxylate superplasticizer

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Abstract. Esterified macromonomers (P1) were obtained from methacrylic acid (MAA), maleic anhydride (MAm) and methoxy polyethylene glycol monomethyl ether (MPEG). A low sensitive polycarboxylate superplasticizer (P-DMG) was prepared by copolymerization of Esterified macromonomers (P1) with acrylic acid (AA), hydroxyethyl acrylate (HEA), acryloyloxyethyl trimethyl ammonium chloride (DAC) and 4-hydroxybutyl vinyl polyoxyethylene ether (VPEG). Compared with the conventional polycarboxylate superplasticizer, P-DMG can reduce the sensitivity to concrete dosage, water consumption, temperature and raw materials, and has good workability. It can be widely used in various concrete projects.

1. Introduction
The domestic research on polycarboxylate superplasticizer began in the late 1990s and early 2000s. As the third-generation concrete admixture, compared with the second-generation admixture, the polycarboxylate superplasticizer has the advantages of high water reduction, low dosage and high slump retention[1-3]. It is widely used in highways, railways, bridges, nuclear power, dams, tunnels, marine engineering and high-rise buildings and other engineering fields.

With the application of polycarboxylate superplasticizer becoming more and more extensive, the differences of raw materials, regional environment, and the limitations of technical personnel's understanding, habits and theoretical knowledge level in the process of ready-mixed concrete, some problems have arisen in the process of using polycarboxylate superplasticizer, which directly affects the use effect of polycarboxylate superplasticizer. At present, the mechanism of action and self-sensitivity of polycarboxylate superplasticizer in China can not be completely controlled. Especially in practical projects, due to various kinds of cement and improper construction operation of workers, when polycarboxylate superplasticizer is directly applied to concrete, the problems such as poor adaptability to cement[4-8], unsatisfactory performance of concrete and possible large collapse often occur, which lead to the failure to meet the requirements of construction site. Therefore, it is of great significance to develop a low sensitive polycarboxylic acid product. Esterified macromonomer (P1) is obtained by esterification of methacrylic acid, maleic anhydride and methoxypolyethylene glycol monomethyl ether (MPEG). And copolymerization of P1, acrylic acid, hydroxyethyl acrylate, acryloyloxyethyl trimethyl ammonium chloride (DAC) and 4-hydroxybutyl vinyl polyoxyvinyl ether (VPEG) to prepare a low sensitive polycarboxylate superplasticizer (P-DMG).

2. Experimental

2.1.Materials
2.1.1. The main synthetic experimental raw materials. 4-hydroxybutyl vinyl polyoxyvinyl ether (VPEG), industrial grade; Methoxypolyethylene glycol monomethyl ether (MPEG), industrial grade; From methacrylic acid (MAA), industrial grade; maleic anhydride (MA), industrial grade; Acrylic acid (AA), industrial grade; p-toluene sulfonic acid (PTSA), industrial grade; Hydroquinone (HQ), industrial grade; Hydroxyethyl acrylate (HEA), industrial grade; Hydrogen peroxide (H₂O₂), industrial grade; Sodium hypophosphite (SHP), industrial grade; Acryloxyethyl trimethyl ammonium chloride (DAC), industrial grade; 3-mercaptopropionic acid (MPA), industrial grade; Sodium hydroxide (NaOH), 30% aqueous solution, industrial grade.

2.1.2. Main performance test raw materials for experiment. Cement (C1): Hua Run P.O 42.5 Cement; Cement (C2): Min Fu P.O 42.5 Cement; Cement (C3): Hong Shi P.O 42.5 Cement; Cement (C4): Hai Luo P.O 42.5 Cement; Cement (C5): Ji Dong P.O 42.5 Cement. Sand: river sand with a fineness modulus of 2.7, containing 2% mud; Small stones: crushed stones with a diameter of 5-20 mm; Large stones: crushed stones with a diameter of 16-31.5 mm. Flyash: class ii; P-JS: Standard polycarboxylate superplasticizer, products of KZJ New Materials Group Co., Ltd.

2.2. Esterification
The esterification product P1 was obtained by adding metered MPEG, MAH, MAA and HQ into the reactor, opening the nitrogen-opening device, heating up to 60°C, adding metered PTSA, slowly heating up to 120°C, constant temperature for a certain time, and cooling down.

2.3. Copolymerization
Metered water, AA and VPEG were added to the reactor, heated and stirred until VPEG was dissolved. After the system temperature reached 10°C, SHP, AA, H₂O₂, HEA, DAC and MPA were added to the reactor respectively. The dropping was controlled within 2 h, then the constant temperature was 0.5 h, and the pH value was adjusted to 5.0-6.0 by adding 30% sodium hydroxide, and then P-DMG was obtained.

2.4. Performance test method

2.4.1. Concrete performance test. Concrete according to GB/T50080-2016 "Standard for test method of performance on ordinary fresh concrete". And according to "Technical Specification for Sensitivity Evaluation of polycarboxylate superplasticizer ", that compiled by Kezhijie New Materials Group Co., Ltd. The concrete mix ratio (kg/m³) is m (cement): m (fly ash): m (small stones): m (large stones): m (sand): m (water) = 260:80:525:525:790:170.

2.4.2. Gel chromatography test. Waters 1515 was used. The column was connected in series by UltrahydragelTM 250 and UltrahydragelTM 500. The mobile phase was 0.1 mol/L sodium nitrate aqueous solution at a flow rate of 0.8 mL/min. The standard calibration curve was sodium polyacrylate and the running time was 60 min.

3. Experimental results and discussion

3.1. Gel chromatography
Gel chromatography was used to test P-DMG. The content of polymer in the spectrogram reflects the conversion rate of P-DMG monomer. The spectrum of P-DMG is shown in Figure 1.
From the experimental results in Figure 1, it can be seen that the content of the polymer is as high as 91.62%, indicating that the monomer conversion rate of P-DMG is high, which can meet the requirement of application.

3.2. Sensitivity test of concrete

3.2.1. Sensitivity of dosage. The laboratory temperature is 20±2°C, keeping the mix proportion of concrete unchanged. By adjusting the dosage of admixture, the initial slump of concrete at (400±10) mm is taken as the starting point A0, and the initial slump of concrete at (550±10) mm is taken as the end point A1. The ratio of the end point of the admixture to the amount of the starting point is used to evaluate the sensitivity of the polycarboxylate superplasticizer (Admixture dosage width Rc= A1/ A0). The larger the Rc is, the less sensitive the content of the polycarboxylate superplasticizer. The results of dosage sensitivity test of P-JS and P-DMG are shown in Fig. 2.

As shown in Figure 1, the content of P-JS is 0.95%-1.3%, RcP-JS is 1.37; the content of P-DMG is 1.0%-2.1%, Rc(P-DMG) is 2.1, RcP-DMG > Rc(P-JS). It can be seen that P-DMG is less insensitive to the dosage.

3.2.2. Sensitivity of water consumption. Keep the concrete mix ratio unchanged and adjust the admixture content. Taking the initial slump of concrete is (450±10)mm as the reference amount, and then adjusting the water consumption of concrete mix proportion, the change of concrete slump with polycarboxylate superplasticizer under different water consumption was investigated. The test results are shown in Fig. 3.
Figure 3. Evaluation results of water consumption sensitivity of P-JS and P-DMG

It can be seen from Figure 3 that for every 10 kg of water added, the concrete slump with P-JS changes by 40-80 mm. For every 10 kg of water added, the slump degree of concrete mixed with P-DMG varies by 20-30 mm. It can be seen that P-DMG is less sensitive to water consumption.

3.2.3. Sensitivity of temperature. Keep the mix ratio of concrete unchanged and adjust the dosage of admixture. Taking the initial slump of concrete is 550±10mm as the reference value, adjusting the laboratory temperature, the slump change of concrete mixed with polycarboxylic superplasticizer at different temperatures was studied. The test results are shown in Figure 4.

Figure 4. Evaluation results of temperature sensitivity of P-JS and P-DMG

It can be seen from Fig. 4 that at a temperature of 0℃ to 40℃, the concrete slump of mixed P-JS is changed by 30 mm to 80 mm for every 10℃ increase in temperature. And the concrete slump degree of mixed P-DMG is changed by 10mm~30mm.

3.2.4. Sensitivity of Raw material. Min Fu cement is used to keep the mix ratio of concrete unchanged and adjust the admixture dosage. Taking the initial slump of concrete is 550±10mm as the reference value. Then replacement of different kinds of cement for testing. And the slump change of concrete mixed with polycarboxylic superplasticizer at different cement variety was studied. The test results are shown in Figure 5.
Figure 5. Evaluation results of cement sensitivity of P-JS and P-DMG

It can be seen from Fig. 5 that with 5 different cements, the concrete slump with P-JS is 420-600mm and that with P-DMG is basically unchanged.

4. Conclusions

(1) The low sensitive polycarboxylate superplasticizer P-DMG was synthesized in this experiment. The content of the product polymer obtained by this synthesis method is as high as 91.62%. It shows that the monomer conversion of P-DMG is high and it can meet the requirements of production and application.

(2) The sensitivity test of P-DMG was carried out, and the sensitivity evaluation of the dosage, water consumption, temperature and raw materials was carried out. The results showed that the low-sensitive polycarboxylate superplasticizer P-DMG was less sensitive to the dosage, water consumption, temperature and raw materials, which was superior to P-JS.

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