Preparation and performance test of multiblock polycarboxylate superplasticizer with low sensitivity

Wenhong Chen [1], Lei Deng[1], Yu Jiang [1], Bo Zhang [1]*

[1] KZJ New Materials Group Guizhou Co., Ltd., Longli, Guizhou, China

* Corresponding author's e-mail: owen@xmabr-kzj.com

Abstract. In order to solve the problems such as wide fluctuation of concrete fluidity, too fast loss and water secretion caused by the variation of polycarboxylate superplasticizer for concrete preparation. In this paper, a kind of polycarboxylate superplasticizer with multiblock low sensitive(PE-K) was prepared by modified polyether (TPEG), acrylic acid (AA), acrylamide (AM), and 2-acrylamide-2-methyl propanesulfonic acid (AMPS) in the presence of initiator at 50 centigrade. Results showed that the PE-K had lower dosage sensitivity, temperature sensitivity and the water consumption sensitivity performance compared with PE-01.

Keywords: low sensitivity; multiblock; polycarboxylate superplasticizer; concrete

1 Introduction

With the accelerated urbanization of our country and the continuous development of the concrete industry, polycarboxylate superplasticizer is the third generation of superplasticizer after lignin and naphthalene superplasticizer[1], which has become the mainstream product of commercially available admixtures because of its high water reduction rate under low admixture conditions[2]. Polycarboxylate superplasticizer is a polymer material containing many "hydrophilic" groups such as carboxyl group (-COOH), hydroxyl group (-OH), amino group ($-NH_2$), sulfonic acid group ($-SO_3H$), etc. In order to adapt to the fluctuation of concrete sand and gravel materials and changes in environmental factors, polycarboxylate superplasticizer is required to have high water reduction, high slump retention, mud resistance [3-5], low sensitivity [6-8] and other characteristics.

At present, construction units require concrete to have the advantages of high fluidity, low water-binder ratio, appropriate amount of admixtures, low sensitivity, high workability, economic benefits, energy saving and environmental protection. However, when the concrete construction environment deteriorates and materials such as sand, stone, and cement fluctuate greatly. The concrete is often prone to problems such as bleeding, sand aggregate separation, and construction difficulties.

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Acrylamide is a bifunctional small molecule containing carbon carbon double bonds (-C=C-) and amino groups (-NH_2), and is also one of the commonly used small monomers in polycarboxylate superplasticizer. Due to the strong hydrophilic effect of amino group (-NH_2) in its molecule, and the carbon-carbon double bond in the molecule can participate in the free radical polymerization of polycarboxylate superplasticizer, it has a high water reduction rate and a low water secretion rate. Tang Xiusheng et al. synthesized acrylamide polymers using acrylic acid and acrylamide as the main raw materials, which have good thickening, wrapping, and reducing bleeding rate of concrete[9]. 2-Acrylamide 2-methylpropanesulfonic acid (AMPS) molecule contains multifunctional groups such as carbon carbon double bonds (-C=C-), amino groups (-NH_2), sulfonic acid groups (-SO_3H). It can be copolymerized with acrylic acid to prepare high water absorption resins and has good adsorption performance for Pb^{2+}, Cu^{2+}, Zn^{2+}metal ions[10]. On the basis of previous studies, in this paper, Polycarboxylate superplasticizer was prepared by modified polyether (TPEG), acrylic acid (AA), acrylamide (AM), and 2-acrylamide-2-methylpropanesulfonic acid (AMPS) were used as raw materials for Radical polymerization.

2 Experiment

2.1 Experimental raw materials

Synthetic raw materials.

The modified polyether (TPEG) with a molecular weight of 2400 was used in this experiment, and the acrylic acid (AA), acrylamide (AM), 2-acrylamide-2-methylpropanesulfonic acid (AMPS), mercaptopropionic acid (TGA), 30% hydrogen peroxide solution (H_2O_2), ascorbic acid (Vc), and sodium hydroxide (PJ) were all of industrial grade.

Performance testing raw materials.

The cement used in this experiment is P. O42.5 silicate cement produced by Guiyang Conch Panjiang Cement Co., Ltd; The mechanism sand is white medium sand produced by Guiyang Municipal Construction Co., Ltd. with Mx= 2.6~3.0; the stone is produced by Guiyang Municipal Construction Co., Ltd. with grain size of 5~35mm; the water is boiler water with pH value of 6.5~8.5.

2.2 The synthesis process of superplasticizer

TPEG (200g), H_2O_2 (1g), and W (265g) were added to the reaction vessel with stirrer, and the temperature was increased to 50°C after TPEG was completely dissolved. At the same time, solution A: AA (16g), AM (5g), AMPS (2.5g), and W (35g) were added dropwise, and solution B: Vc (0.5g), TGA (0.75g), and W (35g) were added dropwise. Solution A was added dropwise for 2.5h, solution B was added dropwise for 3h, and PJ (5g) was added at a constant temperature of 50°C for 1h to obtain a colorless and transparent multi-block low-sensitive superplasticizer with 40% solid content. Polycarboxylate superplasticizer (PE-K) with 40% solid content was obtained.

2.3 Performance test methods

(1) Gel permeation chromatography (GPC) characterization was tested and analyzed using a Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector, USA.

(2) Synthetic samples were analyzed by infrared chromatography (FT-IR) using a PE Spectrum TWO model from PE, USA. The solution was applied to a KBr wafer coated with a thin layer of liquid film and dried under an infrared lamp for determination.

(3) Cement paste fluidity: Tested according to GB/T 8077-2012 "Concrete admixture homogeneity test method", using Conch P. O42.5 cement with water-cement ratio of 0.29.

(4) Concrete performance test: refer to GB/T 50080-2002 "Test method for properties of ordinary concrete mix" and GB/T 50081-2002 "Test method for mechanical properties of ordinary concrete".

(5) Concrete sensitivity evaluation: The sensitivity evaluation was carried out by the C30 concrete test. The larger the absolute value of the difference of concrete expansion, the more sensitive it is, and vice versa, not sensitive. Its concrete fitting ratio (kg/m^3) is: m(cement):m (white sand):m(stone):m(water):m(superplasticizer) = 340:960:960:160, mainly including polycarboxylate superplasticizer admixture sensitivity, water consumption sensitivity and temperature sensitivity.

3 Results and Analysis

3.1 GPC analysis

Carry out GPC test on the multiblock polycarboxylate superplasticizer with low sensitivity (PE-K), and the result shows in Table1.

Table 1. Comparison of GPC data

Sample No.	number-average molecular weight Mn	weight-average molecular weight Mw	Polydispersity coefficient Mw/Mn	Conversion rate %
PE-K	35076	68362	1.95	90.02

We can see from the GPC test data in Table 1, The weight average molecular weight Mn is 35706, and the polydispersity coefficient is 1.95. The molecular weight distribution is narrow and monomer conversion rate of 90.02%.

3.2 Infrared spectroscopy analysis

Carry out infrared spectroscopy analysis to the multiblock polycarboxylate superplasticizer with low sensitivity (PE-K), and Figure 1 shows the result.

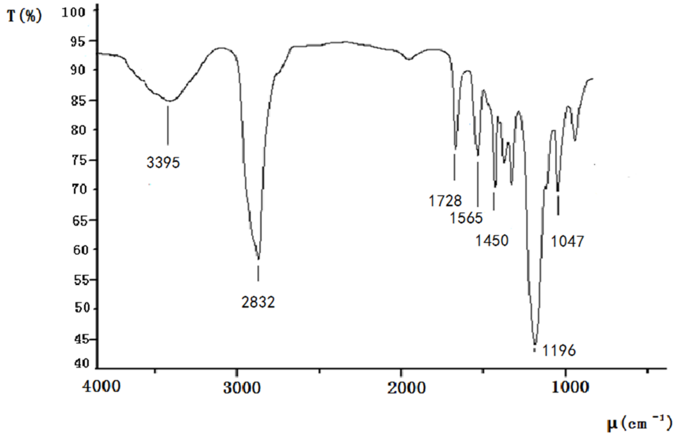

Fig. 1. Infrared spectroscopy of the multiblock polycarboxylate superplasticizer with low sensitivity (PE-K)

We can see From Figure 1, the absorption peaks correspond to the functional groups as follows:3395 cm-1 is the telescopic vibrational absorption peak of hydroxyl-OH and intermolecular association-NH, 2832 cm-1 and 1450 cm-1 are the telescopic vibrational absorption peaks of -CH3,-CH2-, 1728 cm-1 is the characteristic absorption peak of ester group and carboxyl group C=O, 1196 cm-1 is the stretching vibration absorption peak of the ether bond C-O-C,1047 cm-1 is the asymmetric stretching vibrational absorption peak of sulfonate ion R-SO2-O- in -S=O [2].The above characteristic peaks of each group can indicate that TPEG, AA, AM and AMPS have been successfully reacted to form multi-block polymers.

3.3 Cement paste fluidity test

Effect of different AM on the flow of net cement paste.

Through single-factor variable test, without AMPS, 0g, 2.5g, 5g and 7.5g of AM were added, and the polycarboxylate superplasticizer obtained according to 1.2 synthesis process were PE-01, PE-02, PE-03, PE-04 and PE-05 for cement paste fluidity test, and the polycarboxylate superplasticizer folded solid admixture was 0.12%, The fluidity test results of cement paste are shown in Figure2.

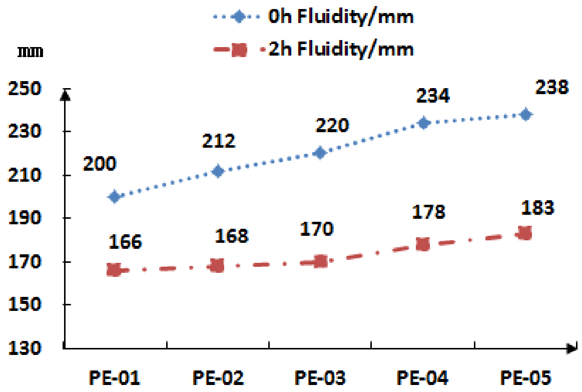

Fig. 2. Effect of different AM on the flow rate of net cement paste

We can see from Figure 2, the 0h net cement flow rate of PE-01 is 200mm, and the 2h net cement flow rate is 166mm. The net cement flow rate of polycarboxylate superplasticizer gradually increases with the increase of AM dosage, and the inflection point appears when the AM dosage is 5g. The net cement flow rate of PE-04 is the most excellent, which indicates that AM can increase the net cement flow rate of polycarboxylate superplasticizer and improve the water reduction rate.

Effect of different AMPS on the flow rate of net cement paste.

Through single-factor variable test, without AM, 0g, 2.5g, 5g, 7.5g of AMPS were added, and the polycarboxylate superplasticizer synthesized according to 1.2 synthesis process were PE-01, PE-05, PE-06, PE-07, PE-08 for cement paste fluidity test, and the polycarboxylate superplasticizer folded solid admixture was 0.12%, The fluidity test results of cement paste are shown in Figure 3.

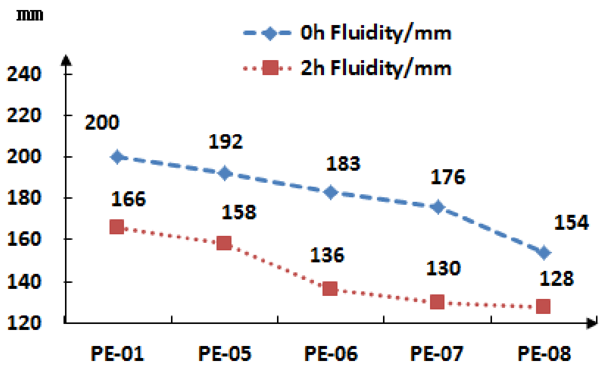

Fig. 3. Effect of different AMPS on the flow rate of net cement paste

We can see from Figure 3, The net cement flow rate of polycarboxylate superplasticizer decreases gradually with the increase of AMPS dosage, and the net cement flow rate of PE-06 is optimal when the dosage of AMPS is 2.5g.

3.4 Concrete performance test

Polycarboxylate superplasticizer dosage sensitivity test.

The synthetic PE-K and the benchmark PE-01 were diluted with water to 15% solution, and the superplasticizer admixtures were 1.1%, 1.2%, 1.3%, 1.4% and 1.5%, respectively, and the test results of C30 concrete were carried out at 22°C as shown in Figure 4.

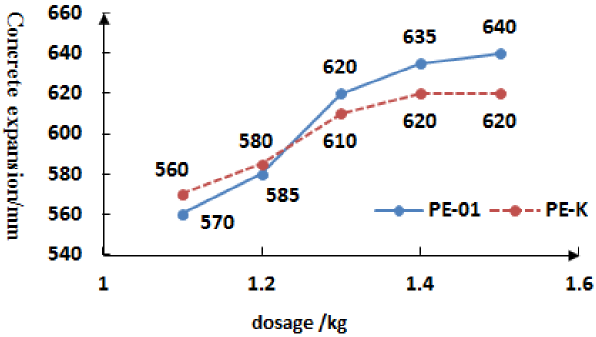

Fig. 4. Different polycarboxylate superplasticizer admixture on concrete expansion test results

We can see from Figure 4, the initial concrete expansion of PE-K is greater than that of PE-01. The intersection of the two occurs when the admixture is 1.2% to 1.3%. When PE-01 dose is greater than 1.2% of the concrete expansion growth trend is obvious, when PE-K dose is greater than 1.2% of the concrete expansion growth trend is slow, when the dose is 1.4% of the initial concrete expansion of concrete is not increasing, indicating that PE-K dose sensitivity is low.

Water consumption sensitivity test.

The water consumption sensitivity test was conducted by diluting the synthetic PE-K and the reference PE-01 with water to 15% solution at 22℃ with water consumption of 150kg, 165kg, 180kg, 195kg and 210kg, respectively, to characterize the sensitivity of the superplasticizer to water consumption by the initial expansion of concrete. See Figure 5.

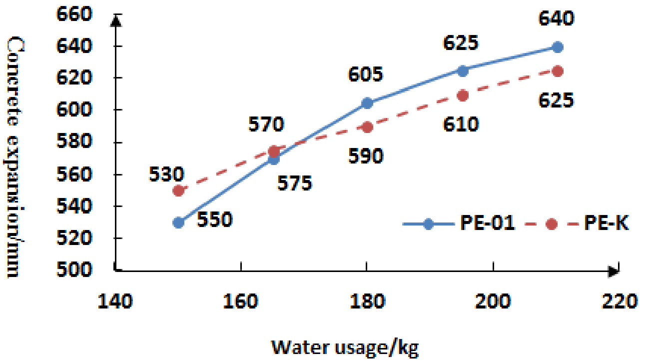

Fig. 5. Concrete expansion test results with different water consumption

We can see from Figure 5, When the water consumption is around 165kg the intersection of the two lines appears, and the rising trend of the two lines shows that the rising trend of PE-k line is obviously slower and less sensitive.

Temperature sensitivity test.

The temperature sensitivity test was conducted by diluting the synthesized PE-K and the benchmark PE-01 with water to 15% solution at 22°C with 1.2 % superplasticizer admixture and temperatures of 2°C, 12°C, 22°C, 32°C and 42°C, respectively, and the results of water sensitivity evaluation of PE-01 and PE-K are shown in Figure 6.

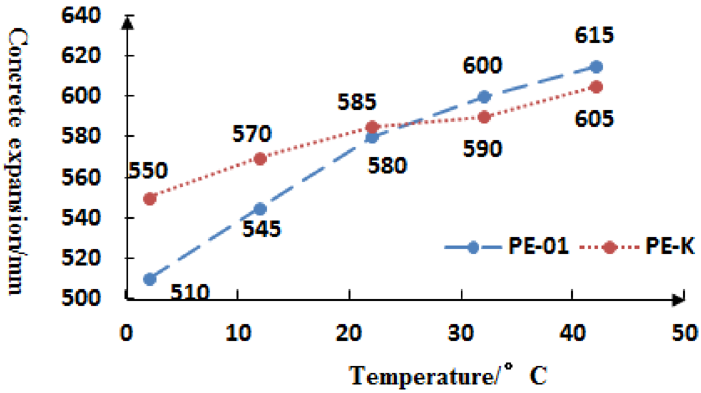

Fig. 6. Test results of concrete expansion at different temperatures

We can see from Figure 6, PE-01 and PE-K both increase in concrete expansion with increasing temperature, but PE-K rises more slowly and has a smaller difference in expansion, which is less sensitive.

4 Conclusion

(1) The multi-block low-sensitive polycarboxylate superplasticizer (PE-K) synthesized with TPEG, AA, AM and AMPS was tested and analyzed by GPC and IR spectroscopy, and the results showed that the obtained multi-block polymers were consistent with the expected design.

(2) The amount of AM and AMPS synthesized was varied by using single factor variables, and the introduction of AM and AMPS could effectively regulate the net cement flow rate of the multi-block polycarboxylate superplasticizer (PE-K) compared with PE-01.

(3) Based on the comparison of concrete sensitivity test between PE-K and PE-01, the concrete admixture sensitivity, water consumption sensitivity and temperature sensitivity of PE-K are lower, which can effectively solve the sensitivity problems arising during the concrete construction.

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