Research on synthesis and property of anti-clay polycarboxylate superplasticizer

Qiumin Xiong, Xiaobin Chen*, Wei Dang, Xiujuan Guo, Han Xu, Guangzhou Li, Jican Guan and Xiaohu Huang
KZJ New Materials Group (Guangdong) Co., Ltd. Foshan 440600, Guangdong, China
*Corresponding author’s e-mail: chenxiaobin0412@yahoo.com.cn

Abstract. With isopentenyl polyoxyethylene polyether (TPEG), maleic anhydride (MAH), acrylic acid (AA) and binary ester (DBE) as monomers, hydrogen peroxide (H₂O₂) as initiator and mercaptoacetic acid (MAA) as chain transfer agent, the anti-clay polycarboxylate superplasticizer (APC) was synthesized. The structure of polymer was characterized by infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). The fluidity of cement paste mixed with montmorillonite (MMT) and the slump of concrete were used as evaluation indicators to investigate its mud resistance and dispersion properties. The results showed that when the content of bentonite (MMT) in the cement was 3% and the content of APC was 0.15% of the cement quality, the initial fluidity of the cement paste was 235 mm and the fluidity in 2 hours was 187 mm. The concrete test was carried out with the machine-made sand with high mud content: the slump flow was 560 mm, and the slump flow was 500 mm after 2 hours. APC has good mud resistance and good dispersion and retention properties.

1. Introduction
With the continuous development of concrete industry, concrete admixture have become an indispensable part of fresh concrete [1, 2]. Polycarboxylate superplasticizer have become the most widely used concrete admixture because of its advantages of low dosage, high water reducing rate, strong designability and environmental friendliness [3-5].

But it was found in the actual production and application of concrete, with the sharp increase in the amount of infrastructure construction, the consumption of sand and gravel is huge, leading to less and less high-quality sand and stone resources and the mud content in sand increases gradually [6, 7]. The polycarboxylate superplasticizer is very sensitive to the mud content in the sand. With the increase of the mud content in the sand, the polycarboxylate superplasticizer was absorbed by a large amount when it was used, which makes the dispersion of the polycarboxylate superplasticizer decline, leading to the decline of the working performance of the concrete [8-10].

In this paper, maleic anhydride (MAH) and dibasic ester (DBE) were used as functional monomers, and the anti-clay polycarboxylate superplasticizer (APC) was synthesized by oxidation-reduction system, and the molecular structure of the synthesized product is characterized. For the determination of relative molecular weight, machine-made sand (mud content 10%) was used to test the dispersion and mud resistance of the APC, and compared with ordinary polycarboxylate superplasticizer (PCE).
2. Experimental

2.1. Experimental raw materials
The main raw materials required for the experiment were as follows: isopentenyl polyoxyethylene polyether (TPEG, molecular weight 2400, industrial grade), maleic anhydride (MAH, industrial grade), acrylic acid (AA, industrial grade), hydrogen peroxide (H$_2$O$_2$, 27.5wt%, industrial grade), binary ester (DBE, industrial grade), Hydroxyethyl acrylate (HEA, industrial grade), mercaptoacetic acid (MAA, industrial grade), sodium hydroxide solution (30% aqueous solution, industrial grade).

2.2. Test raw materials
Cement (C, Feilu brand, P.O 42.5R); Strait sand (S1, river sand with fineness modulus of 2.3 mm and mud content less than 0.4%); Machine made sand (S2, river sand with fineness modulus of 2.7 mm and mud content more than 10%); Gravel (G1, grain size of 5-10 mm; G2, grain size of 10-20 mm); Fly ash (F, Level II); mineral powder (K, Level S95); Water: tap water meeting the test requirements.

2.3. Copolymerization

2.3.1. Copolymerization of PCE
Add TPEG macromonomer and water into the four port flask equipped with agitator, temperature control device and peristaltic pump feeding device, stir until the solution is uniform, directly add H$_2$O$_2$ and AA, drop reducing agent and chain transfer agent MAA, AA and HEA aqueous solutions respectively at room temperature. At room temperature, the copolymerization product was obtained by adding 3 hours, and then the pH value was 5-7 in sodium hydroxide solution. PCE was ordinary polycarboxylate superplasticizer.

2.3.2. Copolymerization of APC
Add TPEG and water into the four port flask equipped with agitator, temperature control device and peristaltic pump feeding device, turn on the agitator, set the synthesis temperature to 50 ℃, add H$_2$O$_2$ and DBE after the monomer dissolves, add solution A (reducing agent and chain transfer MAA), solution B (DBE and HEA), solution C (MAH) at the same time, the dropping time was 3 hours, and the reaction stops after the constant temperature was 1 hour after the dropping. The product was anti-clay polycarboxylate superplasticizer (APC) with pH value of 2.5-3.0.

2.4. Performance test method

2.4.1. Fluidity of cement paste. The fluidity of cement paste is conducted in accordance with GB/T8077-2012 "Test method for homogeneity of concrete admixtures". MMT was displace the corresponding quality of cement by internal mixing method. The water cement ratio is 0.29, and the water reducing agent content is 0.13%.

2.4.2. Concrete test. The concrete test is conducted in accordance with GB/T50080-2016 "Standard Test Methods for Performance of Common Concrete Mixtures" and GB/T 50081-2002 "Standard Test Methods for Mechanical Properties of Common Concrete". Test the performance of concrete mixtures and hardened concrete.

2.4.3. Gel permeation chromatographic (GPC) measurement. American Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector was used for testing and analysis.

2.4.4. Fourier transformer infrared spectra (FTIR) measurement. FTIR were obtained from the pressed disc of PCE and KBr. The spectra in the range of 4000-400 cm$^{-1}$ were recorded on Perkin Elmer Spectrum 100 FTIR spectrophotometer.
3. Experimental results and discussion

3.1. Effect of MAH dosage on cement dispersion

The dosage of MAH in APC-1, APC-2 and APC-3 were 5 g, 10 g and 15 g respectively. PCE was ordinary polycarboxylate superplasticizer. In order to explore the effect of MAH dosage on APC’s dispersibility, APCs and PCE were tested for slurry fluidity was shown in Figure 1.

![Figure 1. Effect of MAH dosage on cement dispersibility](image)

It can be seen from Figure 1 that when MMT was not added to the cement, the net slurry fluidity of APC-2 was the largest. When 3% MMT was added, the loss of PCE was 33%. MMT causes the loss of net slurry fluidity of cement to increase, because the specific surface area of clay was large, and PCE was easy to be adsorbed on the clay surface. Clay is an aluminosilicate mineral, the high valence metal ions such as Al$^{3+}$ and Si$^{4+}$ in its structure are easily replaced by low valence ions such as Fe$^{2+}$, Mg$^{2+}$ and Fe$^{3+}$, which make the surface of clay negatively charged. It is absorb some Ca$^{2+}$ released by cement hydration, which were reduced the fluidity of cement paste.

With the increase of MAH dosage, APC series water reducers increased first and then decreased. When MAH dosage was 10 g, the loss of APC-2 was the smallest, only 6%.

3.2. Concrete test

By regulating the ratio of water to cement and clay, amount of clay, and amount of additive, control the concrete slump fluidity to be (550 ± 10) mm, The concrete test mix proportion (kg/m$^3$) was m (cement): m (fly ash): m (mineral powder): m (strait sand): m (big stone): m (water) = 220: 80: 90: 800: 1050: 160. The concrete test results were shown in Table 1.

| Samples | MAH content | Dosage /% | Slump /mm initial | Slump /mm 2h | Dispersion /mm initial | Dispersion /mm 2h |
|---------|-------------|-----------|-------------------|--------------|----------------------|-------------------|
| PCE     | 0           | 1.2       | 210               | 170          | 540                  | 390               |
| APC-1   | 5           | 1.2       | 215               | 180          | 550                  | 445               |
| APC-2   | 10          | 1.2       | 220               | 200          | 555                  | 490               |
| APC-3   | 15          | 1.2       | 205               | 185          | 545                  | 475               |

As shown in Table 1, the dispersion and slump retention of APC (1-3) were better than PCE. When MAH dosage was 10 g, APC-2 has the best slump retention effect.
Under the same conditions, the concrete test was carried out by replacing 20% straight sand with machine-made sand (mud content more than 10%). The test results show that the less the loss in 2 hours, the less the water reducing agent is sensitive to mud. The concrete test mix proportion (kg/m³) was m (cement): m (fly ash): m (mineral powder): m (straight sand): m (machine made sand): m (big stone): m (water) = 220: 80: 90: 640: 160: 1050: 160. The concrete test results were shown in Table 2.

| Samples | Dosage /% | Slump / mm | Dispersion / mm | Compressive strength / MPa |
|---------|-----------|------------|-----------------|--------------------------|
|         |           | initial 2h | initial 2h      | 3d 7d 28d                |
| PCE     | 1.8       | 205        | 160             | 540 380 29.1 40.3 48.3   |
| APC-1   | 1.5       | 215        | 180             | 545 460 29.3 41.2 47.9   |
| APC-2   | 1.4       | 220        | 200             | 560 500 29.6 42.4 50.6   |
| APC-3   | 1.4       | 210        | 190             | 550 485 29.4 41.7 49.8   |

It can be seen from Table 2 that the dispersion effect of APCs was obviously better than that of PCE under the condition of high mud content of machine-made sand. Compared with PCE, the content of APC-2 was reduced by 20%, which has a good cost performance. APC-2 has no effect on the strength of concrete and the pulp is soft, has better workability of concrete, after 2 hours, the dispersion was 500 mm.

During the mixing of concrete, the clay will adsorb some Ca²⁺ dissociated by cement hydration due to its large specific surface area and negatively charged surface. The carboxyl group on the APC molecule is complexed with Ca²⁺ adsorbed on the clay surface and adsorbed on the clay surface, make the cement completely dispersed and improve the expansion and slump of the concrete.

4. GPC test

Table 3 were gel permeation chromatography data of anti-clay polycarboxylate superplasticizer APC-2 and PCE prepared by the best process conditions.

| Samples | Mₙ | Mₚ | Mₚ/Mₙ | Conversion rate /% |
|---------|----|----|-------|-------------------|
| PCE     | 23457 | 54874 | 2.34  | 83.45             |
| APC-2   | 15298 | 27521 | 1.80  | 89.26             |

It can be seen from Table 3 that the weight average molecular weight (Mₚ) of APC-2 was 27521, the number average molecular weight (Mₙ) was 15298, the polydispersity coefficient (Mₚ / Mₙ) was 1.8 and the conversion rate as high as 89.26%, which was smaller than that of PCE, indicating that the molecular weight distribution of APC-2 was narrow. The molecular weight distribution of the polymer has a great influence on its properties, the appropriate molecular weight distribution and the smaller polydispersity are conducive to its performance.

5. FTIR test

The composition information of PCE and APC-2 was characterized by FTIR. As shown in Figure 2, comparison with PCE, APC-2 at 3396 cm⁻¹, it was the stretching vibration peak of hydroxyl group (-OH), and at 2984 cm⁻¹, it was the stretching vibration absorption peak of alkyl group (-C-H), the absorption peak was small, indicating that the conversion rate of the reaction is high. The absorption peak at 1645 cm⁻¹ was generated by stretching vibration of carboxylate (C=O). At 1455 cm⁻¹ and 1351 cm⁻¹, there were bending vibration absorption peaks of alkyl (-C-H). The stretching vibration absorption peak of ether bond (-C-O-C) was 1105 cm⁻¹. Therefore, the synthesized APC-2 molecule contains -OH, -C-H, -C-O-C, C=O and other groups, which was consistent with the designed molecular structure.
6. Conclusions
(1) The APC was synthesized by oxidation reduction system. The molecular structure and relative molecular mass and its distribution of the synthesized products were characterized by FTIR and GPC respectively. The results showed that the synthesized product accords with the expected design.

(2) When the content of MMT were 3% of the content of cement, APC-2 was added into the cement, the cement particles have better dispersion performance.

(3) APC-2 was better than PCE in mud resistance, slump retention and mud resistance. It shows good performance in machine-made sand materials and has broad application prospects.

References
[1]. Weican Liang. Analysis of the current situation of the development of concrete admixtures [J]. Building materials development orientation (Volume I), 2017 (6).
[2]. Zhenping Sun, Zhengwu Jiang, Zhang Guanlun. Sustainable development of concrete admixtures and concrete materials [J]. Commercial concrete, 2007 (02): 8-12+58.
[3]. Ziming Wang, Huiqun Li. New progress in research and application of Polycarboxylic Water Reducer [J]. Concrete world, 2012, 38 (8): 50-56.
[4]. Papayianni I, Tsahos G, Oikonomou N, et al. Influence of super-plasticizer type and mix design parameters on the performance of them in concrete mixtures [J]. Cement and Concrete Composites, 2005, 27: 217-222.
[5]. Yoshioka K, Tazawa E, Kawai K, et al. Adsorption characteristics of superplasticizers on cement component minerals [J]. Cement and Concrete Composites, 2002, 32: 1507-1513.
[6]. Youzhe Kao. The influence of clay mineral composition on the dispersion of Polycarboxylic Water Reducer [D]. Chongqing University, 2015.
[7]. Bin Liu, Tingshu He, Juan He, et al. Effect of mud content on the performance of concrete mixed with polycarboxylic acid water reducer [J]. Silicate bulletin, 2015:53-57.
[8]. Ziming Wang, Xun Cheng. Effect of different clays on the application performance of Polycarboxylic Water Reducer [J]. Commercial concrete, 2010 (3): 24-26.
[9]. Yuanbing Luo. Study on mud resistance modification of polycarboxylic acid water reducer [D]. Chongqing University, 2017.
[10]. Baoguo Ma, Hu Yang, Hongbo Tan, et al. Adsorption behavior of polycarboxylate water reducer on cement and soil [J]. Journal of Wuhan University of technology, 2012, 5 (34): 1-5.