Study on adsorption and rheological properties of polycarboxylate superplasticizer with different structures

Zhanhua Chen1*, Yue Xiao1, Zhijun Lin1, and Yunhui Fang1
1KZJ NEW MATERIALS CO., LTD., Xiamen, Fujian, 361100, China
*Corresponding author’s e-mail: JYJT@xmabr.com

Abstract. The chemical structures of different types of polycarboxylate superplasticizers were characterized by gel chromatography. The results showed that except PCE-5 was short main chain and short branch chain, the other polycarboxylate superplasticizers were long side chain structures. The properties of the superplasticizer were evaluated by the pulp experiment, and the adsorption and action mechanism were analyzed by testing the adsorption capacity and rheological parameters. The results showed that the order of saturated adsorption capacity of polycarboxylate in cement was PCE-5 > PCE-4 > PCE-3 > PCE-1 > PCE-2. The fluidity of paste is proportional to the adsorption amount of water reducing agent in paste. The thixotropic retention capacity of paste increased with the increase of polycarboxylate adsorption capacity.

1. Introduction
Adsorption is the basis of the interaction between the superplasticizer and cement, and the dispersion of the superplasticizer is realized by adsorption[1-2]. The anion functional group in the molecular structure of polycarboxylate superplasticizer can be adsorbed on the surface of cement. Through static action and spatial hindrance action, the cement particles are temporarily in a stable state of uniform distribution, which improves the structure and uniformity of newly mixed cement concrete and changes the rheological properties of newly mixed cement paste[3-5]. At present, there are few studies on the adsorption and rheology of polycarboxylate superplasticizer with different structures on cement, and it is difficult to study the specific products. In this paper, macro and micro properties of polycarboxylic acid synthesized by five different polycarboxylate superplasticizer monomer were tested and analyzed, and the adsorption and rheological mechanism of polycarboxylic acid on cement were studied.

2. Experimental
2.1. Raw materials
Cement: reference cement P-O 42.5 complying with the Chinese standard GB8076-2016 was used and its composition is listed in Table 1.

PCE-1: synthesized using a TPEG with a molecular weight of 2400. PCE-2: synthesized using HPEG with molecular weight of 2400. PCE-3: synthesized by using EPEG with 2400 molecular weight with 50% solid content. PCE-4: synthesized using VPEG with 2400 molecular weight. PCE-5: synthesized using MPEG with molecular weight of 1200.
Table 1. Chemical and mineral composition of cement.

| Chemical composition (mass %) | Mineral composition (mass %) |
|-----------------------------|-----------------------------|
| SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂Oeq | f-CaO | C₃S | C₂S | C₄AF | C₃A |
| 20.58 | 4.97 | 3.76 | 63.57 | 2.29 | 2.00 | 0.52 | 0.95 | 58.93 | 16.42 | 10.88 | 7.81 |

2.2. Performance test method

2.2.1. GPC test
Using Waters 1515/Waters 2414, the chromatographic column was composed of Ultrahydregel, the flow rate was 0.8 mL/min, and the mobile phase was 0.1 mol/L sodium nitrate aqueous solution.

2.2.2. Fluidity of paste test
According to GB/T 8077-2016 test Method for homogenization of Concrete Admixtures, the water cement ratio is 0.29, and the dosage is tested according to 0.1% ~ 0.15% of cement mass.

2.2.3. Rheological property test
The rheological properties of cement paste, such as plastic viscosity and yield stress, were measured by MCR302 rheometer produced by Anton Pag, Germany, and the experimental data were processed by software. During the test, the paste was prepared according to the method described in Section 2.2.2, and 60 mL of the paste was poured into the sample cup, put into the measuring rotor, and installed on the rheometer as a whole. After the rotor was fastened, the test procedure was started. The thixotropic measurement method was selected, and the shear rate gradually increased from 5s⁻¹ to 131 s⁻¹ and then decreased from 131 s⁻¹ to 5s⁻¹.

2.2.4. Adsorption performance test
The adsorption capacity was measured by the Alimonta TOC-VCPH instrument. Configure different concentrations of water reducing agent solution, take 20 g reference cement into 40 g water reducing agent solution, stir evenly, take out an appropriate amount of liquid into the centrifugal tube, centrifuge centrifuge separation of filtrate (speed of 5000 r/min, centrifuge separation for 10 min), collect the supernatant TOC test, The adsorption amount of polycarboxylate superplasticizer on cement particles was calculated according to the test method of total organic carbon.

3. Experimental results and discussion

3.1. Structure characterization
The molecular weight and molecular weight distribution of PCE-1, PCE-2, PCE-3, PCE-4 and PCE-5 were detected by gel permeation chromatograph, and the results were shown in Table 2.

Table 2. Molecular weight of synthetic polycarboxylate superplasticizer.

| Name | Mn | Mw | Mp | Mn/Mw | Degree of polymerization of main chain/% | Side chain density/% |
|------|----|----|----|-------|--------------------------------------|---------------------|
| PCE-1 | 28484 | 48532 | 39580 | 1.703859 | 20.22 | 19.16 |
| PCE-2 | 30337 | 61407 | 41853 | 2.024172 | 25.59 | 15.53 |
| PCE-3 | 35852 | 69909 | 48578 | 1.949862 | 23.3 | 21.28 |
| PCE-4 | 26396 | 39634 | 60627 | 1.501495 | 13.21 | 31.11 |
| PCE-5 | 12933 | 19663 | 16891 | 1.520411 | 16.36 | 12.89 |

As can be seen from Table 2, Mn, Mw and Mp of PCE-1 and PCE-3 are similar, but all are smaller than PCE-2. PCE-4 has low degree of main chain polymerization and high side chain density. The molecular weight of four kinds of ether polycarboxylate superplasticizer is in the best range. The Mn, Mw and Mp of PCE-5 were all smaller than the other four polycarboxylate superplasticizer, and the degree of main chain polymerization and side chain density were small, and the molecular weight of ester monomer used for synthesis was small, indicating that the ester polycarboxylate superplasticizer
had short main chain, short side chain and low density, and the spatial resistance of the ester polycarboxylate superplasticizer was limited.

3.2. Adsorption performance analysis
The adsorption amount of plasticizer PCE-1, PCE-2, PCE-3, PCE-4 and PCE-5 on the cement surface was tested with the change of the dosage of polycarboxylic acid plasticizer, and the adsorption curve was shown in Figure 1.

![Figure 1. The adsorption amount of polycarboxylate superplasticizer changes with the dosage](image)

It can be seen from Figure 1 that the adsorption amount of cement particles on polycarboxylate superplasticizer increases with the increase of dosage. The order of adsorption capacity of five kinds of polycarboxylate is PCE-5>PCE-4 > PCE-3 > PCE-1> PCE-2. The polycarboxylate superplasticizer is mainly adsorbed on the surface of positively charged aluminate phase by negatively charged functional groups, and adsorbed on the surface of negatively charged silicate phase by Ca$^{2+}$ bridging. With the increase in the concentration of water reducer, the adsorption sites gradually decreased, and the platform structure at the end of the curve represented that the adsorption reached equilibrium. Continued increase in the dosage did not increase the adsorption amount.

3.3. Rheological property

3.3.1. Fluidity of paste analysis
The paste fluidity of PCE-1, PCE-2, PCE-3, PCE-4 and PCE-5 with different dosages was tested. The dosage of polycarboxylate superplasticizer was 0.10 % ~0.15 % of cement dosage. The test results are shown in Figure 2.

![Figure 2. Effect of polycarboxylate superplasticizer on fluidity of cement paste](image)

It can be seen from Figure 2 that when the dosage is low, PCE-1 can make the pulp have better flow ability, and when the dosage is high, PCE-2 can make the pulp have better flow ability. PCE-4 has weak ability to improve the fluidity of paste. Compared with the other four kinds of ether polycarboxylate superplasticizer, PCE-5 needs higher dosage to achieve the same fluidity and water reducing performance is weak.
3.3.2. Correlation analysis between adsorption and fluidity of paste

The fluidity test results of PCE-1, PCE-2, PCE-3, PCE-4 and PCE-5 with different dosages were compared with the adsorption test results of the corresponding dosage. The results are shown in Figure 3.

Figure 3. Comparison of fluidity and adsorption capacity of paste

It can be seen from Figure 3 that the fluidity of paste is proportional to the adsorption amount of polycarboxylate superplasticizer in cement. When the pulp fluidity reached the same level, PCE-2 required the least amount of adsorption, and PCE-5 required the highest amount of adsorption. The order of required adsorption amount was PCE-5 > PCE-4 > PCE-1 > PCE-3 > PCE-2. Compared with other polycarboxylate superplasticizers, PCE-5 contains negatively charged sulfonic acid groups, which improves the adsorption capacity of polycarboxylate superplasticizer on the surface of cement particles.

3.3.3. Analysis of rheological properties

The rheological parameters of PCE-1 to PCE-5 pastes were determined. The dosage of polycarboxylate superplasticizer was 0.10 % ~ 0.15 % of cement dosage. The rheological parameters of polycarboxylate superplasticizer with different dosage were tested, and the results are shown in Figure 4 to Figure 6.
The change of internal structure of fresh pulp can be reflected by the thixotropy of pulp. The shear stress at different rotational speeds was measured by rheometer. It was found that the rising curve did not coincide with the falling curve, but surrounded by a circle, which was called a hysteresis loop. The area of this loop is obtained by instrument test, which can measure the thixotropy of the pulp. The larger the area is, the better the thixotropy is, and vice versa.

It can be seen from Figure 6 that when the dosage of polycarboxylate superplasticizer is 0.10%, the slope of PCE-5 paste curve is much larger than other pastes, and the viscosity of the system is larger. At this time, the overall size of the hysteresis loop area is PCE-5 > PCE-1 > PCE-4 > PCE-3 > PCE-2, and the addition of PCE-5 can significantly improve the thixotropy of the paste. With the increase of polycarboxylate superplasticizer content, the area of hysteresis loop decreases, and the thixotropy of paste decreases. The reason may be that the precipitation of free water increases with the increase of polycarboxylate superplasticizer content. Excessive water precipitation leads to the settlement of the flocculation structure. In the descending shear stage, the flocculation structure settles to the bottom, the resistance decreases, and the shear stress decreases accordingly, which increases the area of the hysteresis loop.

When the dosage of polycarboxylate superplasticizer increased from 0.10% to 0.15%, the descending order of the total area of the hysteresis loop was PCE-5 > PCE-4 > PCE-1 > PCE-1 > PCE-2, which was consistent with the order of the adsorption amount, indicating that the thixotropic retention ability of the paste was positively correlated with the adsorption amount of polycarboxylate molecules on the surface of cement particles. The hysteresis loop area of PCE-5 paste is basically unchanged with the increase of dosage, and the thixotropy is maintained well.
4. Conclusion
From what has been discussed above, we may safely draw the conclusion above:

(1) PCE-1, PCE-2, PCE-3 and PCE-4 are long side chain and long main chain structures, PCE-4 is short main chain structure, PCE-5 is short main chain and short side chain structure.

(2) The adsorption capacity of five polycarboxylic acids was PCE-5 > PCE-4 > PCE-3 > PCE-1 > PCE-2. The adsorption amount increased with the increase of water reducer dosage, and finally reached saturation adsorption.

(3) The fluidity of paste is proportional to the adsorption amount of water reducer in cement. When the pulp fluidity was the same, the required adsorption amount was PCE-5 > PCE-4 > PCE-1 > PCE-3 > PCE-2. In the process of increasing the dosage of polycarboxylate superplasticizer, the area of hysteresis loop decreased, and the thixotropy of paste decreased. The thixotropic retention capacity increased with the increase of adsorption amount of polycarboxylate.

(4) The relationship between the structure and adsorption amount of polycarboxylate superplasticizer synthesized by different polycarboxylate superplasticizer monomers was studied in this project. The relationship between adsorption capacity and thixotropy is of guiding significance for subsequent products and product applications. Subsequently, it is suggested to study the relationship between adsorption and hydration, and further study the mechanism of water reducer on cement.

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