Molecular Structure Influence of Polycarboxylate Superplasticizer on the pump PHC

Yunhui Fang, Xiaofang Zhang, Yuliang Ke, Huazhen Lai, Lina Zhong, Geli Li, Yanmei Lin, Tianxing Lin, Yuanqiang Guo and Xiuxing Ma

KZJ New Materials Group CO., LTD., Fengling Road 760, Xiamen, Fujian, China.
E-mail: fangyunhui@126.com

Abstract. This article disclosed to design a series of polycarboxylate superplasticizer (PHC) by free radical polymerization. The PEO grafting side chain desity and main chain composition of PCE greatly influenced the concrete performance. The PEO long side chain of PCE can produces steric hindrance effect in concrete to provide the flowability. The functional monomer DAC and AMPS incorporated into the main chain can improve the compressive strength. The suitable water dosage in the PHC mix proportion is 145 kg/m$^3$ and 150 kg/m$^3$.

1. Introduction
The prestressed high-strength concrete (PHC) pipe piles have the characteristics of convenience construction speed, high bearing capacity, high density and cost saving. It is widely used in the foundation engineering of various buildings and structures, such as skyscraper, highway, railway and sea port[1,2].

The processes of steam curing and autoclaved curing are used in the fabrication of PHC in order to improve production efficiency, quality control and attaining a sufficient concrete compressive strength[3,4]. The required compressive strength of PHC is above 40 MPa after steam curing process and generally over 80 MPa after autoclaved curing process.

Polycarboxylate superplasticizer (PCE) has excellent molecular designability and high water reduction rate. The PCE has been widely used in ordinary commercial concrete. For the PHC with fine particle and low water binder ratio, the PCE is often hard to disperse and easily to bleed. It is mainly related to the adsorption rate of admixture. A large amount of superfine binding materials will greatly consume PCE, which reducing the free water, making the fluidity decreased, and viscosity increased sharply. Aiming at practical application problems, this paper investigated the influence of molecular structure of PCE on the PHC, such as PEO graft density, side chain length, and etc.

2. Experiments

2.1. Materials
Isopentenylpolyoxyethylene ether (IPEG, molecular weight 2400); Acrylic acid (AA); Acryloxyethyl trimethylammonium chloride (DAC); 2-acrylamido-2-methylpropanesulfonic acid (AMPS); Ammonium persulfate (APS); Thioglycolic acid (TGA); Sodium hydroxide solution, 30 wt% (30 wt% NaOH).

Huarun cement (C), PO 52.5R, the performance indexes are shown in table 1; Ground fine quartz sand powder (GQSP) , specific surface area 435 m$^2$/kg; Ground granulated blastfurnace slag, S95
(GGBS), specific surface area 420 m²/kg; River sand (S), fineness modulus of 2.7; Coarse aggregate 1 (G1), particle size of 10-31.5 mm; Coarse aggregate 2 (G2), particle size of 5-20 mm; Water (W).

| Specific surface area/(m²/kg) | Setting time/min | Flexural strength/MPa | Compressive strength/MPa |
|-------------------------------|------------------|-----------------------|--------------------------|
|                               | Initial  | Final | 3 d          | 28 d | 3 d          | 28 d |
| 362                           | 172     | 234   | 6.2          | 9.7  | 33.7         | 57.5 |

2.2. Synthetic Methods
A detailed description of monomers with mixed proportion to synthesize PCE is described in table 2. An initiator solution with 2.0 wt% was prepared by dissolving APS in deionized water. An unsaturated acid monomers solution with a mass concentration of 80 wt% was prepared by dissolving unsaturated acid monomers in deionized water. In the polymerization process, the molar ratio of initiator to total unsaturated acid monomers was fixed at 2.5 wt%. A four-necks flask with a dropping device filled with macromonomer solution was firstly washed by using nitrogen gas for 3 times and heated up to 60±3 °C in a water bath. Then the initiator solution and the unsaturated acid monomers solution were separately fed into the flask dropwise over 3 h. Kept the reaction at 60±3 °C for 1 h to complete the polymerization. Finally, a proper amount of sodium hydroxide solution was added to adjust the pH value to 6 to 7. The obtained polymer appeared to be yellowish transparent solutions with solid content at 50 wt%.

| Sample | AA/mol | IPEG/mol | DAC/mol | AMPS/mol |
|--------|--------|----------|---------|----------|
| PCE-1  | 0.50   | 0.25     | -       | -        |
| PCE-2  | 0.75   | 0.25     | -       | -        |
| PCE-3  | 1.00   | 0.25     | -       | -        |
| PCE-4  | 1.25   | 0.25     | -       | -        |
| PCE-5  | 1      | 0.25     | 0.03    | -        |
| PCE-6  | 1      | 0.25     | 0.06    | -        |
| PCE-7  | 1      | 0.25     | 0.09    | -        |
| PCE-8  | 1      | 0.25     | 0.12    | -        |
| PCE-9  | 1      | 0.25     | 0.09    | 0.02     |
| PCE-10 | 1      | 0.25     | 0.09    | 0.04     |
| PCE-11 | 1      | 0.25     | 0.09    | 0.06     |
| PCE-12 | 1      | 0.25     | 0.09    | 0.08     |

2.3. Test Methods
The paste test was in accordance with GB/T 8077-2012 (China Standard). The dosage of PCEs was 0.2%. The water binder ratio of paste was 0.29. The concrete test was in accordance with relevant requirements of GB/T 50080-2016 and GB/T 13476-2009 (China Standard). The dosage of admixture in concrete was 0.5% (solid content) according to the binding material. The concrete mix proportion is shown in table 3.

| Material | W | C | GGBS | GQSP | S | G1 | G2 |
|----------|---|---|------|------|---|----|----|
| Dosage/(kg/m³) | 145 | 310 | 50 | 80 | 760 | 800 | 345 |

The concrete blocks were kept at 20±2 °C for 30 min, and then moved into the curing pool (80 °C) for 5 h. And the concrete blocks were placed in the autoclave (180 °C, 1 MPa) for 8 h in the following. Finally the compressive strength could be tested.
3. Results and Discussion

3.1. Influence of PEO Grafting Side Chain Density

The molecular structure of PCE is composed of main chain and side chain. The PEO long side chain of PCE can produce steric hindrance effect in concrete to provide the flowability. The ratio of acid to ether characterizes the PEO grafting side chain density. The PEO grafting side chain density can be adjusted to obtain different performance of PHC. The test results are shown in table 4.

Table 4. Test results of paste and concrete

| Sample | Ratio of acid/ether | Paste fluidity/mm 0 min | Paste fluidity/mm 30 min | Compressive strength/MPa Steam curing | Compressive strength/MPa Autoclaved curing |
|--------|---------------------|-------------------------|--------------------------|--------------------------------------|----------------------------------------|
| PCE-1  | 2                   | 188                     | 172                      | 37.2                                 | 62.6                                   |
| PCE-2  | 3                   | 202                     | 179                      | 38.8                                 | 63.9                                   |
| PCE-3  | 4                   | 217                     | 188                      | 40.4                                 | 77.4                                   |
| PCE-4  | 5                   | 230                     | 195                      | 40.8                                 | 75.3                                   |

It can be indicated from table 4 that the initial paste fluidity increases gradually with the increasing of the ratio of acid to ether, while the paste fluidity retention decreasing after 30 min. The compressive strength raises from 37.2 MPa to 40.8 MPa after steam curing. And the autoclaved curing process also improves the compressive strength from 62.6 MPa to 75.3 MPa. The PCE-3 exhibits higher compressive strength. The optimal ratio of acid to ether is 4.

3.2. Influence of Main Chain Composition of PCEs

3.2.1. Influence of DAC monomer on main chain blocking. Different amount of DAC were introduced basing on the synthetic formula of PCE-3. The test results are shown in table 5.

Table 5. Influence DAC on the test result of paste and concrete

| Sample | Ratio of DAC/AA | Paste fluidity/mm 0 min | Paste fluidity/mm 30 min | Compressive strength/MPa Steam curing | Compressive strength/MPa Autoclaved curing |
|--------|----------------|-------------------------|--------------------------|--------------------------------------|----------------------------------------|
| PCE-5  | 0.03           | 204                     | 150                      | 40.4                                 | 77.4                                   |
| PCE-6  | 0.06           | 192                     | 135                      | 43.5                                 | 77.8                                   |
| PCE-7  | 0.09           | 185                     | 123                      | 46.9                                 | 80.1                                   |
| PCE-8  | 0.12           | 159                     | 80                       | 44.5                                 | 78.5                                   |

The compressive strength of PHC can be effectively improved by introducing DAC into the main chain of PCE molecular structure. Table 5 shows that when the ratio of DAC to AA increasing from 0.03 to 0.12, the initial paste fluidity changes from 204 mm to 159 mm, and varies from 150 mm to 80 mm after 30 min. The PCS-7 exhibits higher concrete strength. The steam and autoclaved curing compressive strength of PCE-7 are 46.9 MPa and 80.1 MPa respectively when the ratio of DAC to AA is 0.09. The DAC will reduce paste fluidity and increase the PHC compressive strength. The optimal ratio of DAC to AA is 0.09.

3.2.2. Influence of AMPS monomer on main chain blocking. Different amount of AMPS were introduced basing on the synthetic formula of PCE-7. The test results are shown in table 6.
Table 6. Influence AMPS on the test result of paste and concrete

| Sample  | Ratio of AMPS/AA | Paste fluidity 0 min | Paste fluidity 30 min | Compressive strength/MPa Steam curing | Compressive strength/MPa Autoclaved curing |
|---------|-----------------|----------------------|-----------------------|----------------------------------------|-------------------------------------------|
| PCE-9   | 0.02            | 180                  | 145                   | 47.1                                   | 78.3                                      |
| PCE-10  | 0.04            | 202                  | 165                   | 47.7                                   | 80.5                                      |
| PCE-11  | 0.06            | 228                  | 187                   | 49.2                                   | 83.8                                      |
| PCE-12  | 0.08            | 238                  | 200                   | 49.8                                   | 82.5                                      |

As can be seen from Table 5, when the ratio of AMPS to AA increasing from 0.02 to 0.08, the initial paste fluidity changes from 180 mm to 238 mm, and varies from 145 mm to 200 mm after 30 min. The compressive strengths after steam and autoclaved curing are 49.2 MPa and 83.8 MPa respectively when the ratio of AMPS to AA is 0.06. The AMPS can improve paste fluidity and increases the PHC compressive strength. The optimal ratio of AMPS to AA is 0.06.

3.3. Chemical Characterization of PCEs

The PCE-3 and PCE-11 were characterized by FT-IR and GPC. The FT-IR spectrums are shown in figure 1 and figure 2. The GPC spectrums are shown in figure 3 and figure 4. The detail GPC data results are shown in table 7.

![Figure 1. FT-IR spectrum of PCE-3](image1)

![Figure 2. FT-IR spectrum of PCE-11](image2)
The peaks of alkyl group (-CH-, -CH2-, -CH3, 2873.12 cm⁻¹, 2872.43 cm⁻¹), ester group (-COOCH2-, 1720.12 cm⁻¹, 1723.96 cm⁻¹), sodium carboxylate (-COONa, 1643.70 cm⁻¹, 1646.20 cm⁻¹) and PEO group (-CH2-CH2-O-, 1106.09 cm⁻¹, 1107.59 cm⁻¹) can be found in figure 1 and figure 2. The FT-IR spectrum well matched the chemical structure of designed PCEs.

As can be seen from figure 3, figure 4 and table 7, the GPC values of Mn, Mw and Mp of PCE-3 are higher than PCE-11, but the Mw/Mn and conversion rate are slightly lower than that of PCE-11.

### Table 7. GPC data of PCE-3 and PCE-11

| Sample  | Mn(Da) | Mw(Da) | Mp(Da) | PD(Mw/Mn) | Conversion rate(%) |
|---------|--------|--------|--------|-----------|--------------------|
| PCE-3   | 20017  | 31928  | 27987  | 1.595     | 82.43              |
| PCE-11  | 17891  | 30756  | 25170  | 1.719     | 85.57              |

3.4. Influence of PCE on Different Water Binder Ratio of PHC

In order to evaluate the performance of PCE-11, the concrete tests of different water binder ratio were designed in practical application. Based on the concrete mix proportion in table 3, the water dosages of concrete mix proportion were adjusted from 135 kg/m³ to 155 kg/m³. The initial slump was controlled to be equivalent by adjusting the PCE-11 content. The results are shown in table 8.
Table 8. Influence of water adjusting in concrete mix proportion

| No. | Concrete water dosage/(kg/m³) | Slump/mm 0 min | Slump/mm 30 min | Pumpability description | Compressive strength/MPa Steam curing | Compressive strength/MPa Autoclaved curing |
|-----|-------------------------------|----------------|----------------|------------------------|---------------------------------------|------------------------------------------|
| T-1 | 135                           | 135            | 100            | High viscosity         | 52.6                                  | 90.4                                     |
| T-2 | 140                           | 165            | 120            | High Viscosity         | 50.2                                  | 85.2                                     |
| T-3 | 145                           | 190            | 165            | Slightly bleeding      | 48.8                                  | 84.1                                     |
| T-4 | 150                           | 205            | 190            | Soft to pump           | 48.4                                  | 83.8                                     |
| T-5 | 155                           | 210            | 195            | Easily to pump         | 47.9                                  | 82.8                                     |

From table 8, it is observed that the higher slump when decreasing the water dosage in the concrete mix proportion. When the concrete water dosage increasing from 135 kg/m³ to 155 kg/m³, the slump changes from 135 mm to 210 mm. The trend of slump retention after 30 min is the same as the initial.

From the pumpability aspect, the higher water dosage, the concrete is easier to pump. The more water dosage can promote the concrete workability and reduce the viscosity the pumping pressure. According to the combination of steam and autoclaved curing strength, the water dosage of 145 kg/m³, 150 kg/m³ and 155 kg/m³ is equivalent. From the perspective of pumppability and compressive strength, the suitable water dosage in the concrete mix proportion is 145 kg/m³ and 150 kg/m³.

4. Conclusions
Based on the above test results, the following conclusions can be drawn:

1. The PEO long side chain of PCE can produces steric hindrance effect in concrete to provide the flowability. The optimal ratio of acid to ether is 4.
2. The DAC monomer in the PCE molecular structure can hinder the flowability, while is effective to improve the compressive strength both after steam curing and autoclaved curing process.
3. The AMPS monomer in the PCE molecular structure can improve both the concrete performance of the flowability and compressive strength.
4. Considering pumppability and compressive strength, the suitable water dosage in the PHC mix proportion is 145 kg/m³ and 150 kg/m³.

5. References
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