The influence of the structural parameters of polycarboxylate superplasticizer on the dispersion and adsorption

Shaohong Zhu 1*, Yanmei Lin 1, Yunhui Fang 1, Yuliang Ke 1, Huazhen Lai 1, Hao Chen 1

1KZJ New Materials Group Co., Ltd., Xiamen, Fujian, 361100
1Email: hong521203402@163.com
1Email: zhushaohong@kzj.lets.com

Abstract. Polycarboxylate superplasticizers with different structural parameters were synthesized by isobutylene polyoxyethylene ether, acrylic acid and ammonium persulfate as raw materials from the perspective of molecular design. The influence of polycarboxylate superplasticizer on cement adsorption was characterized by cement adsorption capacity test and fluidity test, etc. At the same time, the adsorption change of polycarboxylate superplasticizer on the surface of cement particles was also revealed. It was found that the best adsorption and dispersion properties on cement paste were obtained under the heating synthesis process when the structure of the water reducing agent was designed to have a weight average molecular weight of 55128, a macromonomer conversion rate of 84.61%, and a side chain density of 0.1725. For the normal temperature process, when the weight average molecular weight was 103920, the macromonomer conversion rate 92.03%, and the side chain density 0.3115, the best effects in cement can be achieved.

1. Introduction
Polycarboxylate superplasticizer (PCE) have strong attraction and significant adsorption on cement granules. It will have a greater effect on the dispersion and adsorption performance of cement particles, mainly including the three-dimensional repulsion generated by the interaction of the polymer adsorption layer, and the electrostatic repulsion caused by the adsorption of the components in the PCE that were responsible for the dispersion on the surface of the cement granules [1-3]. According to the research, the influence of PCE with different structures on its adsorption and dispersion performance were mainly reflected in the PCE molecular weight, side chain density, conversion rate, and functional monomer structure [4-5]. Therefore, the molecular structure of PCE was adjusted from the perspective of molecular design to further study the adsorption and dispersion of PCE with different structural parameters in cement paste [6]. There were great significances for the development and optimization of new polycarboxylic acid high-performance water reducer.

In this research, the molecular design of the parameters such as the molecular weight, macromonomer conversion rate and side chain density of PCE products were carried out. The influence of the PCE structure parameters on the adsorption capacity was further analyzed to determine the relationship between the composition and structure of PCE and its adsorption and dispersion performance.
2. Materials and Methods

2.1 Experimental raw materials

2.1.1 Synthetic materials
Isobutylene polyoxyethylene ether (HPEG, Fujian Zhongshan Chemical Co., Ltd.), Isopentenyl polyoxyethylene ether (TPEG, Fujian Zhongshan Chemical Co., Ltd.), Acrylic acid (AA, Fujian Binhai Chemical Co., Ltd.), Ammonium persulfate (APS, Zhangzhou Rongcan Trading Co., Ltd.), Sodium hypophosphite (SHP, Chengdu Sanzeng Material Co., Ltd.), Sodium hydroxide solution (NaOH, Quanzhou Lixin Chemical Trading Co., Ltd.), Brygmann chemical reagent TP1351 (Shanghai Kaiyin Chemical Co., Ltd.), Thioglycolic acid (TGA, Nanjing Qicheng New Material Co., Ltd.).

2.1.2 Materials for performance testing
The cement used in the experiment was standard P.I 42.5 cement (China United Cement Group Co., Ltd.), and its properties were shown in Table 1.

| Compressive strength /MPa | Flexural strength /MPa | Water requirement of normal consistency /% | Setting time /min | Density g/cm³ | Fineness /% |
|--------------------------|-----------------------|------------------------------------------|-------------------|--------------|-------------|
| 3 d                      | 28 d                  | 3 d                                      | 28 d              |              |             |
| 23.6                     | /                     | 4.9                                      | /                 | 25.2         | 172         |
| 172                      | 226                   | 3.14                                     | 0.9               |

2.2 Performance testing and characterization

2.2.1 Fluidity test of cement paste
The fluidity of cement paste was tested according to GB/T 8077-2012 "Test Method for Homogeneity of Concrete Admixtures". Among them, the PCE content was 0.2% (reduced solid).

2.2.2 Cement adsorption capacity test
The organic carbon content of PCE were tested the Vario TOC total organic carbon analyzer (Alimenta Trading (Shanghai) Co., Ltd.).

2.2.3 Gel Permeation Chromatography Test
The gel permeation chromatography test (GPC) was tested by U.S. Waters 1515 pump, 2414 differential detector and Breeze acquisition and analysis software. The weight average molecular weight (Mw) and macromonomer conversion rate were measured by GPC, and the side chain density of the PCE molecule was calculated by further analysis.

2.3 preparation of polycarboxylic superplasticizer
AA, SHP (or TGA, TP1351), and TPEG (or HPEG) and initiator APs were copolymerized by free radical copolymerization in aqueous solution at 63 °C (or room temperature). Finally, the reaction product was cooled and neutralized with NaOH solution to a pH of 7 ~ 8 to obtain a PCE solution.

3. Results and discussion

3.1 The structural parameter design of PCE and its influence on the dispersion and adsorption performance
In this paper, TPEG or HPEG was selected as the polyether macromonomer to synthesize PCE by heating (63 °C) or room temperature process. Through the adjustment of these factors, such as n(AA): n(TPEG), n(SHP): n(TPEG), n(APS): n(TPEG), n(AA): n(HPEG), n(TGA): n(HPEG), n(APS): n(HPEG), the changes of different structural parameters of PCE were shown in Table 2 ~ 3.
Table 2 The changes of different parameters under heating process

| samples | n(AA): n(TPEG) | n(SHP): n(TPEG) | n(APS): n(TPEG) | Mw     | macromonomer conversion rate (%) | Side chain density | cement paste fluidity (mm) | Adsorption capacity (mg/g) |
|---------|----------------|-----------------|-----------------|--------|---------------------------------|--------------------|--------------------------|---------------------------|
| A-01    | 3.20           | 0.32            | 0.06            | 52248  | 80.75                           | 0.1792              | 218                      | 2.91                      |
| A-02    | 3.47           | 0.32            | 0.06            | 52968  | 81.78                           | 0.1743              | 220                      | 3.11                      |
| A-03    | 3.72           | 0.32            | 0.06            | 55128  | 84.61                           | 0.1725              | 230                      | 4.77                      |
| A-04    | 4.00           | 0.32            | 0.06            | 56880  | 83.34                           | 0.1720              | 235                      | 4.22                      |
| A-05    | 4.27           | 0.32            | 0.06            | 61488  | 83.38                           | 0.1717              | 242                      | 4.72                      |
| A-06    | 3.72           | 0.17            | 0.06            | 106368 | 84.12                           | 0.1717              | 238                      | 4.90                      |
| A-07    | 3.72           | 0.25            | 0.06            | 57744  | 84.43                           | 0.1723              | 235                      | 4.45                      |
| A-08    | 3.72           | 0.42            | 0.06            | 43728  | 81.58                           | 0.1729              | 227                      | 3.05                      |
| A-09    | 3.72           | 0.50            | 0.06            | 36648  | 80.82                           | 0.1729              | 223                      | 2.89                      |
| A-10    | 3.72           | 0.32            | 0.02            | 50424  | 82.74                           | 0.1760              | 215                      | 2.08                      |
| A-11    | 3.72           | 0.32            | 0.03            | 49896  | 83.05                           | 0.1736              | 225                      | 3.08                      |
| A-12    | 3.72           | 0.32            | 0.07            | 52104  | 84.19                           | 0.1720              | 243                      | 4.24                      |
| A-13    | 3.72           | 0.32            | 0.08            | 61896  | 83.54                           | 0.1714              | 242                      | 4.39                      |

Table 3 The changes of different parameters under room temperature process

| samples | n(AA): n(HPEG) | n(TGA): n(HPEG) | n(APS): n(HPEG) | Mw     | macromonomer conversion rate (%) | Side chain density | cement paste fluidity (mm) | Adsorption capacity (mg/g) |
|---------|----------------|-----------------|-----------------|--------|---------------------------------|--------------------|--------------------------|---------------------------|
| A-14    | 4.05           | 0.10            | 0.09            | 74688  | 90.87                           | 0.3173              | 250                      | 3.03                      |
| A-15    | 4.32           | 0.10            | 0.09            | 88872  | 90.77                           | 0.3158              | 251                      | 3.42                      |
| A-16    | 4.59           | 0.10            | 0.09            | 103920 | 93.00                           | 0.3124              | 260                      | 3.44                      |
| A-17    | 4.85           | 0.10            | 0.09            | 103848 | 92.95                           | 0.3120              | 262                      | 3.41                      |
| A-18    | 5.12           | 0.10            | 0.09            | 104424 | 93.07                           | 0.3127              | 261                      | 3.35                      |
| A-19    | 4.59           | 0.03            | 0.09            | 279048 | 93.08                           | 0.3115              | 270                      | 3.63                      |
| A-20    | 4.59           | 0.07            | 0.09            | 236496 | 93.01                           | 0.3118              | 272                      | 3.39                      |
| A-21    | 4.59           | 0.13            | 0.09            | 58632  | 92.99                           | 0.3130              | 241                      | 3.30                      |
| A-22    | 4.59           | 0.17            | 0.09            | 61152  | 92.93                           | 0.3128              | 219                      | 2.80                      |
| A-23    | 4.59           | 0.10            | 0.05            | 91536  | 90.70                           | 0.3151              | 205                      | 3.38                      |
| A-24    | 4.59           | 0.10            | 0.07            | 74832  | 91.56                           | 0.3129              | 247                      | 3.61                      |
| A-25    | 4.59           | 0.10            | 0.10            | 112728 | 92.03                           | 0.3120              | 263                      | 3.53                      |
| A-26    | 4.59           | 0.10            | 0.12            | 113232 | 92.87                           | 0.3111              | 272                      | 3.32                      |

It can be preliminarily seen from table 2 and table 3 that with the weight average molecular weight increased, the conversion rate of macromonomers enlarged and the side chain density became smaller, the effects of PCE on the adsorption-dispersion performance began to increased.

3.2 The influence of PCE weight average molecular weight on dispersion and adsorption

By adjusting the amount of polyether macromonomer, acrylic acid, initiator, reducing agent and chain transfer agent, the relationships between the weight average molecular weight (Mw) of PCE and the dispersion-adsorption performance were studied, as shown in figure 1.

According to figures 1a, 1c and 1d, the weight average molecular weight also increased with the augment of n(AA): n(TPEG), n(APS): n(TPEG) and n(AA): n(HPEG). It was proved that the increase of carboxyl groups and initiator can promote the Mw, the cement paste fluidity will also be increased with Mw from 218 mm to 242 mm. However, for the amount of adsorption on the surface of cement granules, Mw was not as large as possible. When Mw increased to a certain extent, the increasing trend of adsorption performance remained a steady state. For the heating process, when n(AA): n(TPEG) = 3.72, n(APS): n(TPEG) = 0.06, and Mw reached 55128, the adsorption effect was the best.
If it continued to increase, the adsorption performance will be dropped slightly, and then maintained a stable state. For the room temperature process, when \( n(\text{AA}): n(\text{HPEG}) = 4.59 \) and \( M_w = 103920 \), the flow dispersion adsorption effect was the best.

It can be concluded that with the augment of \( n(\text{SHP}): n(\text{TPEG}) \) and \( n(\text{TGA}): n(\text{HPEG}) \), the \( M_w \) showed a downward trend, which were be inhibited with the increase of the amount of reducing agent or chain transfer agent (figures 1b and 1e). Moreover, the fluidity of purified slurry also dropped with the reduction of \( M_w \), but the adsorption amount changed gradually. When \( n(\text{SHP}): n(\text{TPEG}) = 0.3 \) and \( n(\text{TGA}): n(\text{HPEG}) = 0.08 \), it began to show a significant downward trend.

With the augment of \( n(\text{APS}): n(\text{HPEG}) \), \( M_w \) first decreased and then increased (figure 1f). When it increased to 105,000, the cement paste fluidity will be stabilized. However, the change trend of the adsorption capacity was just the opposite. When \( n(\text{APS}): n(\text{HPEG}) = 0.07 \), \( M_w \) reached 74832, and its adsorption effect was optimal.

![Figure 1 The relationship trends between Mw, cement paste fluidity and adsorption capacity](image)

### 3.3 The influence of macromonomer conversion rate on dispersion and adsorption

The macromonomer conversion rate had increasing trends with the increase of acrylic acid (figures 2a, 2d). When \( n(\text{AA}): n(\text{TPEG}) = 3.72 \) for the heating process, its conversion rate reached the maximum,
Figure 2 The relationship trends between macromonomer conversion rate, cement paste fluidity and adsorption capacity

which was 84.61%. And the trends of dispersion-adsorption performance were be increasing. For the heating process, the adsorption effect was the best, when its conversion rate reached 84.61%. For the normal temperature process, these effects were the best while the conversion was 93.09%.

The macromonomer conversion rate showed a downward trend (2b and 2e) with the augment of n(SHP): n(TPEG) or n(TGA): n(HPEG). When n(SHP): n(TPEG) = 0.32, the maximum macromonomer conversion rate was 84.61% in the heating process. When n(TGA): n(HPEG) = 0.10, the maximum conversion rate was 93.09% in the normal temperature process. Meanwhile, the dispersion-adsorption performance of its PCE products were reduced with the increase of the conversion rate. The adsorption capacity of the heating process had dropped by 2.1 mg/g, while its capacity of the room temperature process had a small change, which only dropped by 0.8 mg/g.

The conversion rate first increased and then dropped with the augment of the initiator (2C and 2F). When n(APS): n(TPEG) = 0.06 or n(APS): n(HPEG) = 0.09, the conversion rate got to the maximum respectively. It was revealed that an appropriate amount of initiator can promote the its conversion, and the over-all change trends will be increased. Combined with the above analyses, the Mw basically continued to increase and its molecular weight distribution will be wider following the increase of the unsaturated acid monomers or initiators. The macromonomer conversion rate gradually increased, however, the effects of reducing agent and chain transfer agent on PCE were completely opposite.

3.4 The influence of side chain density on dispersion and adsorption
The overall change trends of the side chain density decreased with the augment of the unsaturated acid or initiator (figure 3a and 3b). However, the cement paste fluidity was on the rise, indicating that the decrease of side chain density can promote the its dispersibility. In addition, the amount of adsorption on the surface of cement particles also increased with the reduction of the side chain density.
Figure 3 The relationship trends between side chain density, cement paste fluidity and adsorption capacity

The change trends of their adsorption capacity slowed down while the side chain density dropped to a certain value. In the heating process, when the side chain density reached 0.1725, the adsorption capacity was 4.77 mg/g, and the adsorption performance was the best. However, when the side chain density was 0.1720, the dispersibility was better for the dispersibility. There was the best adsorption performance in the normal temperature process when the side chain density reached 0.3124 and the adsorption capacity was 3.44 mg/g.

It can be found from figures 3b and 3E that with the augment of n(SHP): n(TPEG) or n(TGA): n(HPEG), the side chain density also increased, indicating that the addition of reducing agent and chain transfer agent promoted the side chain density. However, the fluidity and adsorption capacity of cement paste gradually became smaller. These showed that the content of carboxyl groups in the water reducer molecule will be dropped, which inhibited the dispersion and adsorption performance.

Meanwhile, the steric hindrance effect and electrostatic repulsion effect in the molecular structure of the polycarboxylate superplasticizer will be gradually increased when the side chain density increased, thereby reducing the adsorption capacity on the surface of cement granules. There were negative correlations between the side chain density, the weight average molecular weight and the macromonomer conversion rate. When the molecular weight reached higher, the side chain density required to achieve higher conversion will be reduced.

4. Conclusions

Based on the heating process and room temperature process, variable structural adjustments were carried out. Combined with the analyses of weight average molecular weight, macromolecular monomer conversion, side chain density, the following conclusions are drawn:

(1) When the weight average molecular weight and the conversion of large monomers were greater, adsorption and dispersion performances will advance greater. However, these increases will be gradually dropped and tended to be flat state. There were the best adsorption and dispersion performance under the heating process, when the weight average molecular weight reached 55128 and
the macromonomer conversion rate was 84.61%. However, with the augment of Mw, the adsorption and dispersion remained unchanged or even decreased. At the normal temperature process, when the weight average molecular weight 103920 and the macromonomer conversion rate 92.03%, the best adsorption and dispersion effects will be achieved.

(2) The influence trend of the side chain density was not obvious under the condition of low content, but with the increase of the content, the side chain density reduced, the adsorption and dispersion performance became better. In the heating process, when the side chain density reached 0.1725, the dispersion and adsorption performance were better. However, there were the best effects at the normal temperature process, when the side chain density reached 0.3115.

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