Effect of sustain-released polycarboxylate superplasticizer on the cement hydration

Y L Ke 1,*, Y H Fang 1, L N Zhong 1, X F Zhang 1, S H Zhu 1, Y Q Guo 1, M M Gui 2, X X Ma 1,2
1 KZJ New Materials Group Co., Ltd., Xiamen 361101, China;
2 Xiamen Academy of Building Research Group Co., Ltd., Xiamen 361004, China;
* Corresponding author (Tel: 86-15959348336; E-mail: yuliang_ke8207@163.com)

Abstract. In order to improve the fluidity retention performance of cement, monomers containing ester groups were introduced into sustain-release polycarboxylate superplasticisers (PCEs). Two different kinds of PCEs were designed and synthesized by free radical polymerization. The chemical structure of PCEs was characterized by FT-IR and GPC, the effect of the amount of hydroxypropyl acrylate of sustain-release PCEs on the retention performance was investigated, and the hydration kinetics of cement with PCEs was observed by hydration heat and SEM. The results showed that the addition of ester group in PCEs can delay the cement hydration process, PCEs with the ester group has less initial dispersion, and the decomposition of the ester group can enhance its later dispersion, which is the main reason for the slump increase of fresh concrete over time. It is suggested that PCE containing the ester group can be used to delay the cement hydration and improve the fluidity loss of fresh concrete.

1. Introduction
Understanding the mechanism of cement hydration is beneficial to both academic research and practical application. Since the chemistry and microstructure of cement are complex and interdependent, it is difficult to determine the mechanism of cement hydration [1]. Moreover, polycarboxylate superplasticizers represent one of the most common and important additives and have been widely applied in concrete operation [2–4]. Undoubtedly, the hydration process of cement with variety of additives is complicated and can be affected by multi-factors.

Several recent studies have focused on cement hydration, which is a complex physical and chemical process with constant heat release [5]. With the hydration process going on, both the hydration temperature and the hydration degree of cement paste would change till the end of hydration [6]. The change in temperature during cement hydration can reflect the hydration degree of cement; hydration heat curves also depict the effects of additives on cement hydration [7,8]. PCEs with various molecular configurations have been widely used, but most investigations on the early hydration behaviour of cement focused on admixtures with a single type of molecular structure [9–10]. The molecular structure of PCEs and their effects on the hydration behaviour of cement remain poorly understood. The current study aims to investigate the effects of PCEs with different densities of ester groups on the hydration behaviour of cement.
2. Experimental

2.1 Materials

(1) An ordinary Portland cement (C) (42.5, Mingfu Cement Co., Ltd.), cement chemical composition was shown in Table 1.

(2) Sand (S), fineness modulus of 2.6 ~ 2.8, the mud content is less than 1%;

(3) Aggregate (G), particle size of 5~31.5mm continuous grading gravel;

(4) Polycarboxylate superplasticizer: PCE-1 was synthesized with AA, hydroxypropyl acrylate (HPA) and IPEG, and the molar ratio was 3:1:1, PCE-2 was synthesized with AA, hydroxypropyl acrylate (HPA) and IPEG, and the molar ratio was 2:2:1. A schematic diagram of the chemical structure of PCE-1 and PCE-2 are shown in figure 1. PC-1 is a commercially available type of water reducing agent.

|                | CaO   | SiO₂  | Al₂O₃ | Fe₂O₃ | SO₃  | MgO  | K₂O | TiO₂ | Na₂O | LOI |
|----------------|-------|-------|-------|-------|------|------|-----|------|------|-----|
| W/%            | 60.44 | 23.36 | 4.84  | 3.37  | 3.82 | 2.44 | 0.803| 0.206| 0.101| 0.621|

![Figure 1: Schematic diagram of chemical structure of PCE-1 (x: y: z=3:1:1, n=53) and PCE-2 (x: y: z=2:1:2, n=53)](image)

2.2 Test methods

2.2.1 FT-IR. The chemical structure of PCE was characterized by using FT-IR (Perkin Elmer Spectrum 100 Fourier transform infrared spectrometer).

2.2.2 GPC. The average molecular weight and molecular weight distribution of PCE were determined through Gel Permeation Chromatography (GPC, Waters 1515 Isocratic HPLP pump /Waters 2414), and the flow phase was 0.1mol/L sodium nitrate solution, while the flow rate was 0.8ml/min.

2.2.3 Paste and Concrete. The paste test was carried out according to the GB/T 8077-2012, while the concrete test was carried out according to GB 8076-2008.

2.2.4 Hydration heat. The hydration heat test was used to measure the hydrothermal curve of cement hydration by TAM-air micro-calorimeter (Thermometric AB, Sweden). The W/C ratio of the cement paste was fixed at 0.4; the heat release rate of cement within 72h was recorded.
2.2.5 Scanning electron microscopy. Cement slurry was prepared and cured at 20°C for 24h, 72h, and 168h, with different type of PCEs. The morphology of hardened cement pastes was observed by Field Emission Scanning Electron Microscope (SEM, EM-20, Korea).

3. Results and discussion

3.1 Characterization of PCEs

PCEs were tested by FTIR and GPC. FT-IR spectrum of PCE-1 and PCE-2 were shown in figure 2, the molecular weight of PCE-1 and PCE-2 were shown in table 2.

![Figure 2. FT-IR spectrum of PCE-1 and PCE-2](image)

| Sample   | Mn(Da)  | Mw(Da)  | Mp(Da)  | PDI(Mw/Mn) | Conversion rate(%) |
|----------|---------|---------|---------|------------|--------------------|
| PCE-1    | 38100   | 77747   | 53229   | 2.04       | 88.60              |
| PCE-2    | 38091   | 77375   | 52718   | 2.03       | 85.70              |

The FT-IR spectrum of PCE-1 and PCE-2 is shown in Fig. 2. The peaks of alkyl group (-CH-, -CH₂-, -CH₃, 2885 cm⁻¹), ester group (-COOCH₂-, 1731 cm⁻¹), sodium carboxylate (-COONa, 1638 cm⁻¹) and polyoxyethylene group (-CH₂-O-CH₂-, 1106 cm⁻¹) can be found in the spectra of both
PCE-1 and PCE-2. The FT-IR spectrum well matched the chemical structure of designed PCEs. As can be seen from Table 2, the GPC values of Mn, Mw and Mp of PCE-1 are similar with PCE-2, but the Mw/Mn and conversion rate are slightly lower than that of PCE-1.

3.2. Hydration heat

The heat evolution of cement was recorded through isothermal calorimetry. It was observed that PCE had a significant effect on the hydration kinetics of cement, which is shown in figure 3.

![Cement hydration exothermic curves with different admixtures](image)

Figure 3. Cement hydration exothermic curves with different admixtures

It is demonstrated that both PCE-1 and PCE-2 delay the hydration of cement paste, while PCE-2 has stronger retarding effect than that of PCE-1. Furthermore, with the increasing of PCEs, the heat flow peak of cement paste moved to the right, the height of peak reduced, and the retardation strength of PCE-2 is higher than that of PCE-1. Then the ester group of PCEs was decomposition as the pH increasing, which are further adsorbed on the surface of the hydration products to restrain the growth of the products [8]. The presence of the ester group provides a stronger retarding effect on early cement hydration.

In order to further investigate the interaction between PCEs and cement, the cement hydration products in the hydration process and morphology of hardened cement pastes were analyzed by SEM.

3.3 The microstructure of hydration products

To further understand the mechanism of the PCE-1 and PCE-2 in cement hydration, SEM was used for the observation of early age hydration products. The experiment was performed at the dosage 0.2 wt.%, and the hydration time was set as 1d, 3d and 7d, respectively. SEM images of hardened cement pastes are exhibited in figure 4.
It can be seen from the SEM morphology of the hydration product that the hydration rate is significantly slower with PCE-1 and PCE-2 than blank. From Fig. 5(a), (d) and (g), there were a large number of needle-like calcium silicate hydrate (C–S–H) in the cement without PCEs, with the addition of PCE-1 and PCE-2, it can be seen that there were fewer needle-like hydration products. Compared with PCE-1 and PCE-2, PCE-2 had a stronger delay of cement hydration characteristics since smallest crystal could be seen in the Fig. 5 (g). After hydration for 3 days, a small amount of acicular hydration products still exist. As the hydration age was extended, the hydration product further filled the voids, and the pore structure of harden cement paste mixed PCE-1 and PCE-2 is denser than that without PCE.

### 3.4 Application results of PCEs used in concrete

The concrete mix and the test results are shown in table 3 and table 4, while the dosage of PCEs was 0.2% (in solid content) according to the cement weight.

| Materials | W | C | S | G |
|-----------|---|---|---|---|
| Dosage(kg/m3) | 175 | 320 | 710 | 1070 |

| Sample | Slump /mm | Setting time /min | Compressive strength/MPa |
|--------|-----------|-------------------|--------------------------|
|        | 0h        | 1h                | 2h                       | 3d | 7d | 28d |
| PC-1   | 210       | 180               | 120                      | 235 | 21.3 | 32.2 | 40.5 |
| PCE-1  | 205       | 200               | 190                      | 235 | 20.6 | 34.8 | 41.2 |
| PCE-2  | 170       | 205               | 200                      | 245 | 22.4 | 33.7 | 39.7 |
As can be seen from the table 4, with the same dosage, the fresh concrete with PC-1 has a 30mm slump loss within 1 h, and it is reduce to 120 mm at 2 h; the initial slump of PCE-1 was higher than that of PCE-2. The fresh concrete with PCE-1 has a slight slump loss within 1 hour, while the slump of PCE-2 is increased; After 2 hour, there is nearly no slump loss within PCE-2, and the fresh concrete with PCE-1 has a little slump loss. It indicates that PCEs with the ester group can significantly improve the slump loss of fresh concrete, and the slump retention performance becomes better, as the ester monomer increases. In addition, with PC-1, PCE-1 and PCE-2, there is little difference in compressive strength for 3d, 7 d or 28 d.

4. Conclusions
The concrete containing PCE-1 and PCE-2 shows good comprehensive performance, particularly the control of slump loss. Besides, PCE-1 and PCE-2 prolong the induction period of cement hydration and improve the pore structure.

(1) As the number of ester group in PCEs increased, the first hydration temperature peak declined, moreover, the appearance of the main hydration peak and maximum elevated temperature was delayed.

(2) PCEs with the ester group have less initial dispersion, and the decomposition of the ester group can enhance its later dispersion, which is the main reason for the slump increase of fresh concrete over time.

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