Study on adsorption, rheology and hydration behaviours of Polycarboxylate(PCE) superplasticizer synthesized by different acid to ether ratio

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Abstract. Polycarboxylate superplasticizer is synthesised by different acid to ether ratio, which is changing the main chain structure parameters, obtained different microstructures. The effect of different microstructure PCE superplasticizer on the fluidity of cement paste, rheological thixotropy, adsorption capacity and hydration heat are studied. The results show that dispersing performance in cement with acid to ether ratio of 3.5 is the best, the molecular weight and side chain density have rather little effect on the cement hydration process.

1. Introduction
Polycarboxylate superplasticizer is a kind of polymer surfactants, which generally has strong polar anionic group such as sulfonic group, carboxylic group which on the hydrophobic main chain and polyoxyethylene side chain [¹]. The effect of anchoring and dissolves which were given by the strong polar anionic group on backbone enabled the polycarboxylate superplasticizer adsorbing to the surface of cement particles or hydration products. Whereas the hydrophilic long-side chain can provide steric stability, which has dispersed and dispersed retention. The microstructure of polycarboxylate superplasticizer affects the performance of cement slurry and concrete. When polycarboxylate superplasticizer is mixed with concrete, adsorption and cement hydration occur simultaneously. Adsorption is the basis of interaction between water reducer and cement particles. The relative molecular mass, main chain polymerization, side chain density and position of the functional group of polycarboxylate superplasticizer all affect the adsorption [²⁻³]. The microstructure of polycarboxylate superplasticizer also affects the process of cement hydration, such as the increase of the length of main chain can effectively inhibit cement hydration. Ding et al. believe that the shorter main chain or longer side chain caused cement early hydration stronger retardation and lesser increase of cement 3 d hydration degree [⁴]. However, Zhang et al believe that Higher side chain density and length lead to lower adsorption amount and consequently higher mortar early strength [⁵]. The results of the above-mentioned studies were different, and the effect of polycarboxylate superplasticizer on cement hydration needs further study.

In this paper, by changing the side chain density, the polymerization degree of the main chain, the influence of various factors on dispersion, rheological thixotropy, adsorption capacity and hydration heat is studied.
2. Experimental

2.1. Raw materials
(1) Reference cement (P. I42.5).
(2) Polyether macromonomer TPEG (industrial grade), sodium hypophosphite (industrial grade), acrylic acid (industrial grade), ammonium persulfate (industrial grade), sodium hydroxide solution (30% aqueous solution, industrial grade).

2.2. Methods

2.2.1. Synthesis technology of PCE
A mixed solution of polyether macromonomer with a relative molecular weight of 2400 and deionized water is added to a 500 mL four-necked flask. After stirring, the temperature is raised to a certain temperature. When the color of the solution becomes clear, add sodium hypophosphite. After uniformly stirring, slowly and uniformly dripping material A (mixed solution of ammonium persulfate and deionized water) and material B (mixed solution of acrylic acid and deionized water) respectively at a constant speed. Both A and B are added dropwise for 3 hours, and keep the temperature same as reaction for one hour. Then add sodium hydroxide solution for neutralization to obtain a polycarboxylate superplasticizer product.

2.2.2. FTIR
The Avatar360 spectrometer, PerkinElmer, USA, has a scanning range of 8000 ~ 400 cm⁻¹ and a spectral resolution of 4 cm⁻¹.

2.2.3. Gel chromatography test
Using Water 1515 Isocratic HPLP pump/Water 2414, the chromatographic column is connected in series with Ultrahydragel 250 and Ultrahydragel 500, the mobile phase consisted of a 0.1 mol/L aqueous solution of sodium nitrate (containing 0.05% sodium azide), and the flow rate is 0.8 mL/min.

2.2.4. Microstructure calculation
The molecular weight and conversion rate of the polycarboxylate superplasticizer molecule can be obtained by gel chromatography test, and then the corresponding side chain density and main chain degree of polymerization can be obtained. The calculation formulas for the side chain density and the degree of polymerization of the main chain are shown in Formula 1 and Formula 2.

\[
\text{Side chain density} = \frac{Z_Z \times n[\text{TPEG}]}{n[\text{AA}] + n[\text{TPEG}] \times Z_Z} \quad (1)
\]

Wherein: \(Z_Z\) represents the conversion rate of the macromonomer TPEG; \(n[\text{TPEG}]\) represents the amount of TPEG during feeding; \(n[\text{AA}]\) represents the amount of acrylic acid during feeding.

\[
\text{Main chain degree of polymerization} = \frac{M_w}{M} \quad (2)
\]

Wherein: \(M_w\) represents the weight average molecular weight of the polycarboxylic acid polymer; \(M\) represents the theoretical molecular weight of the structural unit.

2.2.5. Fluidity of cement paste
The fluidity of cement paste is tested according to GB/T 8077-2012 <Test Method for the Homogeneity of Concrete Admixtures>.

2.2.6. Rheological thixotropy
The test is using the German Anton Paar MCR302 rotary rheometer, and setting the temperature to 20 °C, to record 47 points, and to obtain the rheological thixotropic ring curve.
2.2.7. Adsorption
The water to cement ratio is 2. Weigh the water and cement and add 0.2% cement solid content polycarboxylate superplasticizer, magnetically stir for 5 minutes and then pour it into the centrifuge tube, centrifuge speed 5000 r/min, 10 minutes. Take the supernatant as a sample after adsorption. Configure four water reducing agent solutions with concentrations of 0.5, 1, 1.5 and 2 g/L as standard solutions. Use Shimadzu TOC-VPCH total organic carbon analyzer to measure the standard solution, make a standard curve, measure the TOC area in the sample solution, and substitute this area into the standard curve formula to obtain the adsorption capacity.

2.2.8. Hydration Heat
This test is using TA company TAM Air microcalorimeter to measure cement hydration heat curve. Before the test, put the sample and deionized water into the room with 20 °C constant temperature about 20 °C standing for 24 hours. With a water to cement ratio of 0.35, weight of 100 g of cement and 35 g of polycarboxylate superplasticizer aqueous solution (polycarboxylate superplasticizer solid content is 0.15 wt%), after fully mixing, weight of 3 g of cement paste and put it into the instrument for testing.

3. Results and Discussion

3.1. PCE Structure
In the experiment, polycarboxylate superplasticizer with acid to ether ratios of 2.5, 3.0, 3.5, 4.0 and 4.5 are synthesized respectively, in which the amount of polyether macromonomer remain unchanged, and only the amount of acrylic acid added is changed. The corresponding synthetic samples number are KZJ-1, KZJ-2, KZJ-3, KZJ-4 and KZJ-5. The infrared spectra of polycarboxylate superplasticizer with different acid to ether ratios are tested, and the infrared spectra obtained are shown in Figure 1.

![Fig.1 FTIR of Different acid-to-ether ratio PCE](image)

It can be seen from Figure 1 that near 3510 cm\(^{-1}\) is the \(-\text{OH}\) stretching vibration absorption peak in the associated state, and the 2870 cm\(^{-1}\) absorption peak is caused by the stretching vibration of the C-H bond in the alkane in the polyoxyethylene side chain. 1724 cm\(^{-1}\) is the absorption peak of ester bond or carboxylic acid C=O stretching vibration absorption peak, 1454 cm\(^{-1}\) is also the symmetric stretching vibration absorption peak of carboxyl C=O, 1331~1360 cm\(^{-1}\) is the characteristic absorption peak of polyoxyethylene chain. In the figure, it is 1350 cm\(^{-1}\). Near 1108 cm\(^{-1}\) is the asymmetric stretching vibration absorption peak of ether bond C-O-C, and near 950 cm\(^{-1}\) is the external variable angle vibration absorption peak of trans double bond OH. The presence of the above peaks indicates that there are polyoxyethylene chain, carboxyl groups, ether bonds and hydroxyl groups in different acid to ether ratio water-reducing agents. However, there is no clear peak in the range of 3000~3100 cm\(^{-1}\), indicating that there is no absorption peak of olefinic C-H bonds. There is no absorption peak in the range of 1600~1680 cm\(^{-1}\), indicating that there is no C=C double bond.
Table 1 Microstructure data of polycarboxylate superplasticizer with different acid to ether ratio

| PCE   | M<sub>n</sub> | conversion /% | main chain polymerization degree | side chain density /% |
|-------|--------------|----------------|----------------------------------|-----------------------|
| KZJ-1 | 40721        | 83.13          | 16.96708                         | 24.96                 |
| KZJ-2 | 34643        | 78.48          | 14.43458                         | 20.74                 |
| KZJ-3 | 48532        | 88.13          | 20.22167                         | 19.16                 |
| KZJ-4 | 39308        | 79.96          | 16.37833                         | 16.67                 |
| KZJ-5 | 47309        | 89.00          | 19.71208                         | 16.52                 |

The gel chromatography data is substituting into formulas 1 and 2 to obtain the main chain polymerization degree and side chain density data of polycarboxylate superplasticizer with different acid to ether ratio, which is shown in Table 1.

It can be seen from Table 1 that as the acid to ether ratio increases, the side chain density gradually decreases. But it has little effect on the degree of polymerization of the main chain.

3.2. Adsorption and Rheology

The fluidity and rheology of the cement paste are tested for different acid to ether ratio of polycarboxylate superplasticizer. The water to cement ratio is 0.29, and the solid content is 0.15 wt % polycarboxylate superplasticizer. At the same time, a water to cement ratio of 2 is used to test the adsorption capacity by TOC instrument. The fluidity and adsorption capacity of the cement paste with different acid to ether ratios are shown in Figure 2.

![Fig.2 Adsorption amount and fluidity of cement paste](image)

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![Fig.3 Thixotropic curve](image)

Fig.3 Thixotropic curve

It can be seen from Figure 2 that as the acid to ether ratio increases, the fluidity of cement paste first rises and then decreases, with a maximum value of 265 mm, corresponding to an acid to ether ratio of 3.5. The adsorption capacity also increased first and then decreased, and the adsorption capacity reach the maximum when the acid to ether ratio is 4.0.
A rheological test is also performing on the cement paste. As the shear rate increases whereafter decreases, the corresponding shear stress is tested, and the thixotropic curve and the thixotropic ring area are obtained, which are shown in Figure 3 and Table 2. The larger the area of the thixotropic ring curve, the greater the energy should be required to destroy the structure, reveal more stabler of these structures.

### Table 2 Thixotropic ring area of cement paste with different acid to ether ratios

| PCE  | Acid to ether rate | Thixotropic ring area/Pa.s⁻¹ |
|------|-------------------|-----------------------------|
| KZJ-1| 2.5               | 1859.7                      |
| KZJ-2| 3.0               | 1945.2                      |
| KZJ-3| 3.5               | 1442.6                      |
| KZJ-4| 4.0               | 1607.0                      |
| KZJ-5| 4.5               | 2997.2                      |

It can be seen from Figure 3 and Table 2 that with the increase of the acid to ether ratio, the overall ordinate of the thixotropic ring increases from large to small, which is the opposite trend to the fluidity of the cement paste. When the acid to ether ratio is 3.5, the smallest thixotropic ring area corresponds to the largest fluidity of cement paste, which is indicating that this polycarboxylate superplasticizer has the best dispersibility and the smallest shear stress at the same shear rate. As the acid to ether ratio continues to increase to 4.5, the side chain density decreases to 16.52%. At this time, the fluidity of cement paste become smaller, and the thixotropic ring area reaches 2997.2 Pa. s⁻¹, and the adsorption capacity shows a downward trend. The above data shows that when the side chain density is too large or too small, polycarboxylate molecules have a situation with desorption or insufficient adsorption on the surface of cement particles. The dispersibility of cement particles is poor. The network or gel structure formed by cement particles agglomeration or hydration products makes the area of the thixotropic ring become larger, and the structure is more difficult to destroy. It can be seen that the cement paste with poor dispersibility is more likely to react to form a gel structure.

### 3.3. Hydration heat

Through the microcalorimeter test, polycarboxylate superplasticizer with different acid to ether ratio and blank samples (none of PCE add into cement) are added to obtain the heat flow and accumulated hydrothermal heat curve, which are shown in Figure 4 and Figure 5.

It can be seen from Figures 4 and 5 that the blank sample has a shorter exothermic time during the hydration induction period and an acceleration period than the sample mixed with polycarboxylate superplasticizer. The maximum exothermic peak of the blank sample appears much earlier. It shows that the addition of polycarboxylate superplasticizer can effectively inhibit the early hydration reaction of cement. Compared with other polycarboxylate superplasticizer, the hydration exothermic peak of KZJ-4 is earlier and has a certain early strength effect.

![Fig.4 Heat flow and cumulative heat of PCEs](image-url)
4. Conclusions

(1) Different acid to ether ratios of polycarboxylate superplasticizer affect the density of PCE side chains. When the acid to ether ratio is 3.5, polycarboxylate superplasticizer has the best dispersion performance.

(2) The heat of hydration test results of polycarboxylate superplasticizer with different acid to ether ratios, combined with the adsorption test results, shows that PCE does not form saturated adsorption at a cement content of 0.15 wt.%, so the molecular weight and side chain density affect the hydration heat release rate and accumulated heat have rather little meaning.

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