Molecular Behavior of Different Polycarboxylate Superplasticizers

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Abstract. Four different types of polycarboxylic superplasticizers were synthesized by using different macromonomers, and then the molecular behavior of GPC, infrared, nuclear magnetic, cement hydration heat and micromorphology were characterized. The results showed that different types of PCEs have different molecular behaviors. The research showed that the molecular weight and molecular weight distribution of PCE1 were the smallest, and these four different types of PCEs have better molecular weight and molecular weight distribution. The infrared spectra of the four PCEs were not much different. However, by $^1$H NMR, the macromonomer used in PCE1 when synthesised was MPEG. The macromonomer used in PCE2 and PCE4 when synthesised were TPEG, and the macromonomer used in PCE3 was HPEG. Cement hydration heat and scanning electron microscope data showed that PCE4 has the better early strength.

1. Introduction
Polycarboxylate superplasticizer is a very important chemical substance, which has obvious water reducing effect, due to its excellent properties, such as its low sensitivity, high workability, and good dispersibility. More and more attention is being paid by experts and scholars [1,2].

The polycarboxylic superplasticizer is a surfactant having an asymmetric structure, one portion being soluble in water and the other portion easily escaping from water. Adding a cement slurry of a polycarboxylic superplasticizer, the cement particles are more easily dispersed, the apparent viscosity is lower, and a certain amount of small bubbles can be introduced, which increases the sliding ability between the cement particles [3].

A very important feature of polycarboxylate superplasticizers is the design of molecular structure. It can adjust the superplasticizer products with different properties through molecular structure design to adapt to different materials and different materials. According to the type of macromonomer used, it can be divided into MPEG, HPEG, TPEG, APEG, etc. According to different functions, it can be divided into the preservation type, the early strength type, and the retardation type. Different types of polycarboxylic superplasticizers have different properties and structures [4-6].

The structure of PCE is complex, it consists an anionic polymer backbone and other side chains, which generate electrostatic repulsive forces and steric hindrance to cement particles [7-8]. In order to improve the properties of PCEs, many people studied in preparing new structure materials, and the PCE molecular structure were characterized by infrared spectroscopy and $^1$H NMR resonance, also gel permeation chromatography, scan, cement hydration heat evolution and scanning electron microscopy were used in characterizing the structure [9-10].

In this paper, we synthesized different types of polycarboxylate superplasticizers, and then characterized their molecular behavior. The molecular weight and molecular weight were...
characterized by gel permeation chromatography. The functional groups information was characterized by infrared spectroscopy. The macromonomer type used by $^1$H NMR spectroscopy was analyzed. The mechanism of action was investigated by using cement hydration heat and scanning electron microscopy.

2. Experiment part

2.1 Materials
Maleic anhydride(MA), acrylic acid (AA), hydrogen peroxide (H$_2$O$_2$), ascorbic acid(Vc), thioglycolic acid (TGA) , ammonium persulfate(APS), sodium hydroxide (NaOH) were analytical grade reagents purchased from Aladdin Industrial Corporation, China, MPEG, Isobutanol polyethylene glycol(HPEG), and industry-grade allyl polyethenoxy ether(TPEG) were provided by Liaoning Aoke Chemical, Ultra-pure water was used throughout the experiment.

2.2 Synthesis of PCEs
Four different PCEs were prepared in the lab, PCE1, PCE2, PCE3 and PCE4. A 30% sodium hydroxide solution was used to neutralize the polymer solution.

2.3 Characterization

2.3.1 GPC (gel permeation chromatography)
The molecular weight and molecular weight distribution of PCEs were determined through Waters 1515 gel permeation chromatography with an ultra-hydrogel chromatographic column which combined refractive index detector (RI), laser light scattering detector (LS) and viscosity detector (VIS). The samples were analyzed using a 0.05% NaNO$_3$ aqueous solution as an eluant at a flow rate of 0.8mL/min at 40℃. Glucans with different molecular weights were used as calibration standards.

2.3.2 FTIR (Fourier transform infrared spectroscopy)
The FTIR spectra of the samples were measured on the by the KBr sample holder method in the region of 400~4000cm$^{-1}$ at a resolution of 4cm$^{-1}$.

2.3.3 Nuclear magnetic resonance ($^1$H NMR)
$^1$H NMR spectra of the PCEs were recorded using a Bruker AVANCE III MHz spectrometer with CDCl$_3$/DMSO as the solvent. The PCEs samples were through ultrafiltration membranes of 30KD, 10KD, 5000KD and 3000KD respectively, and then dried in a vacuum overnight to remove the solvent prior to testing.

2.3.4 Cement hydration heat evolution
The cement hydration heat evolution test conforming to GBT 12959-2008 was carried out on cement paste which the water/cement ration was 0.35. The cement pastes were capped and placed into the calorimeter. The heat flow was recorded for 168h. The test temperature was 20℃, different type of PCEs on the hydration heat evolution were examined.

2.3.5 Scanning Electron Microscopy (SEM)
The microscopic characterization of the hydrated cement were observed via SEM(COXEM-20).Cement was mixed with water and PCEs, the dosages of cement and water were 300g and 87g, and the dosage Of PCEs was 0.25%. The mixture was put into the standard curing room for curing. The mixture maintained for 1d, 3d and 7d, and the put the mixture was immersed in absolute ethanol to stop hydration, the placed in an oven at 70℃ for drying. At last, the mixture was crushed into thin pieces and coated with gold prior to characterization.
3. Results and discussion

3.1 GPC characterization

In this paper, GPC was used to measure the molecular weights and molecular distributions of the different PCEs, the results were shown in table 1. From the table, we can see that the different PCEs have different the molecular weights and molecular distributions, PCE1 has the smallest molecular weight and molecular distribution. The distributions of the PCEs were also different, these four different PCEs were around 2.496 to 3.476, the different MWD of PCEs suggested that the uniformity were different, the smaller of MWD, the better uniformity of relative molecular mass, so the PCE3 has the best uniformity of the relative molecular mass; The IV value stands for intrinsic viscosity, the IV value of PCE1 was 0.1224, was smallest in these four PCEs, the relative molecular mass was also the smallest, the result matched the MWD, but others three PCEs IV value did not matched the MWD, such as the IV value of PCE4 was the biggest, but relative molecular mass were not the biggest, it might be due to the difference in molecular weight of each polymer in the sample, and the lengths of the long chain and the side chain were also different. The value of Rh was also different; it was a constant characterizing the molecular size of polymer, the different value of Rh showed different linearity of PCEs.

| Samples | Mw    | Mn    | Mp    | MWD   | IV    | Rh    | M-α   | M-k   |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| PCE1    | 16904 | 6352  | 11153 | 2.661 | 0.1224| 2.962 | 0.471 | -2.683|
| PCE2    | 47960 | 17156 | 37005 | 2.796 | 0.2070| 5.008 | 0.345 | -2.265|
| PCE3    | 79651 | 31390 | 48235 | 2.496 | 0.2669| 6.420 | 0.477 | -2.873|
| PCE4    | 39540 | 58381 | 45980 | 3.476 | 0.2960| 6.212 | 0.306 | -1.956|

Mw-Mass average molecular mass; Mn-Number average molecular mass; Mp-Peak position molecular mass; MWD-Mw/Mn; IV-Intrinsic viscosity; Rh-Hydrodynamic radius; M-α-Mark-Houwink parameterα; M-H- Mark-Houwink parameter H.

3.2 FTIR characterization

The chemical structures of PCE1, PCE2, PCE3 and PCE4 were confirmed by FTIR analysis and the spectra were provided in figure 1. From the figure, we can see that the spectrums of the PCEs were similar, so it was difficult to distinguish these four types of PCEs only by FTIR analysis. The absorption peak around 2880cm⁻¹ correspond to -CH₂ and -CH₃ stretching vibration absorption peaks,
and the absorption peak around 1710cm⁻¹ and 1650cm⁻¹ correspond to C=O stretching vibration absorption peak of ester group and C=C stretching vibration peak, it suggest that the alcoholic hydroxyl group-containing substance and the carboxyl group-containing substance in the PCEs were reacted. The absorption peak around 1110cm⁻¹ correspond to C-O-C stretching vibration absorption peak.

3.3 ¹H NMR characterization

Form the FTIR spectra can not distinguish the difference of different types of PCEs, and to further confirm the chemical structure of PCEs, ¹H NMR spectrum was recorded in figure 2 to figure 5.

![Fig.2. ¹H NMR spectrum of PCE1](image)

![Fig.3. ¹H NMR spectrum of PCE2](image)

It can be seen from Fig.2, the chemical shift at 3.27 (a) has a peak and was a single peak, and the position shift was -CH₃O-, the chemical shift at 3.59(b) was -OCH₂CH₂-. So, it judged that the macromonomer used in PCE1 was MPEG, and the molecular weight of macromonomer was 1350 by calculation.

As can be seen from Fig.3, the chemical shift at 1.69(a) was -CH₃; the chemical shift at 2.2(b) was -CH₂-; the chemical shift at 3.6(c) was -OCH₂CH₂-. So, it can be judged that the macromonomer used in PCE2 was TPEG, and the molecular weight of 6460 was obtained by calculation.

![Fig.4. ¹H NMR spectrum of PCE3](image)

![Fig.5. ¹H NMR spectrum of PCE4](image)

As can be seen from Fig.4, the chemical shift at 4.9(c) was =CH₂, the chemical shift at 3.6(b) was -OCH₂CH₂-, the chemical shift at 1.7(a) was -CH₃. So, it can be judged that the macromonomer used in PCE3 was HPEG, and the molecular weight of 6108 was obtained by calculation.

Form Fig.5, we can see that the chemical shift at 1.83(a) was -CH₃ the chemical shift at 2.2(b) was -CH₂-, the chemical shift at 3.6(c) was -OCH₂CH₂-. So, it can be judged that the macromonomer used in PCE4 was TPEG.

So, ¹H NMR can be used to determine the type of macromonomers used in four PCEs. The difference in chemical shift values was used to judge the functional groups it carried, and the difference in the crown energy groups was used to judge the type of macromonomer used.
3.4 Cement hydration heat evolution characterization

Table 2 showed the cement hydration heat data of different types of PCEs. It can be seen from the table that the data of the four types of PCEs were different. Among them, the heat release of PCE4 was larger at 1d, 3d and 7d. The temperature time of PCE4 was 15h, and the highest temperature time was the earliest. It may be in the process of participating in hydration, which accelerates the process of hydration and has a greater impact on the early strength of hydration. And the other three differences were not big.

| Sample | Maximum temperature/°C | Maximum temperature/h | Q/ (J·g⁻¹) |
|--------|-------------------------|-----------------------|------------|
|        |                         |                       | 1d         | 3d         | 7d         |
| PCE1   | 25.9                    | 23.5                  | 149        | 338        | 453        |
| PCE2   | 35.6                    | 25.5                  | 155        | 355        | 461        |
| PCE3   | 31.4                    | 24.0                  | 145        | 340        | 455        |
| PCE4   | 40.0                    | 15.0                  | 201        | 394        | 494        |

3.5 Scanning Electron Microscopy characterization

Figures 6 to 9 were SEM images of 4 PCEs with a test time of 3 days after treatment. It can be seen from the figure that the hydration process of different types of water reducing agents was different. PCE1 and PCE2 have similar morphology, and only a few irregular needle-like substances appear, which may be AFt in the hydration process. However, more acicular substances appeared in PCE3, indicating that this water-reducing agent promoted the hydration process at this age, and a little plate-like substance appeared in PCE4, indicating that the substance involved in the cement process was more complete, mainly the effect is early strength, and this result is consistent with the cement hydration heat data.
4. Conclusions

(1) Four types PCEs, the molecular weight and molecular weight distribution of PCE1 were the smallest, and these four different types of PCEs have better molecular weight and molecular weight distribution.

(2) The infrared spectra of the four PCEs were not much different.

(3) By $^1$H NMR test, the monomer used in PCE1 when synthesised was MPEG. The macromonomer used in PCE2 and PCE4 when synthesised were TPEG, and the macro monomer used in PCE3 was HPEG.

(4) Cement hydration heat and scanning electron microscope data showed that PCE4 has the better early strength.

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