Research on synthesis and properties of amphoteric early strength polycarboxylate superplasticizer

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Abstract. The amphoteric early strength polycarboxylate superplasticizer (AE-PCE) was synthesized by free radical aqueous solution polymerization, and using acrylic acid (AA), isobutylene alcohol polyoxyethylene ether (HPEG, molecular weight 4000) and dimethyl diallyl ammonium chloride (DMDAAC) as monomers. In this work, the structure of AE-PCE were characterized by FTIR, the hydration behavior of concrete were investigated by using TAM AIR isothermal microcalorimetry and scanning electron microscope, and properties of AE-PCE were studied by cement paste and concrete experimental. The results show that the quaternary ammonium cationic functional group has been successfully introduced into the molecular structure of polycarboxylate superplasticizer. The synthesized amphoteric early strength polycarboxylate superplasticizer (AE-PCE) can accelerate the hydration rate, significantly shorten the setting time and improve the early strength of concrete, and the effect of promoting coagulation and early strength is better than similar foreign products. Applied to the production process of subway shield segments, AE-PCE can effectively shorten the demoulding time of shield segments and improve the production efficiency under low temperature conditions in winter.

1. Introduction
The construction of subway infrastructure involves a variety of methodologies and techniques, with a popular approach being shield tunneling [1-4]. The subway shield segment is the main assembly component of the shield construction. During construction, the shield segment as permanent support structure that prevents its collapse from soil deformation and water infiltration [5]. And the quality of the shield segment is directly related to the overall quality and safety of the tunnel. The shield segments is usually made of high-strength impervious concrete to ensure reliable load-bearing and waterproof performance. The concrete strength of the shield segment is C50-C55, which requires high early strength and meets the cycle within 12 hours under steaming conditions. At present, early strength polycarboxylate superplasticizer is generally used in the production of shield segments [6].

Compared with conventional polycarboxylate superplasticizer, the early strength polycarboxylate superplasticizer has higher early strength and does not affect the medium and late strength of concrete. It is especially suitable for prefabricated concrete and high content mineral blending concrete. Concrete construction and concrete construction under lower temperature conditions, so early-strength polycarboxylate water reducer has become a hot topic at home and abroad [7-9]. However, there are relatively few researches on early strength polycarboxylate superplasticizer to shorten the setting time and improve the construction performance of concrete.

It has been found that increasing the side chain length of the polycarboxylate superplasticizer helps to accelerate the early hydration rate of the cement dispersion system, accelerate the formation
of C-S-H gel and ettringite crystals, and thus improve the early strength of concrete \cite{10,11}, and in the hydration process. Moreover, the addition of a certain amount of cationic monomer can also accelerate the reaction period of hydration and generate C-S-H gel earlier, thereby shortening the setting time and improving the early strength of concrete. In this paper, Isobutenol polyoxyethylene ether with long side chain (HPEG, molecular weight 4000), acrylic acid and diallyldimethylammonium chloride (DMDAAC) were selected as the main raw materials for the preparation of polycarboxylate superplasticizer, and the synthesis was carried out by free radical solution polymerization method.

2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials. Isobutenol polyoxyethylene ether (HPEG, molecular weight 4000, industrial grade), acrylic acid (AA, industrial grade), hydrogen peroxide (H$_2$O$_2$, industrial grade), vitamin C (Vc, industrial grade), thioglycolic acid (TGA, industrial grade), sodium hydroxide solution(30% aqueous solution,, industrial grade), diallyldimethylammonium chloride (DMDAAC, industrial grade).

2.1.2. Main performance test raw materials for experiment. Cement (C, Minfu brand, P.O 52.5R); Sand(S, river sand with fineness modulus of 2.6-2.9 and mud content less than 1%); Gravel(G1, grain size of 5-10mm ; G2, grain size of 10mm-20mm); Fly ash(F, Level II), Slag powder (K, S95); Standard polycarboxylate superplasticizer (HPWR-S, Commercial product); Amphoteric early strength polycarboxylate superplasticizer (AE-PCE, self made); Early strength polycarboxylate superplasticizer (HPWR-A, Commercial product); modified polyether defoaming agent(Commercial product); Air-entraining agent(Commercial product).

2.2. Copolymerization

Add measured water, Isobutenol polyoxyethylene ether (molecular weight 4000), and Hydrogen peroxide into a four-mouth bottle. Raise the temperature to the reaction temperature. After all macromonomers are dissolved, a mixture of acrylic acid and diallyldimethylammonium chloride is added dropwise. Aqueous solution of vitamin C and thioglycolic acid is added dropwise also. Control all materials to complete dropping in a certain period of time. Keep warm for a while,then a 30% aqueous solution of sodium hydroxide was added to adjust the pH to 6.0-7.0, thus obtaining a amphoteric early strength polycarboxylate superplasticizer (AE-PCE).

2.3. Performance test method

2.3.1. Fluidity of cement paste. Cement pastes were prepared at a water cement ratio of 0.29 by adding the tap water with the defined amount of polycarboxylate superplasticizer dosages (0.20% by cement mass).

2.3.2. FTIR measurement. Fourier transformer infrared spectra (FTIR) were obtained from the pressed disc of polycarboxylate superplasticizer and KBr. The spectra in the range of 4000-400 cm$^{-1}$ were recorded on Perkin Elmer Spectrum 100 FTIR spectrophotometer.

2.3.3. Hydration heat determination. The hydration heat determination of cement slurry mixed with polycarboxylate superplasticizer is conducted in accordance with GB/T 12959-2008 " Determination Method for Cement Hydration Heat "

2.3.4. Concrete test. The concrete test is conducted in accordance with GB/T50080-2016 "Standard Test Methods for Performance of Common Concrete Mixtures" and GB/T 50081-2002 “Standard Test
Methods for mechanical properties of Common Concrete”. The concrete mix ratio is shown in Table 1:

| W   | C   | F  | K  | S  | G1 | G2 |
|-----|-----|----|----|----|----|----|
| 145 | 330 | 70 | 40 | 698| 225| 900|

2.3.5. Setting time measurement. The setting time of concrete is conducted in accordance with GB 8076-2008 "Concrete admixture”.

2.3.6. SEM measurement. When the concrete sample is hydrated to set age, remove and terminate the hydration with anhydrous ethanol. Crush and take 3–6mm flakes, place them in a vacuum drying oven. Adjust the temperature to 40°C and dry to constant weight. The sample was taken out and pasted on the copper sample base with conductive adhesive. After vacuum gold-plating, scanning electron microscope (COXEM-20 made in South Korea) was adopted to observe the section micromorphology of the sample.

3. Experimental results and discussion

3.1. Paste fluidity test results

The paste comparison experiment of AE-PCE, HPWR-S and HPWR-A were tested, and the initial paste fluidity were comparable (260±5mm) by adjusting the dosage of polycarboxylate superplasticizer (AE-PCE was 0.31%, HPWR-S was 0.36% and HPWR-A was 0.40%), and the loss of paste fluidity after 30min and 60min was investigated.

![Figure 1. Paste fluidity test of polycarboxylate superplasticizer](image)

It can be seen from Figure 1 that the paste prepared by HPWR-S has a large fluidity loss after 30 minutes, the loss rate is 24%, and the loss rate after 60 minutes is 33%. Compared with HPWR-S, AE-PCE and HPWR-A have less fluidity loss after 30 min, and the loss rate is less than 10%. After 60 min, the loss is increased, and the loss rate is higher than 45%, which meets the construction requirements of shield tunnel segment concrete. In other words, good construction performance in the initial stage and fast setting time in the later stage can shorten the stripping time and improve the production efficiency.
3.2. FTIR measurement results
The structure of amphoteric early strength polycarboxylate superplasticizer (AE-PCE) were characterized by FTIR.

![FTIR spectra of polycarboxylate superplasticizer of AE-PCE](image)

Figure 2. Infrared spectra of polycarboxylate superplasticizer of AE-PCE

As shown in Figure 2: 3444 cm$^{-1}$ (O-H; N-H); 2882 cm$^{-1}$ (C–H); 1730 cm$^{-1}$ (C=O); 1114 cm$^{-1}$ (C–O–C); 1468 cm$^{-1}$, 962 cm$^{-1}$ [-CH$_2$-N’(CH$_3$)$_3$]. The result showed that the quaternary ammonium cation functional group had been introduced into the molecular structure of polycarboxylate superplasticizer. The structure of the obtained product is basically consistent with the molecular structure of the originally designed polycarboxylate superplasticizer.

3.3. The hydration heat test results
The hydration heat test results of cement mixed with different polycarboxylate superplasticizers are shown in Figure 3, and the dosage is 0.8%.

![Hydration heat test results](image)

Figure 3. The hydration heat test results

It can be seen from Figure 3, compared with HPWR-S, AE-PCE significantly accelerates the hydration behavior of cement, the hydration heat exothermic peak is greatly advanced, the main exothermic peak height is increased, and the promoting hydration behavior effect of AE-PCE is better than HPWR-A. During the acceleration period of hydration reaction, large amounts of C$\text{S}$ hydration
to generate C-S-H gel structure that could provide strength. Therefore, the acceleration period of hydration reaction can be advanced by adding AE-PCE and generate C-S-H gel earlier, thereby improving the early strength of concrete specimens.

3.4. Concrete test at room temperature results

At room temperature of 20°C, the concrete comparison experiment of AE-PCE, HPWR-S and HPWR-A were carried out. The concrete mix ratio is shown in Table 1. The slump of concrete is 70±20mm by adjusting the dosage of polycarboxylate superplasticizer, and the concrete setting time and early compressive strength are investigated. The test results are shown in Table 2:

Table 2. Comparison results of superplaster performance at room temperature

| Samples    | Solid dosage/% | Slump /mm | Compressive strength /MPa | Setting time /min |
|------------|----------------|-----------|---------------------------|-------------------|
|            |                |           | 1d | 3d | 7d | Initial | Final |
| HPWR-S     | 0.071          | 60        | 25.6 | 30.2 | 46.6 | 285      | 510   |
| HPWR-A     | 0.073          | 60        | 31.7 | 35.7 | 58.2 | 250      | 415   |
| AE-PCE     | 0.067          | 65        | 32.4 | 37.8 | 58.9 | 240      | 395   |

As shown in Table 2, The concrete slump of AE-PCE is comparable to HPWR-A and HPWR-S at a lower solid dosage, indicating that AE-PCE has a higher water reduction rate. Compared with HPWR-S, the compressive strength of 1d, 3d and 7d concrete prepared by HPWR-A has been increased by 23.83%, 18.21% and 24.89% respectively, and the initial setting time has been shortened by 35min, while the final setting time has been shortened by 95min, indicating that HPWR-A has a better early strength and coagulation effect. Compared with HPWR-S, the compressive strength of 1d, 3d and 7d concrete prepared by AE-PCE has been increased by 26.56%, 25.17% and 26.39% respectively, and the initial setting time was shortened by 45min and the final setting time was shortened by 115min. Compared with HPWR-A, AE-PCE has better effect of promoting coagulation and early strength.

3.5. Concrete test at low temperature results

The low temperature environment will delay the hydration process of concrete, which often causes the setting time of concrete components to be too long, or even unable to condensation, resulting in a longer construction period. Therefore, in order to investigate the coagulation promotion and early strength properties of polycarboxylate superplasticizer synthesized in this study at low temperature, concrete comparison experiments of HPWR-A, HPWR-S and AE-PCE were carried out in a low temperature laboratory at 5°C. The concrete mix ratio is shown in Table 1. The slump of concrete is 70±20mm by adjusting the dosage of polycarboxylate superplasticizer, and the concrete setting time and early compressive strength are investigated. The test results are shown in Table 3:

Table 3. Comparison results of superplaster performance at 5°C temperature

| Samples    | Solid dosage/% | Slump /mm | Compressive strength /MPa | Setting time /min |
|------------|----------------|-----------|---------------------------|-------------------|
|            |                |           | 1d | 3d | 7d | Initial | Final |
| HPWR-S     | 0.071          | 65        | 9.8 | 25.3 | 40.5 | 580      | 820   |
| HPWR-A     | 0.072          | 70        | 15.2 | 30.4 | 51.4 | 475      | 715   |
| AE-PCE     | 0.065          | 75        | 17.3 | 31.7 | 53.6 | 460      | 695   |

It can be seen from Table 3 that AE-PCE still has a higher water reduction rate than HPWR-S and HPWR-A at low temperatures. Compared with the compressive strength of concrete prepared at room temperature for 1d, 3d and 7d, the strength of concrete at low temperature is significantly reduced, especially the strength of 1 day is much lower. In addition, the initial setting time and the final setting time at low temperature are also significantly longer than at room temperature, both extended by 200-300 min. From the values of compressive strength and setting time, it can be seen that, compared with HPWR-S and HPWR-A, AE-PCE still has a better effect of promoting coagulation and early strength at low temperature, which meets the production requirements of shield tunnel segments at low temperature.
3.6. SEM measurement results
After curing concrete mixed with HPWR-S, HPWR-A and AE-PCE for 1d under standard conditions, the morphology of hydration products was tested by scanning electron microscope (SEM), which was shown in Figure 4, Figure 5 and Figure 6.

![Figure 4](image-url) Concrete mixed with HPWR-S
![Figure 5](image-url) Concrete mixed with HPWR-A
![Figure 6](image-url) Concrete mixed with AE-PCE

As shown in Figure 4, Figure 5 and Figure 6, When the concrete mixed with HPWR-S was hydrated for 1d, its structure was relatively loose and there were many pores, some acicular ettringite Aft appeared in the pores, indicating that the hydration products on the surface of cement particles had been formed, but no obvious characteristic hydration products could be seen, indicating low hydration degree. After 1d hydration of concrete mixed with HPWR-A and AE-PCE, there were more needle-shaped and prismatic Aft, moreover, after 1d hydration of concrete mixed with AE-PCE, it can be obviously seen aluminum calcium sulfate AFm with plate structure, indicating that the addition of HPWR-A and AE-PCE can promote the hydration of cement and accelerate the hydration of cement, and the early-strength effect of AE-PCE is better than HPWR-A.

4. Conclusions
(1) The amphoteric early strength polycarboxylate superplasticizer (AE-PCE) was synthesized by using acrylic acid (AA), isobutylene alcohol polyoxyethylene ether (HPEG, Mw = 4000) and dimethyl diallyl ammonium chloride (DMDAAC) as monomers. According to the comparison experiment of paste, the fluidity of paste mixed with AE-PCE had a small loss after 30min, the loss rate was less than 10%, and the loss was accelerated after 60min, which meets the construction requirements of shield tunnel segment concrete.

(2) It can be seen from the infrared spectrum that the quaternary ammonium cationic functional group has been introduced into the molecular structure of the polycarboxylic acid, and the structure of the obtained product is basically consistent with the molecular structure of the originally designed polycarboxylate superplasticizer.
The test results of hydration heat of cement showed that AE-PCE was helpful to accelerate the early hydration of cement.

It can be seen from the test results of shield tunnel segments at room temperature and low temperature that the synthesized AE-PCE has a high water reduction rate, and the prepared concrete has better early strength and coagulation promoting effect than HPWR-A and HPWR-S, and can meet the production requirements of shield tunnel segments at both room temperature and low temperature.

Scanning electron microscope test showed that the addition of HPWR-A and AE-PCE can promote the hydration of cement and accelerate the hydration of cement, and the early-strength effect of AE-PCE is better than HPWR-A.

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