Effect of different synthesis temperature on the bleeding performance of polycarboxylate superplasticizer

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Abstract. In this paper, polycarboxylate superplasticizers were synthesized by free radical solution polymerization under different synthesis temperature conditions. The bleeding performance of polycarboxylate superplasticizers under different synthesis temperature conditions was discussed by paste test and concrete test, and the structure of polycarboxylate superplasticizers was characterized by infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). The results show that the bleeding and slump retention performance of polycarboxylate superplasticizer can be effectively improved by properly increasing the synthesis temperature, and the better synthesis temperature was 55 ℃. With the temperature increase, the molecular weight of polycarboxylate superplasticizers increases first and then decreases. The infrared spectra of polycarboxylate superplasticizers synthesized at different temperatures were not significantly different.

1. Introduction
With the increasing demand for urban traffic facilities and urban buildings, and the demand for low cementitious concrete is increasing rapidly¹,². Therefore, it is the key issue to improve the performance of concrete and meet the use of concrete in various environmental conditions while ensuring the amount of low cementitious concrete. The bleeding rate can affect the performance of concrete in many aspects. In order to control the bleeding rate of concrete, its performance can be adjusted by adding additives³. Among all kinds of concrete admixtures, polycarboxylate superplasticizer (PCE) can control the bleeding performance of concrete very well, and can effectively reduce water consumption, improve slump retention performance and paste flow performance. The amount of water-reducing agent in the concrete industry is increasing year by year, so it is necessary to further improve the performance of the PCE.

The reaction temperature during the synthesis of the PCE has a great influence on its performance. With the deepening of research and the improvement of technology, the synthesis temperature of PCE gradually develops from high temperature to normal temperature, thereby reducing production energy consumption and cost⁴,⁵. The effects of PCE synthesized at different temperatures on the bleeding and retention properties of concrete were studied.
2. Experimental

2.1. Experimental raw materials
The main raw materials required for the experiment were as follows: isopentenyl polyoxyethylene polyether (TPEG, molecular weight 2400, industrial grade), hydrogen peroxide (H₂O₂, 27.5 wt%, industrial grade), ammonium persulfate (APS), sodium hydroxide solution (30% aqueous solution, industrial grade), acrylic acid (AA, industrial grade), mercaptoacetic acid (MAA, industrial grade), sodium hypophosphite (SHP, industrial grade), TP1351 (reductant, industrial grade).

2.2. Test raw materials
Cement (C, Yuexiu brand, P.O 42.5R); Sand (S, river sand with fineness modulus of 2.4 and mud content less than 0.4%); Gravel (G1, grain size of 5-10 mm; G2, grain size of 10-20 mm); Fly ash (F, Level II); Water: tap water meeting the test requirements.

2.3. Copolymerization
The metered TPEG macromonomer and a certain amount of water were added into a four-necked flask. The mixture was stirred and heated in a digital thermostatic water bath at the reaction temperature (the reaction temperatures were 25 ℃, 35 ℃, 45 ℃, 55 ℃ and 65 ℃, respectively). After adding H₂O₂ into the flask, MAA aqueous solution, SHP aqueous solution and TP1351 (reductant), then AA aqueous solution was slowly added dropwise into the flask (dropping time: 3 h) and keep warm for 40 min. By adding a 30% aqueous solution of sodium hydroxide to adjust the pH to 6.0-7.0, and then PCE with solid content of 49% was obtained. According to the initial reaction temperature 25 ℃, 35 ℃, 45 ℃, 55 ℃ and 65 ℃, the polycarboxylate superplasticizers were named PCE-1, PCE-2, PCE-3, PCE-4 and PCE-5, respectively.

2.4. Performance test method

2.4.1. Fluidity of cement paste. The fluidity of cement paste is conducted in accordance with GB/T8077-2012 "Test method for homogeneity of concrete admixtures".

2.4.2. Concrete test. The concrete test is conducted in accordance with GB/T50080-2016 "Standard Test Methods for Performance of Common Concrete Mixtures" and GB/T50081-2002 "Standard Test Methods for mechanical properties of Common Concrete".

2.4.3. Gel permeation chromatographic (GPC) measurement. American Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector was used for testing and analysis.

2.4.4. Fourier transformer infrared spectra (FTIR) measurement. FTIR were obtained from the pressed disc of PCE and KBr. The spectra in the range of 4000-400 cm⁻¹ were recorded on Perkin Elmer Spectrum 100 FTIR spectrophotometer.

3. Experimental results and discussion

3.1. Paste fluidity test
Temperature is an important factor affecting the polymerization during the synthesis, which not only affects the molecular weight of the product, but also affects the dispersion of PCE. The influence of synthesis temperature on the dispersion of PCE was shown in Figure 1.

It can be seen from Figure 1 that with the increase of PCE synthesis temperature, the fluidity of the paste first increases and then decreases. When the synthesis temperature was 55 ℃, the fluidity of the paste reaches the maximum. The reason for the analysis is that when the synthesis temperature was near room temperature, the unsaturated bond of the macromonomer does not break, and the
copolymerization reaction was difficult to occur, resulting in too low conversion rate and low dispersibility of the PCE.

![Figure 1. Fluidity of cement after adding PCEs synthesized at different synthesis temperatures](image)

When the synthesis temperature is enough high, a large number of free radicals produced by TPEG will easily lead to the concentration of local free radicals is too high, resulting in clots, and increase the number of branched chains in the graft, which is unfavorable to the polymerization of macromolecular polymers; High temperature will increase the number of side reactions and the reaction process is difficult to control. The side products produced by these side reactions reduce the dispersibility of cement particles. In addition, the acrylic acid (AA) monomer is easy to self-polymerize with the increase of reaction temperature, which makes it difficult for large monomers to polymerize, therefore, high synthesis temperature results in low fluidity and poor dispersion of cement paste.

3.2. Concrete test

The concrete test was carried out under the same conditions without any slump retaining and retarding components. The concrete test mix proportion (kg/m$^3$) was $m$ (cement): $m$ (fly ash): $m$ (river sand): $m$ (big stone): $m$ (water) = 250: 100: 1050: 165. The concrete test results were shown in Table 1.

| Samples  | Synthesis temperature /°C | Dosage /% | Slump /mm | Dispersion /mm | 1 h Bleeding rate /% |
|----------|---------------------------|-----------|------------|----------------|---------------------|
|          |                           |           | initial | 1 h | initial | 1 h |     |
| PCE-1    | 25                        | 1.6       | 165     | 115 | 520     | 380 | 14.4 |
| PCE-2    | 35                        | 1.5       | 210     | 180 | 510     | 420 | 13.7 |
| PCE-3    | 45                        | 1.5       | 215     | 190 | 525     | 425 | 12.5 |
| PCE-4    | 55                        | 1.4       | 210     | 160 | 540     | 460 | 8.5  |
| PCE-5    | 65                        | 1.4       | 205     | 160 | 520     | 420 | 12.4 |

As shown in Table 1, when the synthesis temperature was low, the polymerization time of PCEs need more time. Therefore, properly increasing the synthesis temperature can effectively improve the reaction rate and shorten the production cycle. The concrete performance of PCEs synthesized at different temperatures was tested. It can be seen from the Table 1 that when the reaction temperature was 55 °C, the synthesized polycarboxylate superplasticizer had a higher water reduction rate, better slump retention effect and lower bleeding rate.
3.3. GPC test
In order to compare the molecular weight and distribution of PCEs synthesized at different temperatures, GPC tests were performed on PCE-1–PCE-5. The results were shown in Table 2.

| Samples  | Synthesis temperature /℃ | Mₙ  | Mₘ  | Mₚ  | Mₘ/Mₙ | Conversion rate /% |
|----------|--------------------------|------|------|------|--------|-------------------|
| PCE-1    | 25                       | 14312| 25237| 21159| 1.76   | 69.61            |
| PCE-2    | 35                       | 15240| 27280| 22617| 1.79   | 80.10            |
| PCE-3    | 45                       | 15192| 27720| 22293| 1.82   | 80.14            |
| PCE-4    | 55                       | 15467| 28614| 22882| 1.85   | 88.85            |
| PCE-5    | 65                       | 14919| 25521| 22051| 1.71   | 77.26            |

It can be seen from Table 2 that the weight average molecular weight ($M_w$) of the PCE synthesized at different temperatures was about 27000. As the temperature increases, the number average molecular weight ($M_n$) of the PCE increases first and then decreased, but they were all around 15000. When the reaction temperature was 55 ℃, the conversion rate of PCE-4 was as high as 88.35% and the material polydispersity index ($M_w/M_n$) was 1.85, the result showed that the PCE synthesized at 55 ℃ had good dispersibility and high conversion rate.

3.4. FTIR test
FT-IR was used to character the compositional information of PCE-1 and PCE-4 and the results were shown in Figure 2. It can be seen from the figure that the positions of the infrared absorption peaks of the PCE-1 and PCE-4 were similar. The change of absorption peak at 3489 cm⁻¹, 2828 cm⁻¹ and 1731 cm⁻¹ ascribed to the stretching vibration of hydroxyl -OH, C-H stretching vibration of methyl and methylene and stretching vibration of C=O in ester bond, respectively. The absorption peak at 1456 cm⁻¹ and 1349 cm⁻¹ were generated by bending vibration of methylene -CH₂ and methyl -CH₃. The position of infrared absorption peak of the PCE synthesized under room temperature and heating conditions basically coincide, but with the increase of temperature, the chemical reaction in the synthesis process was accelerated. Therefore, the peak intensity of the PCE synthesized under heating conditions was slightly higher than that of the PCE synthesized at normal temperature.
4. Conclusions
(1) Proper heating can increase the chemical reaction rate of PCE, promote the polymerization of free radicals, improve the dispersion performance, and then effectively improve the water bleeding, fluidity and slump retention of concrete.
(2) The PCE-4 synthesized at 55 ℃ has low bleeding rate, high water reduction and good slump retention effect.
(3) With the temperature increase, the molecular weight of polycarboxylate superplasticizers first increase and then decrease.
(4) The infrared spectra showed that the peak position of polycarboxylate superplasticizers synthesized at room temperature was basically the same as that synthesized under heating condition, but the peak intensity of the PCE synthesized under heating conditions was slightly higher than that synthesized at room temperature.

References
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