Preparation of solid polycarboxylate superplasticizer

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Abstract. A solid polycarboxylate superplasticizer was synthesized with methacrylic acid, polyoxyethylene(TPEG), and microcrosslinking monomer(P) synthesized by using polyetheramine and croton acid. Studied acid/ether mole ratio, P dosage, rotating speed and reaction temperature on the solid polycarboxylate superplasticizer performance. The results showed that when acid/ether mole ratio was 4.0/1, P dosage was 8% of TPEG, rotating speed was 800rpm and reaction temperature was 60℃, synthetic polycarboxylate superplasticizer had the best comprehensive performance.

1. Introduction
The polycarboxylate superplasticizer is mainly a liquid product on the market currently[1]. The factory liquid product has a solid content of 10-50%, resulting in high cost in the long-distance transportation. In addition, with the large-scale application of grouting, dry mortar and powder coatings in construction projects, the demand for solid polycarboxylate superplasticizers has also expanded year by year, but liquid polycarboxylate superplasticizer cannot meet the needs of these industries.

At present, there are researches on solid polycarboxylic superplasticizer in China. We use spray drying technology or bulk polymerization to obtain powder polycarboxylic superplasticizer usually[2]. However, the powder polycarboxylic superplasticizer obtained by spray drying technology undergoes molecular chain transfer reaction, and it is partially converted into high molecular weight polymer, resulting in decline in quality and agglomeration. Bulk polymerization process is not easy to control, then the product has a wide molecular weight distribution and poor performance.

In this paper, the kneading machine is used for bulk polymerization to overcome the problems of high viscosity of the reactants in the bulk polymerization process of polycarboxylate superplasticizer, difficulty in stirring and difficulty in heat dissipation. At the same time, self-made micro-crosslinking monomer is introduced into the copolymerization reaction to synthesize solid polycarboxylic acid. The product has excellent comprehensive properties in concrete.

2. Methods

2.1. Materials
Prenol polyoxyethylene ether TPEG(Mn: 3000), industrial grade; methacrylic acid (AA), industrial grade; dibenzoyl peroxide (BPO), industrial grade; polyetheramine(Mn: 800), industrial grade; crotonic acid, industrial grade; hydroquinone, industrial grade; concentrated sulfuric acid, industrial grade; thioglycolic acid (TGA), industrial grade; cuprous naphthalate, industrial grade.

Sand (S), river sand, fineness modulus 2.5 to 2.8; cement (C), mingfu P.O42.5; counterattack stone (G): 5-22 mm continuous gradation; Point-MS: polycarboxylate superplasticizer, manufacturer: Kezhijie New Material Group Co., Ltd.
2.2. Synthetic process

2.2.1. Micro-crosslinking monomer
Performing an amidation reaction of polyetheramine, crotonic acid, hydroquinone and concentrated sulfuric acid at a temperature of 100°C for 5h where water is removed by vacuuming, obtaining a micro-crosslinked monomer p.

2.2.2. Copolymerization
Copolymerization: performing a bulk polymerization of TPEG, a micro-crosslinked monomer and TGA at a temperature of 60°C and a stirring speed of 800rpm, obtaining a liquid polycarboxylate superplasticizer; wherein dropping the methacrylate in 2h and adding BPO and cuprous naphthalate in three equal portions at intervals of 18min after the reactants being in a liquid state, then keeping the temperature constant to react for 1h; Finally, a product with a solid content of 100% is obtained.

cooling slice: the liquid polycarboxylate superplasticizer flows into the slicer through the kneading machine discharge pipe for cooling slice, obtaining a micro-crosslinked solid polycarboxylate superplasticizer.

2.3. Performance testing and characterization
(1) IR
The infrared spectrometer model is Spectrum 100, and the manufacturer is American PE company. The test was carried out using a film method.

(2) Zeta potential measurement
The zeta potential of the cement surface was measured by a JS94K2 microelectrophoresis apparatus from Shanghai Zhongchen Company.

The measurement steps are as follows:
(1) According to the designed water-cement ratio and the amount of PCE, weigh an appropriate amount of PCE and deionized water, and manually mix and stir for 3 minutes;
(2) Weigh 1 g of the slurry and dilute it in 100 g of water, centrifuge it for 1 min, take a certain amount of the middle layer liquid, inject it into the electrophoresis cup, measure the zeta potential of the sample, and record the stable zeta potential value.
(3) Performance testing
Test of mechanical properties of concrete: the compressive strength of concrete is determined according to the provisions of GB50081-2002 "Test methods for mechanical properties of ordinary concrete", According to GB8076-2008 "Concrete admixture" requirements to determine other performance indicators. The concrete mix ratio is shown in Table 1. The macromonomer conversion rate of the synthetic product was tested using GPC.

Table1. Concrete mix ratio
| Material | C | S | G | W |
|----------|---|---|---|---|
| Dosage kg/m³ | 330 | 698 | 1126 | 145 |

3. Results and discussion

3.1. Factors influencing the copolymerization reaction

3.1.1. Effect of acid ether ratio on performance of solid PCE
### Table 2. Concrete experiment results

| Number | Acid ether ratio | Initial slump /mm | slump after 1h/mm | Compressive strength /MPa 7d | Compressive strength /MPa 28d | Macromonomer conversion rate/% |
|--------|------------------|--------------------|-------------------|------------------------------|------------------------------|-------------------------------|
| 1      | 3.0:1            | 160                | 95                | 32.5                         | 41.2                         | 84                            |
| 2      | 3.5:1            | 170                | 120               | 29.3                         | 42.9                         | 86                            |
| 3      | 4.0:1            | 215                | 185               | 29.4                         | 43.8                         | 89                            |
| 4      | 4.5:1            | 195                | 155               | 26.8                         | 41.4                         | 88                            |
| 5      | 5.0:1            | 180                | 130               | 26.5                         | 40.4                         | 86                            |

The macromonomer TPEG with a molecular weight of 3000 was selected, and solid polycarboxylate superplasticizers was copolymerized according to different acid-ether ratios. The concrete comparison experiments of the PCE were carried out, and the results are shown in Table 2. It can be seen from Table 2 that as the ratio of acid to ether increases, the initial slump of concrete increases first and then decreases, and the conversion rate of macromonomer increases first and then decreases, and the 7d compressive strength of concrete decreases. The slump retention performance of the PCE is less affected by the ratio of acid to ether. The lower the ratio of acid to ether, the main chain of the PCE is shorter, and the branching is longer. Theoretically, the longer the main chain of the polycarboxylate superplasticizer, the better the dispersion performance, but the slump retention performance decreases as the main chain grows. In addition, the shorter the main chain, and the longer the branching, PCE can increase the early strength of concrete. Therefore, in order to obtain a solid PCE with excellent comprehensive performance, it is necessary to determine a suitable acid-ether ratio. It can be seen from Table 2 that the optimum ratio of acid to ether is 4.0:1, and the synthesized solid PCE has higher conversion rate of macromonomer and the best comprehensive performance.

### 3.1.2. Effect of micro-crosslinking monomer on the performance of solid PCE

| Number | P dosage/% | Initial slump /mm | slump after 1h/mm | Compressive strength /MPa 7d | Compressive strength /MPa 28d | Macromonomer conversion rate/% |
|--------|------------|--------------------|-------------------|------------------------------|------------------------------|-------------------------------|
| 1      | 5          | 185                | 150               | 28.5                         | 40.2                         | 82                            |
| 2      | 8          | 200                | 195               | 30.3                         | 41.9                         | 88                            |
| 3      | 11         | 170                | 105               | 32.4                         | 42.3                         | 86                            |
| 4      | 14         | 165                | 90                | 32.7                         | 41.7                         | 82                            |
| 5      | 17         | 150                | 90                | 33.5                         | 40.9                         | 79                            |

Note: The amount of P is the mass percentage to the macromonomer.

The micro-crosslinking monomer P is introduced in the solid PCE, thereby introducing an amide group and a micro-crosslinked structure into the molecular structure to improve slump retention performance, and to improve early strength of concrete. Different amounts of P were copolymerized with the macromonomer to obtain a solid PCE, and concrete comparison experiments were carried out. The results are shown in Table 3. It can be seen from the table 3 that with the increase of P dosage, the initial slump and 1h slump of concrete first increase and then decrease, and the conversion rate of macromonomer increases first and then decreases, and the compressive strength is increasing. The micro-crosslinked monomer P has a large steric hindrance and a small reactivity. The addition of an appropriate amount of P can introduce an amide group and a micro-crosslinked structure on the molecular chain of the solid PCE to improve the dispersion performance and slump retention performance. With the increase of the addition amount of P, a large amount of micro-crosslinking monomer P can not participate in the reaction, affecting the active ingredients in the final product, then concrete comprehensive performance is degraded. The amide group in the molecular structure of the solid PCE promotes the formation of ettringite and increases the amount of ettringite formation. The crystal morphology of ettringite also changes, and a large parallel packing turn into a smaller twisted radial shape. Therefore, as the amount of micro-crosslinking monomer P is increased, and the early
compressive strength of the concrete with the synthesized solid PCE is increased. According to the test results, in order to obtain a solid PCE with the best comprehensive performance, the optimum amount of the micro-crosslinking monomer P is 8% of the mass of the macromonomer.

3.1.3. Effect of rotating speed on performance of solid PCE

Fig. 1 shows the effect of the kneading machine speed on the performance of the synthetic solid PCE. It can be seen from the fig 1 that as the rotational speed increases, the initial slump of the concrete increases first and then decreases, and the macromonomer conversion rate also shows a trend of increasing first and then decreasing. When the rotation speed is low, the dispersion performance of the PCE is poor. This is because the bulk polymerization reaction of the solid PCE has a large viscosity and is difficult to stir and dissipate. The low rotation speed is not conducive to the reaction heat dissipation and the polymerization degree of the synthesized product is relatively high, but monomer conversion rate is lower. As the rotation speed increases, the degree of polymerization of the product becomes smaller, the conversion rate of macromonomer increases, and the dispersion performance becomes better. When the rotation speed reaches a certain value and continues to increase, the macromonomer conversion rate is lowered, the molecular weight of the synthesized product is too low, and the dispersion performance is lowered. Therefore, the optimum speed of the kneader is 800 rpm.

![Fig.1 Effect of Rotating Speed on Performance of solid PCE](image1)

3.1.4. Effect of reaction temperature on performance of solid PCE

![Fig.2 Effect of Reaction Temperature on Performance of solid PCE](image2)
Fig 2 shows the effect of reaction temperature on the properties of synthetic solid PCE. It can be seen from the figure that as the reaction temperature increases, the initial slump of concrete increases first and then decreases. The monomer conversion rate first increases and then decreases. When the temperature is lower than the decomposition temperature of the BPO initiator, the initiation efficiency of the initiation system is very low, and the performance of the synthetic PCE is poor. When the temperature is too high, the explosion may occur, resulting in poor performance of the synthetic PCE. Therefore, the optimum reaction temperature of the system is 60 °C.

3.1.5. concrete performance
According to the above test results, TPEG3000 is used as the macromonomer, the ratio of acid ether is 4:0:1, the amount of micro-crosslinking monomer is 8% of the mass of macromonomer, the speed of kneading machine is 800rpm, and the reaction temperature was 60°C, then a PCE X was synthesized. The PCE X and the Point-MS were tested for concrete under the same amount of solidification. Table 4 shows the concrete test results.

| Number | Sample  | Initial slump /mm | Slump after 1h/mm | Compressive strength /MPa |
|--------|---------|-------------------|-------------------|---------------------------|
| 1      | X       | 185               | 150               | 27.5                      | 41.5                      |
| 2      | Point-MS| 180               | 150               | 27.3                      | 40.9                      |

It can be seen from Table 4 that the initial slump, 1h slump and compressive strength of the concrete obtained by mixing the two PCE are similar, and it can be seen that the PCE X reaches the Point-MS performance.

3.1.6. Effect of solid PCE on Zeta Potential of Cement Paste

As shown in Fig 3, when the concentration of the PCE reaches a certain value, the Zeta potential tends to be basically stable due to the adsorption of the cement particles to the PCE, and the PCE X has a basic stability value of 6mv, the basic stability value of ordinary PCE is 8mv. It can be seen that the effect of PCE X on the zeta potential of cement paste is not as great as that of ordinary PCE. Mainly because, compared with ordinary PCE, PCE X introduces micro-crosslinking monomer, and its molecular configuration is relatively large. Its adsorption on the surface of cement particles is basically monolayer adsorption, and the effect of zeta potential is small.

3.2. Molecular structure analysis

3.2.1. IR
The above PCE X and Point-MS were analyzed by infrared spectroscopy. The results are shown in Fig.4. As can be seen from Fig.4, the infrared spectrum of PCE X and Point-MS is similar. Wherein the absorption peak of carboxylate is near 1643 cm\(^{-1}\) and the characteristic absorption peak of ether bond CO is at 1100.00 cm\(^{-1}\). It is indicated that PCE X is similar in structure to the common ether polycarboxylate superplasticizer. PCE X can achieve the performance of the liquid polycarboxylate superplasticizer.

![Infrared spectrum](image)

**Fig.4 infrared spectrum**

### 3. Conclusions

1. The best process recipe for solid PCE: the ratio of acid to ether is 4.0:1, the amount of micro-crosslinking monomer is 8% of the mass of macromonomer, the kneader rotation speed is 800 rpm, and the reaction temperature is 60°C. The synthesized solid PCE has the best comprehensive performance.

2. Through study on the performance of concrete, it is found that the properties of PCE X and Point-MS are similar, and it can be seen that PCE X reaches Point-MS performance.

3. The effect of PCE X on the zeta potential of cement paste is not as great as that of ordinary PCE. Mainly because, compared with ordinary PCE, PCE X introduces micro-crosslinking monomer, and its molecular configuration is relatively large. Its adsorption on the surface of cement particles is basically monolayer adsorption, and the effect of zeta potential is small.

4. It was found by IR analysis that PCE X has a similar structure to the ordinary ether PCE, and can achieve the performance of the liquid PCE.

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