Synthesis and Characterization of A Slowly-Released Polycarboxylate Superplasticizer with High Slump Retention

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Abstract. A slowly-released polycarboxylate superplasticizer with high slump retention was obtained at room temperature by using Isomyl enol polyoxyethylene ether (TPEG), 2-hydroxyethyl acrylate (HEA), acrylic acid (AA), and acrylamide (AM) as the main raw material, and using hydrogen peroxide (H₂O₂) as initiator and mercaptoacetic acid as the chain transfer agent. The effect of initiator dosage, chain transfer agent dosage and acrylamide dosage on the performance of the product were investigated. The results showed that under the optimum polymerization conditions of the slowly-released polycarboxylate superplasticizer with high slump retention, the dosage of initiator, chain transfer agent and acrylamide was 0.3%, 0.25% and 0.9% based on the mass of the macromonomer, respectively. The molecular weight distribution under the optimum synthesis conditions was determined by gel permeation chromatography (GPC) and the structure of the polymer was characterized by spectroscopy (FTIR). Compared with commercial similar produces and other synthesized slowly-released polycarboxylate superplasticizer, the test results showed that the developed superplasticizer had an excellent slump retention ability.

1. Introduction
Polycarboxylate superplasticizers, as an important raw material in concrete, have become an indispensable new material for national capital construction because of their high water-reducing rate, low admixing volume, and environmental protection [1-4]. Because of the great difference of concrete raw materials, in the hot weather or long-distance transportation, the slump loss of concrete is too fast and the workability is poor, resulting in the failure of normal pouring of fresh concrete, which significantly wastes human and material resources [5-7]. In order to reduce the slump loss of concrete, the methods of increasing the amount of polycarboxylate superplasticizer and adding compounding retarding ingredients are adopted, which not only increase the cost of concrete production but also have serious side effects on the strength and durability of concrete [8-10]. Therefore, it is an urgent need to develop a slow-release and slump maintaining polycarboxylate superplasticizer.

In this paper, through the design of the molecular structure and the introduction of unsaturated ester group and amide group monomers, a kind of slowly-released polycarboxylate superplasticizer with high slump retention was investigated through experiments, and the best ratio and process conditions were selected. The concrete test results show that the slowly-released polycarboxylate superplasticizer has excellent comprehensive performance, good slow-release slump retention performance and wide application prospect.
2. Experimental

2.1. Experimental raw materials.
Isopentenyl polyoxyethylene polyether (TPEG, \(M_w = 2400\) g/mol, industrial grade), acrylic acid (AA, industrial grade), hydrogen peroxide (\(\text{H}_2\text{O}_2\), 27.5 wt\%, industrial grade), sodium hypophosphite(SHP, industrial grade), mercaptoacetic acid (95% aqueous solution, industrial grade), Hydroxyethyl acrylate (HEA, industrial grade), acrylamide (AM, industrial grade), sodium hydroxide solution (30% aqueous solution, industrial grade).

2.2. Test raw materials.
Cement (C, Yuexiu brand, P.O 42.5R), strait sand (S, river sand with fineness modulus of 2.3 and mud content less than 0.4%), gravel (G1, the grain size of 5-10 mm; G2, the grain size of 10-20 mm), fly ash (F, Level II), slag powder (K, Level S95), tap water met the test requirements, PCE-1, PCE-2, PCE-3 are slump retaining polycarboxylate superplasticizers on the market, with solid contents of 39.8%, 40%, and 42%, respectively, PCE-JS is an ordinary polycarboxylate superplasticizer with a solid content of 48.6%.

2.3. Copolymerization of PCE-SR.
A certain amount of TPEG and deionized water were added into a 250mL three-necked flask. The quantitative amount of \(\text{H}_2\text{O}_2\) and AM were subsequently added into the reaction vessel. After the solution was uniformly mixed, a prepared solution of A (AA and HEA) and B (SHP and chain transfer agent) were added dropwise to the system. The polymerization reaction was completed in 3h at room temperature. Then a 30% aqueous solution of sodium hydroxide was added to adjust the pH to 6.0-7.0, thus obtaining a slowly-released of polycarboxylate superplasticizer with high slump retention (PCE-SR).

2.4. Performance test method

2.4.1. Fluidity of cement paste. The fluidity of cement paste is tested according to GB/T8077-2012 "Test method for homogeneity of concrete admixtures" at 0, 0.5, 1, 1.5, 2 and 2.5 hours. The water-cement ratio is 0.29 and the polycarboxylate superplasticizer content is 0.45%.

2.4.2. Concrete test. The concrete test is conducted according to 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". Test the performance of concrete mixtures and hardened concrete. The concrete test mix proportion (kg/m³) was shown in Table 1.

| W | C | S | G | F |
|---|---|---|---|---|
| 170 | 270 | 800 | 1050 | 80 |

2.4.3. Gel permeation chromatographic (GPC) measurement. GPC was measured and analyzed by using American Waters 1515 Isocratic HPLP pump/glassed of water 2414 differential detector.

2.4.4. Fourier transformer infrared spectra (FTIR) measurement. PCE-SR and PCE-3 were pressed disc with KBr to obtain FTIR data, respectively. 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. Effect of initiator dosage on cement dispersion

![Figure 1. Effect of initiator dosage on cement dispersibility.](image)

It can be seen from Figure 1 that when the initiator dosage is 0.3%, the dispersion of polycarboxylate superplasticizer can reach the best within two hours. When the dosage of the initiator is 0.2%, the release rate of the unsaturated double bond is slow and the fluidity is reduced due to the low initiation rate and incomplete free radical polymerization. When the dosage of initiator is higher than 0.3%, the instantaneous particles in the reaction system are too concentrated and the dispersion performance began to decline due to the increase of initiator concentration and free radical growth rate.

3.2. Effect of chain transfer agent dosage on cement dispersion

![Figure 2. Effect of chain transfer agent dosage on cement dispersibility.](image)
As shown in Figure 2, with the increase of the dosage of the chain transfer agent, the fluidity of slump-retaining polycarboxylate superplasticizer tends to be first increasing and then decreasing. When the amount of chain transfer agent is 0.25%, the slump-retaining performance of the synthesized product is the best. The dosage of the chain transfer agent has a great influence on the molecular weight of the product. The low amount of the chain transfer agent results in the excessive molecular weight and high molecular side density of the synthetic product, which leads to winding and poor slump retention performance. With the increase of the chain transfer agent dosage, the molecular weight of the synthesized product tends to appropriate and the slump retention is enhanced. When the amount is excessive, the molecular weight of the synthesized product is too low, which leads to the decreased of the steric resistance effect of the synthesized product adsorbed on the cement particles and the decrease of the dispersion effect.

3.3. Effect of acrylamide dosage on cement dispersion

![Figure 3. Effect of acrylamide dosage on cement dispersibility.](image)

It can be seen from Figure 3 that a small amount of AM has little effect on the dispersion of polycarboxylate superplasticizer. When the dosage of AM is 0.90%, the initial dispersion of polycarboxylate superplasticizer increased obviously. It is worth noting that with the increase of AM usage, it not only has little effect on improving the fluidity of cement mortar but also increases the loss. The charge density of the main chain of polycarboxylate superplasticizer is reduced by adding AM, and under the alkaline condition of cement hydration, the amide group hydrolyzed into the carboxyl group to improve the slump retention of cement paste.

3.4. Concrete test

The concrete comparison experiment of PEC-1, PEC-2, PEC-3 and PCE-SR were respectively mixed with PCE-JS at room temperature. The concrete test results were shown in Table 2.

| Samples    | Dosage /% | Slump / mm | Dispersion / mm | Compressive strength / MPa |
|------------|-----------|------------|----------------|----------------------------|
|            |           | initial    | 2h             | initial 2h 3d 7d 28d       |
| PCE-1      | 1.4       | 210        | 190            | 550        470 23.2 28.9 36.2 |
| PCE-2      | 1.4       | 210        | 195            | 545        505 23.1 26.6 37.9 |
| PCE-3      | 1.4       | 205        | 195            | 550        495 22.2 27.0 36.8 |
| PCE-SR     | 1.4       | 220        | 210            | 550        520 23.6 29.3 38.5 |
Compared with other slump retention polycarboxylate superplasticizers, the slump loss of the synthesized PCE-SR is the least, and the slump retention performance is better than that of the similar products on the market in Table 2. In addition, the compressive strength of concrete mixed with PCE-SR is improved, and the compressive strength concrete reaches 38.5 MPa at 28d. At the same time, the concrete with PCE-SR has excellent workability, almost no bleeding after two hours, and has good concrete application performance.

4. GPC measurement
Table 3 was gel permeation chromatography data of PCE-SR and PCE-1, PCE-2, and PCE-3, respectively.

| Samples | $M_n$ | $M_w$ | $M_w/M_n$ | Conversion rate /% |
|---------|-------|-------|-----------|--------------------|
| PCE-SR  | 23092 | 69048 | 2.99      | 96.01              |
| PCE-1   | 22547 | 53671 | 2.38      | 84.39              |
| PCE-2   | 23303 | 65874 | 2.83      | 92.87              |
| PCE-3   | 11367 | 31556 | 2.78      | 87.68              |

It can be seen from Table 3 that the weight average molecular weight ($M_w$) of PCE-SR is 69048, the number average molecular weight ($M_n$) is 23092, the polydispersity coefficient ($M_w/M_n$) is 2.99, and the conversion rate is as high as 96%, which is more than that of PCE-1, PCE-2 and PCE-3, indicating that the molecular weight distribution of PCE-SR is wide.

5. FTIR measurement

FTIR spectra of PCE-3 and PCE-SR are shown in Figure 4. The peak at about 3414 cm$^{-1}$ is the stretching vibration peak of hydroxyl (-OH) in the mother liquor of slump maintaining agent, and the characteristic vibrational absorption peak of C-H stretching vibration of methyl and methylene is at 2864 cm$^{-1}$. The stretching vibration absorption peak of the double bond (C=C) at 1730 cm$^{-1}$, and the peak at 1450 cm$^{-1}$ is corresponding to the C-H bending vibration absorption peak of methylene (-CH$_2$-), meanwhile the
stretching vibration absorption peak ether (-C-O-C) is detected at 1110cm⁻¹. The result showed that the molecular structures of PCE-3 and PCE-SR contain hydroxyl, carboxyl, ether, and other functional groups. While the difference between the infrared spectra of PCE-SR and PCE-3 is that there is a single peak of PCE-SR at 1600cm⁻¹, which is the characteristic absorption peak of amine (-NH₂), indicating that acrylamide is indeed introduced into PCE-SR in the substructure.

6. Conclusions
(1) The slowly-released polycarboxylate superplasticizer with high slump retention was synthesized by free radical polymerization. FTIR spectrum analysis of the products showed that the polymerization of the monomers proceeded smoothly. The optimum synthesis process was the dosage of initiator, chain transfer agent and acrylamide were 0.3%, 0.25%, and 0.9% of the monomer mass, respectively.

(2) Under the optimal synthesis conditions, the fluidity of the cement paste corresponding to the synthesized product has better retention performance and fluidity when the water-cement ratio is 0.29 and the output is 1.2% of the cement mass.

(3) PCE-SR has a good slump retention performance. The combination of PCE-SR and polycarboxylic acid water reducer can greatly improve the slump retention of water reducer, and there is almost no loss of concrete within two hours.

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