Study on Synthesis and Performance of Slump Retention Polycarboxylate Superplasticizer

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Abstract. A polycarboxylate superplasticizer with high slump retention capability was prepared and the effect of the ratio of acid to ether, L-type ascorbic acid and acrylic acid was discussed. The results showed that the optimum acid-ether ratio of the water reducing agent was 2.44, the amount of L-type ascorbic acid was 0.35, and the amount of acrylic acid was 9%. The results of C30 concrete test showed that the initial slump of PC-1 was slightly larger than that of the same kind of PC-2 and PC-3.

1. Introduction

Polycarboxylate superplasticizers are more and more widely used in concrete engineering because they have many advantages, such as low content, high water reduction rate, dispersing cement particles and environmentally friendly properties [1]. Besides, the unique molecular structure of polycarboxylate superplasticizer could be modified or redesigned by changing the composition of functional groups, length or density of the side chain and length of backbone [2-4]. The polycarboxylate superplasticizers have made remarkable progress in the synthesis of raw materials and methods. For example, the synthetic raw materials have evolved from the earliest the polyethylene glycol methacrylate ester (MPEG) and allyl polyethylene glycol (APEG) to the current isobutenyl polyethylene glycol (VPEG) and methylallyl polyoxyethylene ether (HPEG), isopentenol polyoxyethylene ether (TPEG) [1], and the synthesis methods also include bulk polymerization, solution radical polymerization and normal temperature initiated polymerization [5-6]. However, the large slump loss of concrete often appears during long-time and long-distance transportation due to the existence of large differences in concrete raw materials. In addition, the complexity of the concrete components, such as, the unreasonable particle grading of machine-made sand, high stone powder content and poor particle morphology, and the diversification of the structure have made it more and more difficult to control the performance of concrete. Traditional water-reducing agents can no longer meet the needs of modern concrete production, which would result in concrete segregation, bleeding, poor water retention and workability, although some additives have been used to improve the partial performance of concrete, but still unable to fundamentally enhance the performance of concrete.

Due to long time transportation in a hot weather, the slump loss of concrete was large. Thus, the amount of superplasticizer is usually increased to maintain the working performance of the concrete and make the concrete have good fluidity. However, the increase of the dosage of water-reducing agent can easily lead to the segregation and bleeding of concrete, and reduce the compressive strength of concrete. Another way is to solve the slump loss of concrete by adding appropriate retarders, such
as sodium citrate, sucrose and sodium citrate [7-8]. However, the related results showed that the addition of retarder not only could not effectively solve the problem of slump loss concrete, but would affect the performance of the water reducing agent.

In this work, the synthesis of water-reducing agent was studied. The water-reducing agent with slump retention was synthesized by polymerization at room temperature. The polymerization reaction between TPEG and acrylic acid takes place in the redox-initiated system. By optimizing the synthetic parameters such as acid-to-ether ratio, the problem of rapid slump loss of polycarboxylate superplasticizer in fresh concrete is solved, and the slump retention performance of polycarboxylate superplasticizer is improved.

2. Experiment

2.1. Materials
TPEG-2400 (isopentenol polyoxyethylene ether with molecular weights of 2400, industrial grade), acrylic acid (AA, analytical grade, Shanghai Lingfeng Chemical Reagent Co., Ltd), hydrogen peroxide (H₂O₂, industrial grade), L-type ascorbic acid (industrial grade), thioglycolic acid (industrial grade), fly ash (Type II, Jiaxing Power Plant,), PC-2 (Shanghai Taijie Chemical Co., Ltd.), PC-3 (Jiangsu Nigao Science & Technology Co., Ltd).

Cement: cement type P·O 42.5 was used. Chemical composition and particle size distribution of cement are shown in Table 1 and Table 2, respectively.

Fine aggregates: manufactured sand with a fineness modulus of 2.9 to 3.0 and a clay content of less than 1% was used. Coarse aggregates: the grading of the coarse aggregates shall meet the particle size of 5 to 20 mm.

Mixture proportions: All concrete should be proportioned to the following the Table 3 requirements.

| Material         | Content (kg·m⁻³) |
|------------------|------------------|
| Cement           | 280              |
| Fly ash          | 74               |
| Sand             | 780              |
| Coarse aggregates| 1047             |
| Water            | 170              |

2.2. Synthesis of the polycarboxylate superplasticizers
First, TPEG-2400 and water were added into the reactor, and then hydrogen peroxide was added at one time when TPEG-2400 has been uniformly dissolved. Secondly, the mixture of A and mixture of B was introduced respectively after 10 minutes, A was a mixed solution of acrylic acid and water, B was a mixed solution of L-type ascorbic acid, thioglycolic acid and water. The mixture solution of A was added dropwise for 3 hours, the mixture solution of B was added dropwise for 3 hours and 20 minutes, and reacted at a constant temperature for 1 hour after the mixture solution of B was added dropwise. Finally, sodium hydroxide solution (30%) was added neutralized to a pH of 6—7 to obtain high slump retention capability polycarboxylic superplasticizer (PC-1).
2.3. Properties of concrete testing

2.3.1. Cement paste fluidity. Cement paste fluidity was carried out with reference to GB 8077-2012 "Methods for testing uniformity of concrete admixture", water-cement ratio was 0.29.

2.3.2. Concrete test. Concrete test was tested with reference to GB 8076-2008 "concrete admixtures".

3. Results and discussion

3.1. Influence of the ratio of acid to ether

The initial fluidity of polycarboxylate superplasticizer is mainly related to the molecular density of the polymer. The decomposing group mainly plays the role of anchoring and electrostatic repulsion, and the long side chain ether bond has a steric hindrance. The effect of different ratio of acid to ether on the fluidity of polycarboxylate superplasticizer was studied. The results were shown in Table 4.

It can be seen from Table 4 that with the increase of acid-to-ether ratio, the initial fluidity of cement paste mixed with water reducing agent gradually increases, and the fluidity of cement paste no longer increases or even decreases when the acid-to-ether ratio increases to 2.44. Since the dispersion between the polycarboxylate superplasticizer and the cement was mainly determined by the adsorption groups such as carboxyl groups, the density of the carboxyl group would affect the adsorbability of the polycarboxylate superplasticizer, and then affect the dispersibility of the cement paste. Besides, it can be found that when the acid-to-ether ratio was 2.44, 1h cement paste fluidity retention was the best. Therefore, the optimal acid-to-ether ratio was 2.44.

Table 4. Influence of the ratio of acid to ether on the fluidity of polycarboxylate superplasticizer.

| The ratio of acid to ether | 1.77 | 2.00 | 2.22 | 2.44 | 2.66 |
|---------------------------|------|------|------|------|------|
| Initial cement paste fluidity (mm) | 196  | 216  | 234  | 246  | 238  |
| 1 h cement paste fluidity (mm) | 188  | 204  | 221  | 244  | 228  |

3.2. Influence of the dosage of L-type ascorbic acid

The effect of the dosage of L-type ascorbic acid on the fluidity of the water reducing agent was studied, and the ratio of acid to ether was 2.44. The test results were shown in Table 5. As can be seen from Table 5 that with the increase in the amount of L-type ascorbic acid, the initial and 1h fluidity of the cement paste gradually increase, and when the amount of ascorbic acid increases to 0.35, the dispersion performance was best. Therefore, the optimal dosage of L-type ascorbic acid was 0.35, and the slump of the polycarboxylate water reducing agent was best.

Table 5. Influence of the dosage of L-type ascorbic acid on the fluidity of polycarboxylate superplasticizer.

| The dosage of ascorbic acid (%) | 0.15 | 0.25 | 0.35 | 0.45 |
|-------------------------------|------|------|------|------|
| Initial fluidity of cement paste (mm) | 192  | 225  | 230  | 206  |
| 1 h fluidity of cement paste (mm) | 185  | 234  | 256  | 192  |

3.3. Influence of the dosage of AA

The carboxyl group density of the polymer could be adjusted by the amount of AA, and then improve the dispersion performance of the water reducing agent. The dosage of L-type ascorbic acid and the acid-to-ether ratio were 0.35 and 2.44, respectively. The effect of the dosage of AA of polycarboxylate superplasticizer was studied, and the results were displayed in Table 6. The results showed that with the increase of dosage of AA, the initial fluidity of the cement paste increased gradually, and when the
dosage of AA was 9%, 1 h fluidity of cement paste increased significantly. Therefore, the optimal addition of AA was 9%, and the slump of the polycarboxylate water reducing agent was best.

| The dosage of AA (%) | 7   | 9   | 11  | 13  |
|----------------------|-----|-----|-----|-----|
| Initial fluidity of cement paste (mm) | 216 | 236 | 241 | 256 |
| 1 h fluidity of cement paste (mm)     | 223 | 264 | 200 | 213 |

### 3.4. Properties of concrete testing

PC-1 was the polycarboxylic water reducing agent prepared by the optimal synthesis condition, and PC-2 and PC-3 were selected. The properties of concrete with the same solid content (0.3%) were tested, such as the slump, workability and compressive strength. The properties of concrete were shown in Table 7. The results displayed that the initial slump of PC-1 was slightly larger than that of similar PC-2 and PC-3 under the same solid content, and the slump after 1 h of PC-1 was significantly better than similar national products PC-2 and PC-3. The concrete mixed with these products exhibited good workability, and the 3 d, 7 d, and 28 d compressive strengths of 3 kind of superplasticizer were equivalent.

| Polycarboxylate superplasticizer | Slump/Slump flow (mm) | Workability | Compressive strength (MPa) |
|----------------------------------|------------------------|-------------|----------------------------|
|                                  | Initial                | 1 h         | 3 d | 7 d | 28 d |
| PC-1                             | 235/605                | 180/580     | good workability           | 18.7 | 28.5 | 37.6 |
| PC-2                             | 225/575                | 145/560     | good workability           | 18.3 | 27.6 | 35.4 |
| PC-3                             | 220/565                | 145/540     | good workability           | 18.4 | 28.1 | 36.7 |

### 4. Conclusions

The best preparation parameters of polycarboxylate superplasticizer with high slump retention were that the acid-to-ether ratio, the dosage of L-type ascorbic acid and AA dosage was 2.44, 0.35 and 9%, respectively. The initial slump of PC-1 was slightly greater than that of similar national products PC-2 and PC-3, and the compressive strengths of 3 d, 7 d, and 28 d were equivalent.

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