Study on performance stability of Polycarboxylate Superplasticizer prepared at different temperatures

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Abstract—The effects of initial dropping temperature, amount of ferrous sulfate and dropping time on the performance of Polycarboxylate Superplasticizer were studied, and the measures to maintain the performance stability of Polycarboxylate Superplasticizer from 15 ℃ to 40 ℃ were discussed. The results show that the stability of the process is better when the initial dropping temperature is 20 ℃-30 ℃. When the temperature is higher than 30 ℃, the stability of the process can be achieved by prolonging the dropping time or reducing the amount of FeSO4. When the temperature is lower than 15 ℃, the performance can be improved by increasing the amount of FeSO4, so as to achieve the stability of the process.

1. Introduction
Polycarboxylate Superplasticizer has the advantages of designable molecular structure, good dispersion and dispersion retention, green environmental protection and so on. It meets the needs of modern concrete engineering and is gradually becoming the preferred admixture for preparing high-performance concrete [1-4]. In recent years, the function of polycarboxylate Superplasticizer has been continuously developed, and the preparation technology has been continuously improved. The preparation process has gradually changed from early heating process to normal temperature process [5-6]. In different seasons, the normal temperature ranges from 15 ℃ to 40 ℃. When polycarboxylate Superplasticizer is prepared by room temperature process, different reaction temperature will directly affect the activity of free radical and comonomer, so as to affect the performance of water reducer [7-9]. Therefore, the study of reaction temperature and factors affecting process temperature plays an important role in maintaining the stability of polycarboxylic acid high-performance water reducer.

In this project, the effects of initial dropping temperature, FeSO4 dosage and dropping time on the performance of water reducer were studied, and the measures to maintain the performance stability from 15 ℃ to 40 ℃ were discussed.

2. Experimental

2.1. Raw material
Raw materials include Methyl allyl polyethylene glycol ether (HPEG, Mn=2400), Acrylic acid (AA), Hydrogen peroxide solution (H₂O₂), Vinyl acetate, mercaptoacetic acid, ascorbic acid, FeSO₄, Sodium hydroxide solution (NaOH), 30 wt%. All raw materials are industrial grade.
2.2. Test raw materials
Cement (C): The physical performance of cement is shown in Tab 1.

| Varieties | Specific surface area / (g/cm²) | Standard consistency water consumption/% | Setting time/min | Flexural strength/MPa | Compressive strength/MPa |
|-----------|--------------------------------|------------------------------------------|-----------------|----------------------|-------------------------|
|           |                                |                                          | Initial | Initial | 3d | 28d | 3d | 28d |
| Hongshi P.O 42.5 | 368                           | 27.8                                    | 230     | 355     | 5.5   | 8.7   | 29.3  | 52.4  |

Sand (S): Natural sand, fineness modulus is 2.7, mud content is 0.8%.
Stone (G): Crushed stone G1 with a nominal diameter of 5mm-20 mm, and G2 gravel with a nominal diameter of 16mm-31.5 mm.
Water (W): Tap water.

2.3. Synthetic route
Firstly, a certain amount of water, HPEG, FeSO₄ and H₂O₂ are added to the reactor, and the aqueous solution of VC, aqueous solution of mercaptoacetic acid and mixed aqueous solution of acrylic acid and vinyl acetate are added to the reaction vessel by dropping for room temperature reaction. The dropping time is 2h, and then the constant temperature is 1h. The obtained product is neutralized with Sodium hydroxide solution to pH 6 ~ 7. Finally, polycarboxylate Superplasticizer PCE with solid content of 50% was prepared.

2.4. Concrete test
The slump, expansion and strength of concrete shall be tested according to the methods specified in GB 8076 “concrete admixtures”. The concrete mix ratio (kg/m³) is m(C) : m(S) : m(G1) : m(G2) : m(water) = 360:770:742: 318:175, and the amount of PCE is 0.2% of the amount of cementitious material.

3. Results and discussion
3.1. Effect of initial dropping temperature on properties of PCE
The initial reaction temperature will affect the activation energy and free radical decomposition rate of the polymerization system [10]. The higher the temperature, the lower the activation energy required by the system, and the faster the free radical decomposition rate, which will affect the performance of the prepared water reducer. In this project, the effects of different initial temperatures of 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C and 45 °C on the performance of water reducer are studied. The test results are shown in Table 2.

| Temperature/°C | (Slump and Slump expansion)/mm 0h | 1h | 3d | 7d | 28d |
|----------------|----------------------------------|----|----|----|----|
| 15             | 210                              | 570| 195| 370| 26.9| 30| 39.4|
| 20             | 210                              | 590| 205| 410| 26.8| 31.1| 39.2|
| 25             | 210                              | 600| 210| 390| 27.7| 31.5| 40.6|
| 30             | 215                              | 590| 180| 390| 26.7| 30.8| 39.7|
| 35             | 220                              | 585| 205| 340| 27.7| 31.7| 39.4|
| 40             | 215                              | 560| 180| 300| 27.6| 31.3| 39.8|
| 45             | 195                              | 510| 165|    | 27.2| 31.3| 39.9|
The results show that when the process temperature is lower than 20℃ and higher than 35℃, the 0h slump expansion of concrete will become smaller, that is, the dispersion effect of water reducer will be reduced. When the temperature is lower than 20℃ and higher than 30℃, the 1h slump expansion of concrete will become smaller, that is, the dispersion retention of the water reducer decreases. Considering comprehensively, the process has good stability from 20℃ to 30℃.

3.2. Effect of FeSO4 dosage on the performance of PCE

Some studies have shown that [9-10], FeSO4 will coordinate with the carboxyl group of acrylic acid, shift the common electron cloud of carbon carbon double bond in the monomer to carbonyl carbon, enhance the activity of double bond, and improve the conversion rate of monomer. FeSO4 can accelerate the decomposition of hydrogen peroxide and the production of active free radicals. FeSO4 will reduce the energy barrier of the reaction and promote the progress of the reaction, resulting in more concentrated heat release, which is not conducive to the control of reaction temperature under high temperature conditions. Therefore, the effect of ferrous sulfate content on the performance of water reducer was investigated at 40℃. The test results are shown in Table 3.

| FeSO4/wt% | (Slump and Slump expansion)/mm | Compressive strength/MPa |
|-----------|--------------------------------|--------------------------|
|           | 0h   | 1h   | 3d   | 7d   | 28d  |
| 0         | 210  | 585  | 205  | 385  | 27.5 | 30.7 | 39.5 |
| 0.0015    | 210  | 590  | 205  | 380  | 27.2 | 30.3 | 39.8 |
| 0.003     | 215  | 570  | 200  | 345  | 27.1 | 31.4 | 39.6 |
| 0.0045    | 215  | 555  | 185  | 310  | 28.0 | 31.8 | 41.0 |
| 0.006     | 205  | 520  | 165  |      | 27.0 | 31.1 | 40.1 |
| 0.0075    | 220  | 480  | 140  |      | 28.0 | 32.0 | 39.8 |

The results show that under the condition of 40℃, with the increase of the amount of FeSO4, the dispersion and dispersion retention of PCE decrease, indicating that the amount of FeSO4 should be reduced or not used under the condition of high temperature.

3.3. Effect of dropping time on the performance of PCE

The length of dropping time will affect the exothermic reaction of polymerization, and then affect the performance of water reducer [11]. Under the condition of 40℃, when the dosage of ferrous sulfate is 0.0045%, the effect of dropping temperature on performance is investigated. The test results are shown in Table 4.

| time/h | (Slump and Slump expansion)/mm | Compressive strength/MPa |
|--------|--------------------------------|--------------------------|
|        | 0h   | 1h   | 3d   | 7d   | 28d  |
| 2      | 220  | 550  | 205  | 310  | 26.2 | 31.5 | 41.2 |
| 2.5    | 205  | 560  | 205  | 360  | 26.2 | 31  | 40.7 |
| 3      | 220  | 580  | 200  | 385  | 26.2 | 32  | 40.6 |
| 3.5    | 210  | 575  | 195  | 380  | 26.4 | 30.5 | 39.6 |

The results show that the dispersion and dispersion retention of the samples are improved with the extension of dropping time, which shows that prolonging the dropping time is conducive to the stability of the polymerization reaction at higher temperature, and the performance of dropping time of 3H is the best.
4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) The initial dropping temperature of the process is between 20 °C and 30 °C, and the stability of the process is good.

(2) When the temperature is higher than 30 °C, the stability of the process can be achieved by prolonging the dropping time or reducing the amount of ferrous sulfate.

(3) When the temperature is lower than 15 °C, the performance can be improved by increasing the amount of ferrous sulfate, so as to achieve the stability of the process.

References

[1] Shanshan Qian et al. Synthesis, characterization and working mechanism of a novel polycarboxylate superplasticizer for concrete possessing reduced viscosity[J]. Construction and Building Materials, 2018, 169 : 452-461.

[2] Lina Zhong. Synthesis and properties of mud resistant polycarboxylate superplasticize [J]. New building materials, 2018,45 (05): 41-44 + 48.

[3] Yunhui Fang. Preparation and characterization of viscosity reducing polycarboxylate superplasticize with different molecular structures [J]. New building materials, 2017,44 (06): 104-108 + 121.

[4] Yunhui Fang. Application of polycarboxylate superplasticize molecular design in prestressed high strength concrete pipe pile [J]. New building materials, 2012,39 (08): 32-35 + 67.

[5] Hao Wang, Jianjun Yun, Ranran Ye, et al. Theoretical study on the process of synthesizing polycarboxylate superplasticizer at room temperature [J]. Commercial concrete, 2014 (5): 27-29.

[6] Shunguan Lin. Study on process and performance of polycarboxylate superplasticizer synthesized at room temperature [J]. Concrete, 2020 (12): 77-79 + 84.

[7] Shaomin Zhang. Preparation and properties of polycarboxylate superplasticizer from new polyether macromonomer at low temperature [J]. Silicate bulletin, 2020,39 (09): 2844-2848.

[8] Xiaolu Chen. Study on the method and performance of synthesizing polycarboxylate superplasticizer at room temperature [J]. New building materials, 2014,41 (12): 80-83.

[9] Qiumin Xiong, Xiujuan Guo, Wei Dang, Xiaobin Chen, Jican Guan, Guangzhou Li, Han Xu. Effect of synthesis temperature on the performance of polycarboxylate superplasticizer [J]. Guangdong building materials, 2020,36 (07): 2-4.

[10] Jianjun Yun, Jianshu Tang, Meiqing Xu, Shumeng Min, Jingyao Wang. Temperature rise influencing factors and control measures for the preparation of polycarboxylate superplasticizer at room temperature [J]. Concrete world, 2021 (10): 61-64.

[11] Yu Zeng, You Sun, Ao Fan, Long Xiao, Wang Yuanfu, Fang Shichang. Synthesis and dispersion of new polycarboxylate superplasticizer [J]. Shandong chemical industry, 2021,50 (19): 12-13 + 16.