Study on the Influencing Factors of Mildew of Polycarboxylate Superplasticizer

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Abstract. This article discusses the effect on the mildew of polycarboxylate superplasticizer under different environmental temperature, sealing conditions, reaction temperature, acid-ether ratio, initiation system and compounding with different dosage of sodium gluconate. The results of the study indicate that the polycarboxylate superplasticizer should be kept as tightly as possible when not in use. In the case of the same cost performance, it can be selected to appropriately increase the acid-ether ratio, the reaction temperature, and reasonably select the additives with bactericidal effect for production.

1. Introduction
Due to its outstanding advantages such as high water reduction rate, good adaptability to cement, and excellent slump retention, Polycarboxylate superplasticizer has become the most important product in the admixture market for concrete. With the construction of my country's nuclear power, water conservancy, bridges, tunnels and other large-scale infrastructure, especially the planning and implementation of the railway passenger dedicated line network project, the market demand for Polycarboxylate superplasticizer continues to grow. However, the polycarboxylic acid water-reducing agent contains sugars, hydroxy carboxylates and other slow-setting and plastic-retaining components, which have the nutrients required for the growth of microorganisms, which is likely to cause a large number of microorganisms to multiply and the product is prone to mildew[1~4]. The spoilage of concrete admixtures not only affects the quality of the admixtures, but also may cause the quality of the final commercial concrete to be seriously affected. Especially after entering the summer, with the addition of retarding materials and other factors, Polycarboxylate superplasticizer is more prone to spoilage and deterioration under high temperature environment[5], and there will also be odor, resulting in the performance of Polycarboxylate superplasticizer reduced, affecting the concrete produce.

In this paper, through the experiment of the polycarboxylic acid water reducing agent mother liquor, the paper discusses the mildew of the polycarboxylic acid water reducing agent under the conditions of different ambient temperature, sealing conditions, reaction temperature, acid-ether ratio, initiation system and the combination with sodium gluconate impact. Through research on the influencing factors of mildew, it provides technical support for preventing mildew of Polycarboxylate superplasticizer.
2. Test materials and test methods

2.1. Raw materials
Polycarboxylate superplasticizer mother liquor: PCE-1 (solid content 40%, room temperature process), PCE-2 (solid content 40%, room temperature process), PCE-3 (solid content 40%, room temperature process), PCE-4 (solid content 40%, room temperature process), PCE-5 (solid content 40%, 63°C synthesis process), PCE-6 (solid content 40%, room temperature process), PCE-7 (solid content 40%, room temperature process), Hunan Kezhijie New Material Co., Ltd.; Sodium gluconate (industrial grade).

2.2. Test method
Store the Polycarboxylate superplasticizer in a 2000mL food grade plastic bottle, as shown in Figure 1. Store in open mode at different ambient temperatures, study and observe the mildew of the product; store in an open and airtight room at a temperature of 25±2°C, study and observe the mildew of the product; mix different amounts of sodium gluconate to study the effect of sodium gluconate on product mildew. Through the above observation and test results, the effects of different reaction temperatures, acid-ether ratios, and initiation systems on mildew of carboxylic acid water reducer are analyzed.

Fig 1. Mother liquor storage container

3. Test results and analysis

3.1. Influence of ambient temperature
Weigh an equal amount of PCE-1, store it in a 2000mL food-grade plastic bottle, and put it in an environment of 5, 15, 20, 25, 30, and 35°C under open conditions, observe and record the time of mildew generation (The time from the beginning of the test to the first visual observation of mildew).

| Sample No. | Temperature /°C | Mildew start time /D |
|------------|-----------------|----------------------|
| 1-1        | 5               | 102                  |
| 1-2        | 15              | 70                   |
| 1-3        | 20              | 30                   |
| 1-4        | 25              | 35                   |
| 1-5        | 30              | 36                   |
| 1-6        | 35              | 49                   |

It can be seen from Tab 1 that as the temperature increases, the rate of mildew of Polycarboxylate superplasticizer gradually accelerates. Mildew is most likely to occur when the temperature is 20 ~
After the temperature is higher than 35°C, the rate of mildew begins to decrease. It can be seen that polycarboxylic acid water-reducing agents are more prone to mildew in spring or in areas with more comfortable temperatures in summer.

### 3.2. Influence of different sealing conditions

Weigh equal amounts of PCE-1, PCE-2, PCE-3, PCE-4, and PCE-5, and keep them in a sealed and open room at an indoor temperature of 25±2°C, while ensuring that other experimental conditions are the same. In the experiment, observe the time for the water reducer to produce mildew under different confined conditions. The test results are shown in Tab 2.

| Sample No. | Sample name | Mildew start time /Day | Exposure | Airtight |
|------------|-------------|------------------------|----------|----------|
| 2-1        | PCE-1       | 35                     | 90       |
| 2-2        | PCE-2       | 28                     | 85       |
| 2-3        | PCE-3       | 24                     | 80       |
| 2-4        | PCE-4       | 30                     | 92       |
| 2-5        | PCE-5       | 55                     | 122      |
| 2-6        | PCE-6       | 24                     | 77       |
| 2-7        | PCE-7       | 29                     | 85       |

It can be seen from Tab 2 that these 7 kinds of Polycarboxylate superplasticizers start to mold 53 to 67 days later in the closed state than in the open state. It can be seen that when the water reducer is exposed to the air, it is more prone to mildew, and it should be kept sealed as far as possible without use to reduce the impact of the air on the product.

### 3.3. Effect of acid-ether ratio

Under the condition where the other experimental conditions are the same, the water-reducing agents PCE-1, PCE-2, PCE-3 and PCE-4 are obtained by adjusting the acid-ether ratio, and the effects of different acid-ether ratios on the mildew of water-reducing agent are studied. The results are shown in Tab 3.

| Sample No. | Sample name | Acid-ether ratio | Mildew start time /Day |
|------------|-------------|------------------|------------------------|
| 3-1        | PCE-1       | 4.3              | 35                     |
| 3-2        | PCE-2       | 4.0              | 28                     |
| 3-3        | PCE-3       | 3.7              | 24                     |
| 3-4        | PCE-4       | 3.4              | 30                     |

It can be seen from Tab. 3 that as the acid-to-ether ratio increases, the time for the start of mildew is gradually extended. It can be seen that the higher the acid-to-ether ratio, the less likely to be mildew.

### 3.4. Effect of synthesis reaction temperature

Under the condition that the other test conditions are the same, the water reducing agents PCE-1 and PCE-5 are obtained by adjusting the synthesis reaction temperature, and the effects of different synthesis reaction temperatures on the mildew of water reducing agent are studied. The test results are shown in Tab 4.

| Sample No. | Sample name | temperature reflex /℃ | Mildew start time /Day |
|------------|-------------|------------------------|------------------------|
| 4-1        | PCE-1       | homoeothermy           | 35                     |
| 4-2        | PCE-5       | 63                     | 55                     |
It can be seen from Tab 4 that the polycarboxylic acid water-reducing agent synthesized by the heating process is less prone to mildew than the one synthesized by the normal temperature process. It can be seen that the heating synthesis conditions can kill part of the mold carried in the synthetic raw materials, and can inhibit the product from mildew.

### 3.5. Initiating the impact of the system

Under the condition that the other experimental conditions are the same, the moldy properties of the water reducing agents PCE-1 and PCE-6 synthesized by different initiation systems are compared and studied. The test results are shown in Tab 5.

| Sample No. | Sample name | Priming system                  | Mildew start time /Day |
|------------|-------------|---------------------------------|------------------------|
| 5-1        | PCE-1       | Hydrogen peroxide system        | 35                     |
| 5-2        | PCE-6       | Non-hydrogen peroxide system    | 24                     |
| 5-3        | PCE-7       | Non-hydrogen peroxide system    | 29                     |

It can be seen from Tab 5 that the polycarboxylic acid water reducing agent synthesized by the hydrogen peroxide system is less tolerant to mildew than the non-hydrogen peroxide system, and the synthesis process of the hydrogen peroxide system can suppress the occurrence of mildew.

### 3.6. Effect of sodium gluconate

Make PCE-1 into a 10% solution, mix it with 0%, 1%, 2%, 3% and 4% sodium gluconate respectively and put it in a room with a temperature of 25±2℃ to study the effect of sodium gluconate on mildew of water reducing agent, the test results are shown in Tab 6.

| Sample No. | Sample name | Sodium gluconate dosage /% | Mildew start time /Day |
|------------|-------------|----------------------------|------------------------|
| 6-1        | PCE-1-0     | 0                          | 30                     |
| 6-2        | PCE-1-1     | 1                          | 25                     |
| 6-3        | PCE-1-2     | 2                          | 22                     |
| 6-4        | PCE-1-3     | 3                          | 18                     |
| 6-5        | PCE-1-4     | 4                          | 10                     |

It can be seen from Tab 6 that as the amount of sodium gluconate increases, PCE-1 is more prone to mildew. Introducing sodium gluconate during product compounding will promote the growth of microorganisms and accelerate product deterioration.

### 4. Conclusion

Mildew of Polycarboxylate superplasticizer is closely related to ambient temperature, sealed storage layer, material-to-ether ratio, synthesis reaction temperature, initiation system, etc. In this paper, the following conclusions and suggestions are formed by studying the influencing factors of mildew of Polycarboxylate superplasticizer:

1. With the increase of the ambient temperature, the mold rate of Polycarboxylate superplasticizer accelerates. The temperature is most prone to mold at 20-30℃, and the mold rate begins to decrease after being higher than 35℃.

2. The polycarboxylic acid water-reducing agent should be kept sealed as far as possible when not in use to reduce the influence of air on the product.

3. The higher the acid-ether ratio, the better the effect of inhibiting mildew. The acid-ether ratio can be appropriately increased without affecting the product performance.

4. After increasing the synthesis reaction temperature, the product is less prone to mildew, so under the same cost performance, the heating production process is preferentially used to extend the shelf life of the product.
(5) When adjusting the synthesis process, using hydrogen peroxide as an initiator can play a sterilizing role while ensuring the cost-effectiveness of the product, and it is less prone to mildew.

(6) When mixing sodium gluconate as a retarder during compounding, it is more prone to mildew. Especially in areas or seasons where the temperature is between 20 and 30°C, sodium gluconate should be used less as a retarder.

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