Study on mildew of polycarboxylic acid water reducing agent

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Abstract: In practical applications, polycarboxylic acid water-reducing agents are susceptible to microbial contamination and mildew. Through the mold test on the polycarboxylate water-reducing agent with different storage time, the effect of reaction temperature, chain transfer agent type, solid content, compound components and preservatives on the mildew of the polycarboxylate water-reducing agent is studied. The research results can provide technical guidance for long-term storage of polycarboxylic acid superplasticizer and have important application significance.

1. Introduction
At present, with the development of the concrete industry, polycarboxylic acid water-reducing agents are widely used in many projects. As a high-performance water-reducing agent, polycarboxylic acid water-reducing agents have the advantages of low dosage, high water reduction rate, strong dispersion ability, good workability of concrete, good slump protection performance and so on[1]. However, in practical applications, polycarboxylic acid water-reducing agent products are prone to mildew and deterioration, which reduces the water-reducing rate of polycarboxylic acid water-reducing agent, or even completely loses water-reducing performance[2-3]. In view of this, this article has carried out research on the cause of mildew of polycarboxylic acid water-reducing agent, and provided technical support for the anti-mildew of polycarboxylic acid water-reducing agent.

2. Experimental
2.1. Materials
Polycarboxylic acid water reducing agent (PC, 40% solid content, colorless transparent liquid, KZJ New Materials Group Co., Ltd.; Bit E11 preservative, Shanghai Bit Biological Technology Co., Ltd.; Wanhou HS-AF anticorrosion Agent, Shanghai Wanhou Biological Technology Co., Ltd.

2.2. Mold test
The polycarboxylic acid water-reducing agent under different conditions is put into plastic bottles with caps, but not sealed, and placed outdoors for storage. Mold tests were carry out at 30d, 60d and 90d respectively.

2.3. Mold test
Refer to the detection of the total number of bacteria in water, plate colony counting method GB/T 5750.12-2006, detection conditions: bacteria culture temperature 32±1℃, culture period 48-72 hours; mold yeast culture temperature 28±1℃, culture period 72 hours perform the determination of the number of colonies.
3. Results and discussion

3.1. The influence of reaction temperature on mildew of polycarboxylate water-reducing agent
The same process was used to synthesize under normal temperature and heating, and the influence of reaction temperature on the mildew of the polycarboxylate water-reducing agent was investigated. The mold test results under different storage times are shown in Table 1.

Table 1. The influence of reaction temperature on mildew of PCE

| Sample | Reaction temperature/°C | Storage time/d | Mold test/ (cfu/g) | Bacteria content | Mold content | Yeast content |
|--------|-------------------------|---------------|--------------------|------------------|---------------|---------------|
| PC-1   | 25                      | 30            | <10                | 1.0×102          | <10           | <10           |
| PC-2   | 45                      | 30            | <10                | <10              | <10           | <10           |
| PC-1   | 25                      | 60            | 9.2×102            | 1.4×104          | <10           | <10           |
| PC-2   | 45                      | 60            | <10                | 1.0×102          | <10           | <10           |
| PC-1   | 25                      | 90            | 5.0×10^2           | 1.0×106          | <10           | <10           |
| PC-2   | 45                      | 90            | 6.5×10^3           | <10              | <10           | <10           |

It can be seen from the test results that PC-1 is synthesized at room temperature, and PC-2 is synthesized by heating at elevated temperature. With the extension of storage time, the low reaction temperature of the synthesis process is prone to deterioration, and the main types of microorganisms are bacteria and molds. This is because the lower the synthesis process temperature, the greater the chance of infection of microorganisms during the synthesis process, and the more likely it is to deteriorate during storage. The higher the temperature of the synthesis process, the inactivation of microorganisms will be promoted, and the effect of partial sterilization will be achieved, so that the shelf life of the polycarboxylic acid water-reducing agent will be prolonged.

3.2. Influence of chain transfer agent on mildew of polycarboxylate water-reducing agent
Synthesized by the same process, in which the chain transfer agent used in PC-2 is non-sulfhydryl type, and the chain transfer agent used in PC-3 is sulfhydryl type. The effect of chain transfer agent on the mildew of polycarboxylic acid water-reducing agent is investigated, and the storage time is different. The following mold test results are shown in Table 2.

Table 2. The influence of chain transfer agent on mildew of PCE

| Sample | Chain transfer agent | Storage time/d | Mold test/ (cfu/g) | Bacteria content | Mold content | Yeast content |
|--------|----------------------|---------------|--------------------|------------------|---------------|---------------|
| PC-2   | Non-sulfhydryl type  | 30            | <10                | <10              | <10           | <10           |
| PC-3   | Sulfhydryl type      | 30            | <10                | <10              | <10           | <10           |
| PC-2   | Non-sulfhydryl type  | 30            | <10                | 1.0×10^2         | <10           | <10           |
| PC-3   | Sulfhydryl type      | 30            | <10                | <10              | <10           | <10           |
| PC-2   | Non-sulfhydryl type  | 30            | 5.0×10^2           | 6.5×10^3         | <10           | <10           |
| PC-3   | Sulfhydryl type      | 30            | 10~100             | 9.7×10^2         | <10           | <10           |

It can be seen from the test results that with the extension of storage time, the mother liquor of non-sulfhydryl chain transfer agents is more prone to deterioration. Polycarboxylic acid water reducing agents using sulfhydryl chain transfer agents are compared with products of non-sulfhydryl chain transfer agents. The shelf life will be longer, and the types of microorganisms that spoilage are mainly bacteria and molds. This is because the addition of sulfhydryl chain transfer agent will form a protective film in the upper space of the mother liquor to prevent microorganisms in the air from contacting the polycarboxylic acid product, thereby prolonging the shelf life of the product.

3.3. Influence of solid content on mildew of polycarboxylate water-reducing agent
Dilute the polycarboxylate water-reducer synthesized by PC-3 to 10% solid content, PC-4, and investigate the effect of solid content on the mildew of the polycarboxylate water-reducer. The mold
test results under different storage times are shown table 3.

Table 3. The effect of solid content on mildew of PCE

| Sample | Solid content/\% | Storage time/d | Bacteria content (<10) | Mold content (1.5×10^2) | Yeast content (<10) |
|--------|-----------------|----------------|------------------------|-------------------------|-------------------|
| PC-3   | 40              | 30             | <10                    | <10                     | <10               |
| PC-4   | 10              | 30             | <10                    | 1.5×10^2                | <10               |
| PC-3   | 40              | 60             | <10                    | <10                     | <10               |
| PC-4   | 10              | 60             | 10~100                 | 2.4×10^5                | <10               |
| PC-3   | 40              | 90             | 10~100                 | 9.7×10^2                | <10               |
| PC-4   | 10              | 90             | 5.5×10^3               | 1.1×10^6                | 1.5×10^3          |

It can be seen from the test results that the product with 10% solid content is more prone to spoilage than the product with 40% solid content, and the spoiled sample contains a lot of mold and bacteria. This is because products with low solid content are more likely to infect mold when they come into contact with the air. Conjugation on the surface of the product isolates the product from the air. The surface of the film is prone to infection of bacteria and breeds mold and bacteria. The main components of polycarboxylic acid products are used as nutrients, so that the content of mold and bacteria in each stage of mildew multiplies and expands exponentially.

3.4. Effect of compound components on mildew of polycarboxylate water-reducing agent

Add the air-entraining component sodium dodecyl sulfonate and the retarding component sodium gluconate to PC-4 with a solid content of 10%. The combined water reducer codes are PC-5 and PC-6. To investigate the influence of the compound components on the mildew of the polycarboxylic acid water-reducing agent. The results of the mold test under different storage times are shown in Table 4.

Table 4. Effect of compound components on mildew of PCE

| Sample  | Solid content/% | Storage time/d | Bacteria content (<10) | Mold content (5.5×10^3) | Yeast content (Full) |
|---------|-----------------|----------------|------------------------|-------------------------|---------------------|
| PC-4    | Blank           | 30             | <10                    | 1.5×10^2                | <10                 |
| PC-5    | Sodium Dodecyl  | 30             | <10                    | 4.3×10^3                | 7.8×10^2            |
| PC-6    | Sodium Gluconate| 30             | <10                    | 8.3×10^3                | 1.8×10^3            |
| PC-4    | Blank           | 60             | 10~100                 | 2.4×10^5                | <10                 |
| PC-5    | Sodium Dodecyl  | 60             | 10~100                 | 2.4×10^6                | <10                 |
| PC-6    | Sodium Gluconate| 60             | <10                    | 7.6×10^6                | 2.5×10^4            |
| PC-4    | Blank           | 90             | 5.5×10^3               | 1.1×10^6                | 1.5×10^3            |
| PC-5    | Sodium Dodecyl  | 90             | 5.5×10^3               | Full                    | Full                |
| PC-6    | Sodium Gluconate| 90             | 6.2×10^3               | Full                    | Full                |

It can be seen from the test results that the air-entraining component sodium dodecyl sulfonate and the retarding component sodium gluconate are more prone to deterioration in the polycarboxylate water-reducing agent, and the mold mainly contains yeast and mold. Therefore, if the sodium lauryl sulfonate and or sodium gluconate are added in the compound, the lag period of the growth of yeast and mold will be greatly shortened, and the microorganisms will enter the exponential growth phase, thereby accelerating the deterioration of the polycarboxylic acid water-reducing agent.

3.5. Influence of preservatives on mildew of polycarboxylate water-reducing agent

Add E11 preservative and HS-AF preservative to PC-6 with a solid content of 10%, and investigate the effect of preservatives on the mildew of polycarboxylic acid water-reducing agent. Different
storage. The mold test results under time are shown in Table 5.

Table 5. Effect of preservatives on mildew of PCE

| Preservative | Dosage/% | Storage time/d | Bacteria content | Mold test/ (cfu/g) | Yeast content |
|--------------|----------|----------------|------------------|-------------------|---------------|
| Blank        | 0.1      | 30             | <10              | 8.3×10³           | 1.8×10³       |
| E11          | 0.1      | 30             | <10              | <10               | <10           |
| HS-AF        | 0.1      | 60             | <10              | <10               | <10           |
| Blank        | 0.1      | 90             | 6.2×10³          | Full              | Full          |
| E11          | 0.1      | 90             | 10~100           | <10               | <10           |
| HS-AF        | 0.1      | 90             | 10~100           | 5.6×10³           | <10           |

It can be seen from the test results that the polycarboxylate water-reducing agent without preservatives is more susceptible to mold erosion during storage. This is mainly due to the fact that the polycarboxylate water-reducing agent contains sugar retarding components, which provide mold growth. The nutrients needed. After adding preservatives to the polycarboxylate water-reducing agent, the growth of mold is obviously inhibited, and the antiseptic effect of E11 preservative is better. Therefore, a reasonable choice of high-quality preservatives, taking into account rapid sterilization and long-term bacteriostasis, can ensure that a large number of microorganisms are killed before storage and can be free from microbial contamination during storage.

4. Conclusion
The reaction temperature of the polycarboxylic acid water reducing agent, the type of chain transfer agent used in production, the solid content of the mother liquor, and the compound components can all cause the mildew of the polycarboxylic acid water reducing agent. Therefore, the polycarboxylic acid water reducing agent Anti-mildew measures may include heating process production, the use of sulfhydryl chain transfer agents, the production of mother liquor with high solid content, and the addition of preservatives.

References
[1] Ouyang Xinping, Li Jia, Qiu Xueqing. The development and greening of concrete water reducing agent[J]. World Science and Technology Research and Development, 2006(28): 3036.
[2] Zhao Tingting, Dong Jinlong, Wang Song, etc. Storage stability research and countermeasures of polycarboxylate water reducing agent [J]. Guangzhou Chemical Industry, 2015, 43(12): 100-101.
[3] Ma Baoguo, Li Gaoming, Li Xiangguo, et al. Study on the compound effect of sodium gluconate and polycarboxylic acid water reducer [J]. Journal of Wuhan University of Technology, 2011, 33(1): 52-55.
[4] Peng Jinping, Yu Qian, Guan Hanju, etc. Study on the antibacterial effect of two isothiazole preservatives [J]. Guangzhou Chemical Industry. 2003, 31(1): 34-36.