Synthesis and Application of Aliphatic Superplasticizer by Two-stage Acetone Process

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Abstract: Aliphatic superplasticizer is a kind of admixture that is widely used in concrete. This article proposes a two-stage acetone method based on existing raw materials and technology. An aliphatic superplasticizer with higher water reduction rate and slump retention performance. It has been verified by experiments that compared with the aliphatic superplasticizer collected in the market, it has obvious advantages in the initial water reduction rate and slump retention performance.

1. Introduction
At present, there is a trend of mainly NSF type high-performance superplasticizer in the application of domestic and gradually in-depth research and application of polycarboxylic acid high-performance superplasticizer. However, there are still many problems in the application of various types of high-efficiency superplasticizer: in addition to the high alkali content of the NSF type superplasticizer, the fresh concrete tend to bleeding and segregation, which affect the compressive strength of concrete, Durability issues. Polycarboxylic Superplasticizer has high sensitivity to raw materials and other issues. In contrast, aliphatic superplasticizers have a wide source of raw materials, low prices, small dosages, high water reduction rates, good adaptability to cement, no pollution and the cost performance is better than NSF products and other advantages, and it is becoming more and more popular in society. In order to achieve the purpose of improving product performance, it is necessary to conduct in-depth research on the synthesis process of aliphatic superplasticizer. In response to these problems, the synthesis process of the aliphatic superplasticizer is studied and analyze the synthesis mechanism. This article proposes a two-stage acetone addition process and carried out the synthesis test.

2. Situation Analysis
Analyze the main feeding method and the product performance advantages and disadvantages method 1:
1. Add a metered amount of sulfonating agent (sodium bisulfite, sodium sulfite or sodium metabisulfite) and water into the reaction flask in turn, heat to 30-40°C for 30 minutes.
2. Add acetone, heat the specified temperature and hydrolyze for 30 minutes, stop heating, adjust to the specified pH with caustic soda solution.
3. Slowly add formaldehyde. The initial dripping rate is slow. Pay attention to the temperature of the material in the reaction bottle. After the temperature rises steadily, accelerate the dropping rate. After the formaldehyde is added within the specified time, the material should automatically rise to 80-90°C, then gradually increase the temperature to about 95°C, keep it for about 4h.
4. Stop heating and cool naturally, when the temperature drops to 50-60℃ stop stirring, obtain aliphatic superplasticizer product.[3]

method 2:

1. Add sulfonating agent (sodium bisulfite, sodium sulfite or sodium metabisulfite) and water into the reaction flask, heat to the specified temperature for hydrolyze for 30 minutes, adjust pH with caustic soda solution.
2. Simultaneously add formaldehyde, acetone and sulfonating agent into the beaker and mix at 40°C.
3. After the solid components are dissolved, add the mixture dropwise to the reaction flask within the specified time. Raise the temperature to about 95°C, keep it for 4h, stop heating, cool naturally, and stop stirring when the temperature drops to 50-60°C. Cool to room temperature to obtain an aliphatic superplasticizer product.[4]

Although the aliphatic sulfonate superplasticizer has been produced and used to a certain extent as a new type of cement concrete admixture, this kind of superplasticizer also has its own shortcomings to be solved. For example, the brown-red color of this superplasticizer agent will cause the concrete or mortar to appear red[5]and it will also cause the problem of large loss of concrete slump. In the manufacturing process, the types of raw materials will affect the performance of synthetic products. Further research is needed to improve product performance and application technology.

3. Research content of this project

3.1. experiment synthesis research

Combining the above several dropping methods and analyzing the product performance, the water reducing rate of the aliphatic superplasticizer produced by method 1 is higher than method 2, but the slump retention performance is poor; the slump retention performance of method 2 is better. Combining method 1 and method 2, a newly developed two-step acetone dripping method was developed. The sulfonation temperature is controlled at 75-80°C, the dropping time is 90min, the condensation temperature is 90-95°C, and the condensation time is 60min. Cool to room temperature to obtain aliphatic superplasticizer product.

1. Add measured amounts of sodium metabisulfite, water, and formaldehyde into the erlenmeyer flask. The temperature of the materials in the erlenmeyer flask rises rapidly. Cool the erlenmeyer flask to 32°C, add measured amounts of acetone, and stir for 30min to obtain a mixed solution A.
2. Add measured amounts of sodium sulfite, water and acetone to the reaction flask, control the temperature at 45°C, and stir for 30 minutes;
3. Add the mixed solution A dropwise to the reaction flask at a constant speed. The temperature of the reaction flask will rise rapidly in the early stage. When the temperature rises to 75-80°C, the temperature of the reaction flask will slowly rise through circulating cooling water and the mixed solution A will be added dropwise. The temperature of the materials in the reaction flask is controlled at 90-95°C when the mixed solution A is end of infusion, the condensation time is 60min. Cool to room temperature to obtain aliphatic superplasticizer product.

3.2. Performance verification

The experiment synthetic samples, market-collected samples and similar products of the company has verified by cement paste fluidity and concrete tests.

In order to verify the performance of the process product (B06), the cement paste fluidity and concrete tests were carried out with our company's similar product B01 and the aliphatic superplasticizer samples collected in the market. The homogeneity test was carried out on B06 samples, B01 samples and samples of aliphatic superplasticizer collected from the market. The solid content of the sample is mainly tested according to the national standard GB/T 8077-2016"Test Method for Homogeneity of Concrete Admixtures". The test results of the sample solid content are listed in Table 1.
Table 1. Aliphatic superplasticizer solid content test

| Sample       | Collect sample 1 | Collect sample 2 | B06 |
|--------------|------------------|------------------|-----|
| Solid content/% | 36.5             | 34.5             | 37.0| 34.5 |

The fluidity test of cement paste was conducted on B06 sample, B01 sample and market collected sample, according to the national standard GB/T 8077-2016 "Test Method for Homogeneity of Concrete Admixtures". The specific data on the cement paste fluidity test is shown in Table 2.

Table 2. Fluidity test of cement paste

| Sample type | Dosage/g | Cement paste initial fluidity/mm | Cement paste 60min fluidity/mm |
|-------------|----------|----------------------------------|---------------------------------|
| B06         | 5.10     | 225                              | 182                             |
| B01         | 4.60     | 223                              | 199                             |
| sample 1    | 5.40     | 221                              | 188                             |
| sample 2    | 5.10     | 228                              | 171                             |

From the data in Table 1 and table 2, it can be seen that the slump retention performance of this product is better than the similar products and market samples under the same initial water reduction rate. On the premise of ensuring the same performance of concrete, the dosage of this product is obviously lower than that of other products. It shows that the product has higher water reduction rate and slump retention performance.

The concrete test of the invention sample is carried out according to the operation method specified in the national standard GB / T 50080-2016 “standard for performance test methods of ordinary concrete mixture”, the specific comparative data are shown in Table 3.

Table 3. Water-reducing agent concrete test (grade strength C30)

| Type of superplasticizer | Dosage/g | Concrete slump/mm | Compressive strength/MPa |
|--------------------------|----------|--------------------|--------------------------|
|                          |          | Initial slump /expansion | 40min slump /expansion | 7d  | 28d |
| B06                      | 64       | 220/580            | 210/560                  | 24.56 | 35.33 |
| B01                      | 70       | 220/590            | 210/480                  | 24.02 | 35.01 |
| sample 1                 | 74       | 220/580            | 205/500                  | 24.86 | 35.88 |
| sample 2                 | 70       | 220/600            | 210/430                  | 24.03 | 36.06 |

It can be seen from Table 3 that under the condition of ensuring the same initial fluidity of concrete, the concrete slump retention performance of this product is better than similar products of the company and the samples collected in the market; the solid content of this product is significantly lower than that of similar products and samples collected in the market, but the amount of superplasticizer is significantly lower than the other products. Which is consistent with the results of the cement paste fluidity test. Through the product cost calculation, the production cost of this product is equivalent to the production cost of the company's similar products, but it shows a higher water reduction rate and slump retention performance, showing a higher product cost-effectiveness.

Compare the impact of this superplasticizer with the company's similar products and market samples on the compressive strength of concrete. Through the 7d and 28d compressive strength tests of concrete test blocks, the strength of this product test block is equivalent to that of other product concrete test blocks. The aliphatic superplasticizer of this product has no adverse effect on the strength of the test block.
4. Performance characterization

4.1. GPC Analysis
Molecular weight and its distribution are important parameters that affect the performance of aliphatic superplasticizer [6,7]. The molecular weight and distribution of samples of the aliphatic superplasticizer synthesized in the laboratory and the company's similar products were determined by GPC method, as shown in Figure 1 and Figure 2, respectively.

![Figure 1. GPC analysis of aliphatic superplasticizer for this project (B06)](image1)

![Figure 2. GPC analysis of similar aliphatic superplasticizer products (B01)](image2)

According to the data of GPC analysis, the main molecular weight peak of B01 is concentrated at 3340; the main molecular weight peak of B06 is concentrated at 3450; but the aliphatic water-reducing agent shows different water reduction rates and slump retention performance, which may be due to the fact that if the molecular weight of B01 is too small or too short, it will affect the water retention and seepage of concrete. Increasing the molecular weight of the aliphatic superplasticizer, the dispersion effect and the slump retention performance are all improved, and the content of macromolecules in the polymer helps to improve the dispersion performance of the aliphatic superplasticizer. According to the theory of the relationship between relative molecular weight and surfactant performance, it is consistent with Chen Jiankui's proposal that the relative molecular weight suitable for superplasticizers is 1500~10000.[7]

4.2. IR Analysis
In order to determine the functional groups contained in the aliphatic superplasticizer, the synthesized aliphatic superplasticizer sample was precipitated with ethanol, filtered, dried and compressed with
KBr, and then analyzed with an infrared spectrometer. The infrared spectra of the aliphatic superplasticizer (B06 and B01) are shown in Figure 3.

![Figure 3. IR analysis of project products(B06) and similar products(B01)](image-url)

It can be seen from the infrared spectrogram of Figure 3 that the infrared spectra of the aliphatic superplasticizer samples are relatively similar, but the peak intensity is slightly different, and the overall difference is not big; the peak of Stretching vibration absorption are about 3450cm⁻¹ of the hydroxyl group. The peak around 2930 cm⁻¹ is the (-CH) stretching vibration absorption peak on the aliphatic molecular chain. The peaks around 2850cm⁻¹ and 2860cm⁻¹ are the stretching vibration peak of -CH₃. The peak around about 1643cm⁻¹ is the carbonyl stretching vibration absorption peak. The peaks around 1450cm⁻¹ and 1410cm⁻¹ are the flexural vibration absorption peaks of alkyl (-CH). The peaks around 1185cm⁻¹ and 1045cm⁻¹ are the stretching vibration peak of the alkyl sulfonic acid salt (-SO₃); in summary, the functional group structure of the two samples is consistent, so it is speculated that the two samples are the same kind aliphatic superplasticizer.

5. conclusion

By adopting the two-step acetone dripping method, the obtained aliphatic superplasticizer has a higher water reduction rate and better slump retention performance than the existing aliphatic superplasticizer production process.

Through infrared spectroscopy and GPC analysis of synthetic samples, the synthetic samples of this method have the same functional groups as the aliphatic superplasticizer on the market, they are all polymer compounds containing hydrophilic groups (such as hydroxyl, carbonyl and sulfonic acid groups). Through GPC analysis, the molecular weight distribution is basically the same, the molecular weight is basically 3500–4000, which basically conforms to Chen Jiankui's theory.

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