Study on Preparation of Low Sensitive and Stable Type Polycarboxylate Superplasticizer Small Monomers

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Abstract. Acrylic acid and p-hydroxybenzenesulfonic acid were esterified with ethyl sulfonic acid as catalyst and hydroquinone as inhibitor for 3 hours at 90°C. Low sensitive and stable type polycarboxylate superplasticizer small monomers (P1) with double-layer dispersion structure was obtained after esterification. A low sensitive and stable type polycarboxylate superplasticizer (P-WD) can be obtained by using P1. The experimental results show that the synthesized P-WD has better adaptability to cement than PCE without P1, and better control of the time-dependent fluidity of cement paste.

1. Introduction
Polycarboxylate superplasticizer has been applied in high-speed railway, hydropower, nuclear power and other key national projects since 2006 because of its excellent performance, energy saving, environmental protection and good durability of concrete[1-3]. However, with the shortage of resources and the increasing demand for concrete performance, the application of polycarboxylate superplasticizer in the promotion process also often has the problems of insufficient slump-retaining effect and too sensitive to materials[4-7]. Therefore, it is of great significance to develop low sensitive and stable type polycarboxylate superplasticizer with excellent slump retention and insensitive to cement changes. In this paper, unsaturated monomers (P1) with double-layer dispersion structure were synthesized by esterification of acrylic acid with p-hydroxybenzenesulfonic acid. And then, a low sensitive and stable type polycarboxylate superplasticizer (P-WD) was prepared by copolymerization of P1 with acrylic acid and 4-hydroxybutyl vinyl polyoxyvinyl ether.

2. Experimental
2.1. Materials
2.1.1. The main synthetic experimental raw materials. 4-hydroxybutyl vinyl polyoxyvinyl ether (VPEG), industrial grade; Acrylic acid (AA), industrial grade; p-hydroxybenzenesulfonic acid (PHSA), industrial grade; p-toluene sulfonic acid (PTSA), industrial grade; sulphuric acid (H2SO4), industrial grade; benzenesulfonic acid (BSA), industrial grade; ethanesulfonic acid (ESA), industrial grade; hydroquinone (HQ), industrial grade; ferrous sulfate (FeSO4), industrial grade; 3-mercaptopropionic acid (MPA), industrial grade; Hydrogen peroxide (H2O2), industrial grade; Sodium formaldehyde sulfonate dihydrate (SFD), industrial grade; Sodium hydroxide (NaOH), 30% aqueous solution, industrial grade.
2.1.2. Main performance test raw materials for experiment. Cement(C1): Hai Luo P.O 42.5 Cement; Cement(C2): Min Fu P.O 42.5 Cement; Cement(C3): Hong Shi P.O 42.5 Cement.

2.2 Esterification
The esterification product P1 was obtained by adding metered AA, PHSA and HQ into the reactor, opening the nitrogen-opening device, heating up to 50°C, adding metered PTSA, slowly heating up to the reaction temperature, constant temperature for a certain time, and cooling down.

2.3 Copolymerization
Metered water and VPEG were added to the reactor, heated and stirred until VPEG was dissolved. After the system temperature reached 30°C, P1, AA, H₂O₂, SFD, FeSO₄ and MPA were added to the reactor respectively. The dropping was controlled within 1 h, then the constant temperature was 1 h, and the pH value was adjusted to 6.0-7.0 by adding 30% sodium hydroxide, and then P-WD was obtained.

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2.4. Performance test method
2.4.1. Cement paste fluidity determination. Cement paste fluidity according to GB/T8077-2012 "Concrete admixture homogeneity test method" was carried out, W/C was 0.29.

2.4.2. Esterification rate test. The acid value before and after esterification was tested by acid-base titration, and the esterification rate was calculated according to the change of acid value.

2.4.3. Double bond retention rate test. The double bond values before and after esterification were measured by iodine value method, and the retention rate of double bond was calculated according to the change of double bond values[8].

3. Experimental results and discussion
3.1. Effect of esterification catalyst types on esterification rate
The amount of fixed esterification catalyst is 1.0% of the total mass of acrylic acid and p-hydroxybenzenesulfonic acid. Other experimental conditions are the same. The effects of different kinds of esterification catalysts on the esterification rate are studied. The experimental results are shown in Table 1.

| Esterification catalyst type   | Esterification rate(%) |
|-------------------------------|------------------------|
| Blank                         | 68                     |
| Sulfuric acid                 | 88                     |
| p-Toluene sulfonic acid       | 87                     |
| Benzenesulfonic acid          | 85                     |
| Ethanesulfonic acid           | 93                     |

From the experimental results in Table 1, it can be seen that the esterification rate of the product obtained by using ethyl sulfonic acid as esterification catalyst is the highest, so ethyl sulfonic acid is chosen as esterification catalyst for this reaction.
3.2. Effect of the dosage of inhibitor on the retention rate of double bond
Fixed other experimental conditions unchanged, adjusted the amount of inhibitor used in esterification reaction (the amount of inhibitor is expressed as a percentage of the total mass of acrylic acid and p-hydroxybenzenesulfonic acid), the effect of the amount of inhibitor on the retention rate of double bonds was studied. The experimental results are shown in Figure 1.

As shown in Figure 1, with the increase of inhibitor dosage, the double bond retention rate of esterification products increases gradually and then tends to be stable. This is because the inhibitor can prevent the copolymerization of acrylic acid when heated and protect its double bond. Therefore, the addition of the inhibitor is conducive to improving the double bond retention rate. When the dosage of the inhibitor is 0.4%, the dosage of the inhibitor is enough to keep the double bond retention rate in a relatively high range. Continuing to increase the dosage of the inhibitor does not contribute significantly to the improvement of the double bond retention rate. Moreover, too much of the inhibitor will affect the subsequent copolymerization, so choose the dosage of the inhibitor is 0.4%.

3.3. Effect of esterification temperature on esterification rate and double bond retention rate
Fixed other experimental conditions unchanged, adjusted the esterification reaction temperature, the effect of esterification reaction temperature on the esterification rate and double bond retention rate was studied. The experimental results are shown in Figure 2.

As shown in Figure 2, with the increase of esterification temperature, the esterification rate increases and the double bond retention rate decreases. This is mainly because the higher the reaction temperature, the easier the water in the system is to be separated, and the more conducive to improving the esterification rate. However, the higher the esterification temperature is, the easier the
double bond of acrylic acid will be reacted, and the double bond retention rate will gradually decrease. Therefore, considering the two factors of esterification rate and double bond retention rate, it is appropriate to choose the esterification reaction temperature of 90°C.

3.4. Effect of esterification time on esterification rate and double bond retention rate

Fixed other experimental conditions unchanged, adjusted the esterification reaction time, and studied the effect of esterification reaction time on the esterification rate and double bond retention rate. The experimental results are shown in Figure 3.

As shown in Figure 3, with the extension of esterification time, the esterification rate increases and the double bond retention rate of decreases. This is mainly because the longer the reaction time, the more water brought out by nitrogen, the more conducive to improving the esterification rate. However, the longer the esterification time is, the easier the double bond of acrylic acid will be reacted, and the double bond retention rate of will gradually decrease. Therefore, considering the two factors of esterification rate and double bond retention rate, it is appropriate to choose the esterification reaction time of 3 hours.

3.5. Performance test of low sensitive and stable type polycarboxylate superplasticizer synthesized by P1

The preparation conditions of P1 were as follows: the esterification catalyst was ethyl sulfonic acid, the dosage of which was 1.0% of the total mass of acrylic acid and \( p \)-hydroxybenzenesulfonic acid, and the inhibitor was hydroquinone, and the dosage of which was 0.4% of the total mass of acrylic acid and \( p \)-hydroxybenzenesulfonic acid. the reaction temperature was 90°C, the reaction time was 3 h, and the molar ratio of acrylic acid to \( p \)-hydroxybenzenesulfonic acid was 4:1. The low sensitive and stable type polycarboxylate superplasticizer P-WD was synthesized by copolymerization of P1 and VPEG. The PCE was synthesized by copolymerization of acrylic acid and VPEG under the same conditions. Hai Luo cement, Min Fu cement and Hong Shi cement were used to test the fluidity of cement paste mixed with P-WD and PCE to characterize the properties of low sensitive and stable type polycarboxylate superplasticizer P-WD synthesized by P1. The test results are shown in Table 2.

| Cement  | Polycarboxylate superplasticizer | Dosage/% | Cement paste fluidity /mm |
|---------|----------------------------------|----------|--------------------------|
|         |                                  | 0h       | 0.5h         | 1h         | 1.5h       | 2h         | 3h         |
| C1      | PCE                              | 0.15     | 242          | 221        | 189        | 131        | -a         | -a         |
| C2      | P-WD                             | 0.15     | 253          | 248        | 243        | 236        | 225        | 201        |
| C3      | PCE                              | 0.15     | 252          | 227        | 193        | 142        | -a         | -a         |
|         | P-WD                             | 0.15     | 257          | 252        | 247        | 238        | 227        | 206        |
|         | PCE                              | 0.15     | 218          | 197        | 162        | 118        | -a         | -a         |
|         | P-WD                             | 0.15     | 243          | 245        | 238        | 232        | 220        | 198        |

*a"**" means that the fluidity of the slurry is too small to be measured.
As shown in Table 2, when PCE and P-WD are used for Hai Luo cement, Min Fu cement and Hong Shi cement, respectively, PCE initially has good dispersion effect. However, with the time going on, because of the gradual consumption of water reducer molecules in PCE, the loss of fluidity is obvious, and no net cement paste fluidity can be measured by 2h. The initial dispersion effect of P-WD is slightly better than that of PCE, and the change of the net cement paste fluidity within 3 hours is obviously smaller than that of PCE, which indicates that the control of P-WD on the cement paste fluidity is more stable. Compared with the data of the same polycarboxylate superplasticizer used in different cement, the change of the fluidity of P-WD in different cement is smaller than that of PCE, which shows that P-WD is less sensitive to the change of cement and more stable to the control of the fluidity of cement paste.

4. Conclusions

(1) Compared with other esterification catalysts, ethyl sulfonic acid has a better effect on this esterification reaction, making the esterification rate of the product the highest.

(2) With the increase of the amount of inhibitor, the retention of double bonds of esterification products increased gradually and then stabilized. Considering that too much inhibitor would affect the subsequent copolymerization, the dosage of the inhibitor of 0.4% is more appropriate.

(3) With the increase of esterification temperature, the esterification rate increases and the double bond retention rate decreases. Therefore, considering the two factors of esterification rate and double bond retention rate, the esterification temperature of 90°C is more appropriate.

(4) With the extension of esterification time, the esterification rate increased and the double bond retention rate decreased. Therefore, considering the two factors of esterification rate and double bond retention rate, the esterification time of 3h is more appropriate.

(5) Compared with PCE synthesized without P1, the initial water reducing rate of P-WD synthesized with P1 is higher, the control of cement paste fluidity is more stable, and it is less sensitive to the change of cement.

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