Research on the Effect of Different Esters on the Synthesis of Polycarboxylate Superplasticizer at Low Content

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Abstract. This article uses three ester monomers, hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate (HEA), and hydroxypropyl acrylate (HPA), mixed with 2% of the mass of the macromonomer to synthesize Polycarboxylate Superplasticizer (PCE), compared with the blank sample without esters. The GPC technology was used to investigate the influence of different ester monomers on the molecular weight and distribution of PCE and the polymer yield at low dosages. The cement paste and concrete tests were carried out for testing the performance of PCE. Experiments proves that HEMA affects initial dispersion performance at low dosage. The article concludes that HEA and HPA indeed played a slow-release effect at low content.

1. Introduction
Polycarboxylates high performance water-reducing admixture is widely used in the field of construction engineering because of its high water reduction rate and good slump performance[1-3]. In actual production applications, Polyether monomer and unsaturated ester monomers are usually used to copolymerize to form a slow-release polycarboxylic acid water-reducing agent, which maintains the working performance of concrete through ester group hydrolysis in an alkaline environment.

At present, the content of unsaturated ester monomers in the slow-release polycarboxylate water-reducer process is about 10%-15% of the mass of the monomer. Studies have shown that the slow-release polycarboxylate water-reducer can avoid concrete the strong adsorption of stone powder and soil at the initial stage of mixing effectively keeps the concrete in a stable working state[4,5].

In this experiment, three esters of 2% of the mass of the monomer will be added to the high performance water-reducing admixture with an acid-to-ether ratio of 5.0. Through molecular characterization and application research, the effect of these three esters on polycarboxylate water-reducer products at low content is obtained.

2. Experiment
2.1. Raw materials and equipment
Synthetic raw materials: Methacrylate (HPEG), industrial grade; Acrylic acid (AA), industrial grade; Hydroxyethyl methacrylate (HEMA), industrial grade; Hydroxyethyl acrylate (HEA), industrial grade; Hydroxypropyl acrylate (HPA), industrial grade; Sodium hypophosphate (SH), industrial grade; Hydrogen peroxide, industrial grade; Vitamin C (VC), industrial grade; Sodium hydroxide (NaOH), 30%, industrial grade; Deionized water, self made.
Instruments: Peristaltic pump (BT100-2J type); Constant temperature water bath (HH-1 type); Electric stirrer (JJ-1 type); Electronic balance (JJ1000Y type).

2.2. Synthetic sample
First, prepare an aqueous solution of VC as A solution, and prepare an aqueous solution of three esters and AA as B solution. Second, add deionized water and HPEG to a 1000 mL flask, and stir to dissolve at elevated temperature, add SH and Hydrogen peroxide to the bottle. Third, when the temperature rises to 40℃, drop A solution and B solution into the bottle respectively.
A solution was added for 3.5h, B solution was added for 3h, and then kept at constant temperature for 1h. Add sodium hydroxide to adjust its pH to 6.0-7.0, and finally get the product.

2.3. performance evaluation
Performance test raw materials: Cement: Tianya P·O42.5; Sand: Standard sand.
Cement paste evaluation: Performance evaluation according to GB/T 8077-2012 "Methods for testing uniformity of concrete admixture";
Concrete evaluation: Performance evaluation according to GB/T 50080-2011 "Standard for test method of Performance on ordinary fresh concrete".

2.4. Sample characterization
GPC analysis: Using American Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector and Breeze software system. The column is composed of Ultra-hydragel™250 and Ultra-hydragel™500 in series. At the same time, the mobile phase is 0.1mol/L sodium nitrate aqueous solution (containing 0.05% sodium azide). The flow rate is 0.8 mL/min; the injection volume is 200μL; the oven temperature is 40 ℃; the internal temperature of the differential indicator is 40 ℃.

3. Results and discussion

3.1. GPC analysis results
Perform two GPC tests on blank samples and HEMA, HMA and HPA with 2% of the mass of monomers, take the arithmetic average of the test results. The molecular mass of the water-reducer and its distribution, and the polymer yield are shown in Table 1.

| sample  | Mn   | Mw   | MP   | D  | %Yield |
|---------|------|------|------|----|--------|
| Blank   | 30355| 58019| 45519| 1.90| 93.66  |
| HMA     | 29420| 52541| 43313| 1.79| 89.70  |
| HPA     | 30120| 52508| 43531| 1.74| 87.83  |
| HEMA    | 31169| 59117| 45911| 1.90| 86.80  |

It can be seen from Table 1 that the molecular weight of the two acrylates is smaller than the blank sample, while the molecular weight of the hydroxyethyl methacrylate is slightly larger than that of the blank sample, and the D value is the largest. This may be because the steric hindrance of HEMA and the electron-withdrawing effect of methyl groups increase the reactivity, which leads to a larger molecular weight of the polycarboxylic acid water reducer. Compared with the blank sample, the polymer yield is significantly reduced after adding esters, indicating that the addition of esters will also change the reactivity rate of the entire reaction system at low dosages, resulting in incomplete monomer reaction.

3.2. Test of fluidity and loss of cement paste over time
The fluidity of the cement paste was tested three times on the four samples, and the arithmetic average of the test results was taken, and the experimental results as shown in Figure 1 were obtained.

It can be seen from Figure 1 that at the same dosage, the initial dispersion performance of the HEMA sample is better than that of the blank sample. The initial dispersion of HEA and HPA is worse than the blank sample, indicating the molecular weight of the HEMA synthesized sample is large, strong steric hindrance, so the net slurry dispersion effect is better. At 30 min, the loss of the mother liquor synthesized with the three esters is equivalent to that of the blank sample. After 60 min, it can be clearly seen that the loss of the three samples using esters is smaller than that of the blank sample. Under the dosage, the ester group can still make up for the loss of cement paste fluidity through ester group hydrolysis, but the degree of compensation is small.

![Figure 1. Cement paste fluidity and loss over time](image)

3.3. Concrete test results
Carry out three concrete evaluations respectively, and take the arithmetic average of the test results. The concrete mix ratio is as follows: m (cement): m (sand): m (stone): m (water) = 340: 920: 920: 170. The experimental conditions are the same, and no slump retention and retarding components are added. The test results are shown in Figure 2.

![Figure 2. Concrete test results](image)

It can be seen from Figure 2 that the initial slump results of the blended esters are consistent with the pure slurry results. The initial slump of HEA and HPA samples is smaller than that of the blank sample. This is because the molecular weight is small and the initial steric hindrance is small, so the dispersion performance of the product is poor. It shows that at low dosage, the influence of esters on the structure of polycarboxylic acid water reducer is also obvious. From the point of view of loss, combined with the GPC results, HEMA samples have the highest low-dispersibility, fewer low molecular weight parts, the lowest yield, incomplete monomer reaction, and reduced active ingredients,
resulting in the largest loss of slump of HEMA samples. The low dispersion of HEA and HPA is less than that of the blank sample, but the slump retention ability in the later stage is better, indicating that the ester group has a hydrolysis reaction in an alkaline environment at a low content.

4. Conclusion

(1) The addition of 2% low-volume esters to the high-performance polycarboxylic acid water-reducing agent has a significant impact on the molecular mass and its distribution. Among them, HEMA has the greatest impact.

(2) For the initial fluidity, it can be proved from the results of the pure paste and the concrete that, at a low content, the addition of HEMA can significantly improve the initial dispersion performance, followed by HPA, and HEA is the worst.

(3) At low content, it can be seen from the results of concrete that HEA and HPA have a significant improvement in the later retention ability.

(4) Through the above research, it can be proved that the low dosage of different esters in the high-performance polycarboxylic acid water reducer can indeed have a certain impact on the performance of the product. In actual production applications, you can choose to incorporate HEMA to significantly improve the dispersion performance. In actual production applications, the required product performance can be obtained through reasonable molecular design results. The dispersion performance should be improved.

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