Preparation and study of chemical functional materials for wet mixed mortar

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Abstract. The wet mixed mortar chemical functional material PC-2 was synthesized by monomers including 4-hydroxybutyl vinyl ether polyoxyethylene ether, acrylic acid, 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate. The effects of different side chain lengths, the dosage of 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate on the properties of wet-mixed mortar chemical functional materials were investigated. It had been verified by test that compared with PC-1, PC-2 could effectively reduce the consistency loss rate of wet mixed mortar, improved the water retention rate of wet mixed mortar, the tensile bond strength of 14d and the compressive strength of 7d and 28d. In the process of pumping and spraying construction, PC-2 had better performance and could meet the requirement of continuous supply.

1. Introduction

With the acceleration of urban development, the number of urban municipal infrastructure and housing will increase significantly, and building energy consumption has occupied a considerable part of the overall energy consumption. As a large building material second only to wall materials and concrete, construction mortar is used in quantities of hundreds of millions of tons per year. Therefore, the promotion of wet mixed mortar as a green building material is imperative[1,2].

The wet mixed mortar has the same timeliness as the commercial concrete. It needs to be used up within a certain period of time after the completion of the mixing, and the mortar construction process is generally long. This requires measures to ensure the application performance of the wet mixed mortar and an admixture is needed to extend the age of use. The chemical function material of the premixed wet mortar can be said to be the key to the premixed mortar, which mainly plays the role of water reduction, thickening, water retention and retardation. At present, there are few researches and applications on the chemical functional materials of premixed wet mortar. The existing mortar admixtures have low performance and uneven levels, and their development lags far behind concrete water reducers[3,4]. The traditional wet mixed mortar construction operation time is short and the performance loss is fast, which restricts its rapid development[5]. In order to prolong the working time of the commercial wet mixed mortar, a common method is to add a retarder having excellent performance or a method of protecting the raw material as a basic raw material. Therefore, a wet-mixing chemical functional material with good workability, strong work performance retention and long working time has been developed, which has considerable practical value and economic significance.
In this paper, 4-hydroxybutyl vinyl ether polyoxyethylene ether, acrylic acid, 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate were used to synthesize wet-mix mortar chemical functional materials. The effects of different side chain lengths, the dosage of 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate on the properties of wet-mixed mortar chemical functional materials were investigated. By introducing a mono-2-(methacryloyloxy)ethyl succinate, the flexibility of spatial conformation can be increased, the curl of molecular chain can be increased, and a new releasing mechanism of stable plastics groups can be created, which is conducive to reducing the loss rate of consistency of wet-mixed mortar and improving the water retention rate and the compressive strength of 28d of wet-mixed mortar.

2. Experimental

2.1 Materials

2.1.1. The main synthetic experimental raw materials
4-hydroxybutyl vinyl ether polyoxyethylene ether (The relative molecular masses are 600,1200, 2400, 3000,4000),4-vinylbenzenesulfonic acid, mono-2-(methacryloyloxy)ethyl succinate, potassium persulfate, sodium hypophosphite, sodium hydrogen sulfite, dodecyl mercaptan, Sodium hydroxide (32% aqueous solution): industrial grade.

2.1.2. Main performance test raw materials for experiment
An ordinary Portland cement (C) (42.5, Mingfu Cement Co., Ltd.), Sand (S, fineness modulus of 3.1), Fly ash(F, Level II), Tap water (W), Wet mixed mortar admixture(PC-1, Imported commercial products).

2.2. Copolymerization
Add the weighed polyether macromonomer and water into a four-mouth bottle equipped with a stirrer. After dissolving, potassium persulfate and sodium hypophosphite were added into a four-mouth bottle. Under normal temperature conditions, a mixed aqueous solution of acrylic acid, 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate, and an aqueous solution of dodecyl mercaptan were added dropwise, and the dropping time was 2.5 h. After constant temperature reaction for 0.5 h, a 32% sodium hydroxide was added to obtain a wet mixed mortar chemical functional material PC-1.

2.3. Performance test method

2.3.1. Wet mixed mortar performance test
The consistency, consistency loss rate, water retention rate, setting time, compressive strength, and tensile bond strength of wet mixed mortar were measured according to JGJ/T 70-2009 "Test Methods for Basic Performance of Building Mortar". The wet mix mortar as shown in Table 1 (In addition to the engineering application research mix ratio, the performance verification of other wet mixed mortars was based on the above mix ratio.).

| W (kg/m³) | C (kg/m³) | S (kg/m³) | F (kg/m³) |
|-----------|-----------|-----------|-----------|
| 230       | 230       | 1350      | 80        |

2.4 Test methods

2.4.1 Hydration heat.
The hydration heat test was used to measure the hydrothermal curve of cement hydration by TAM-air micro-calorimeter (Thermometric AB, Sweden). The W/C ratio of the cement paste was fixed at 0.35, the heat release rate of cement within 72h was recorded.

2.4.2 Scanning electron microscopy.
When the sample was hydrated to each age, it was taken out and the hydration was terminated with absolute ethanol. Fragmented 3–6nm flakes, placed in a vacuum drying oven, adjusted to a temperature of 40℃, dried to constant weight. The sample was taken out and adhered to a copper sample holder with a conductive paste. After vacuum gold plating, a scanning electron microscope (COXEM-20 type manufactured by Korea) was used to observe the microscopic morphology of the sample.

3. Experimental results and discussion

3.1 Influence of different side chain lengths on the properties of wet mixed mortar chemical functional materials
Reaction conditions: according to n (acrylic acid): n (4-hydroxybutyl vinyl ether polyoxyethylene ether) = 2.5: 1, The amount of 4-vinylbenzenesulfonic acid and mono-2-(methacryloyloxy)ethyl succinate was 0.8% and 2% of the total mass of the polyether macromonomer, potassium persulfate, sodium hypophosphate and tert-dodecyl mercaptan were respectively 1.0%, 1.5% and 1.0% of the total mass of the polyether macromonomer. The effects of different side chain lengths on the properties of wet mixed mortar chemical functional materials were investigated. The test results are shown in Table 2.

| Molecular Weight of 4-Hydroxybutyl Vinyl Ether Polyoxyethylene Ether | A/g | 0h consistency /mm | 4h consistency /mm | Consistency loss rate /% |
|---|---|---|---|---|
| 600 | 3.15 | 90 | 42 | 53.3 |
| 1200 | 2.89 | 88 | 43 | 51.1 |
| 2400 | 2.62 | 92 | 50 | 45.7 |
| 3000 | 2.58 | 89 | 51 | 42.7 |
| 4000 | 2.43 | 93 | 56 | 39.7 |

As shown in Table 2, as the length of the side chain increases, the consistency loss rate gradually decreases. Mainly because of the increase in side chain length, the steric hindrance of the side chain of the wet mixed mortar chemical functional material is enhanced, and the cement particles have a good dispersion effect, which shows that the consistency loss rate is small. Therefore, 4-hydroxybutyl vinyl ether polyoxyethylene ether with a molecular weight of 4000 was selected.

3.2 Influence of the Amount of 4-Vinylbenzenesulfonic Acid on the properties of wet mixed mortar chemical functional materials
Reaction conditions: The other conditions were unchanged. The molecular weight of 4-hydroxybutyl vinyl ether polyoxyethylene ether was 4000. The effect of the amount of 4-vinylbenzenesulfonic acid on the properties of the wet functional mortar was investigated. The test results are shown in Table 3.

| 4-vinylbenzenesulfonic acid dosage% | A/g | 0h consistency /mm | 4h consistency /mm | Consistency loss rate /% |
|---|---|---|---|---|
| 0.8 | 2.43 | 93 | 56 | 39.7 |
| 1.2 | 2.05 | 92 | 61 | 33.7 |
| 1.6 | 1.88 | 92 | 71 | 22.8 |
| 2 | 1.96 | 91 | 64 | 29.6 |
| 2.4 | 2.15 | 93 | 60 | 35.4 |
As shown in Table 3, under the same initial consistency, with the increase of the amount of 4-vinylbenzenesulfonic acid, the blending amount of wet-mixed mortar chemical functional materials first decreased and then increased, and the consistency loss rate trend was the same. When the amount was too large, the larger the amount of wet-mixed mortar chemical functional materials could reach the same initial performance mainly because the amount of 4-vinylbenzenesulfonic acid increased, and the chemical chain of wet chemical mortar was in the molecular chain. The majority of the 4-vinylbenzenesulfonic acid structure lead to a decrease in the side chain structure of 4-hydroxybutyl vinyl ether polyoxyethylene ether, thereby weakening the steric hindrance. Therefore, the optimum amount of 4-vinylbenzenesulfonic acid was 1.6%.

3.3 Influence of the Amount of mono-2-(methacryloyloxy)ethyl succinate on the properties of wet mixed mortar chemical functional materials

Reaction conditions: The other conditions were unchanged, the optimum amount of 4-vinylbenzenesulfonic acid is 1.6%. The effect of the amount of mono-2-(methacryloyloxy)ethyl succinate on the properties of the wet functional mortar was investigated. The test results are shown in Table 4.

| mono-2-(methacryloyloxy)ethyl succinate dosage/% | A/g | 0h consistency/mm | 4h consistency/mm | Consistency loss rate/% |
|-----------------------------------------------|-----|-------------------|-------------------|------------------------|
| 2                                             | 1.88| 92                | 71                | 22.8                   |
| 2.5                                           | 1.76| 95                | 80                | 15.8                   |
| 3                                             | 1.55| 96                | 85                | 11.5                   |
| 3.5                                           | 1.72| 90                | 80                | 11.1                   |
| 4                                             | 2.12| 95                | 86                | 11.1                   |

As shown in Table 4, with the increase of the amount of mono-2-(methacryloyloxy)ethyl succinate, the amount of chemically mixed materials of wet mixed mortar first decreased and then increased, and the consistency loss rate gradually decreased and then tend to balance. Mainly because when the amount of mono-2-(methacryloyloxy)ethyl succinate was too small, the number of small molecular monomers between adjacent macromonomers was too small, the side chain density was too large, and there was steric hindrance during adsorption, so that the adsorption capacity of the wet mixed mortar chemical functional material on the surface of the cement particle was insufficient. Therefore, a higher amount of wet mixed mortar chemical functional materials was required to achieve comparable performance. When the amount of mono-2-(methacryloyloxy)ethyl succinate was too large, the density of the side chain of the polymer decreased, and the molecules of the wet-mixed mortar chemical functional material adsorbed on the surface of the cement particle could not obtain a good steric hindrance effect, thereby causing a decrease in performance. As the amount of mono-2-(methacryloyloxy)ethyl succinate increased, the loss of consistency decreased gradually, mainly because with the increase of the amount of mono-2-(methacryloyloxy)ethyl succinate, the molecular chain had more ester groups. Under alkaline conditions of the cement, the ester group was continuously hydrolyzed to release a carboxylic acid group that act on water reduction, thereby reducing the rate of consistency loss. Therefore, the overall use of mono-2-(methacryloyloxy)ethyl succinate was 3%.

4. Hydration heat analysis

The best preparation process of wet mixed mortar chemical functional material PC-2:n (acrylic acid):n (4-hydroxybutyl vinyl ether polyoxyethylene ether-4000) = 2.5:1. 4-vinylbenzene sulfonic acid, mono-2-(methacryloxy) ethyl succinate, potassium persulfate, sodium hypophosphite and Tert-dodecyl mercaptan accounted for 1.6%, 3%, 1.0%, 1.5% and 1.0% of the total mass of polyether macromonomers.

Microcalorimeter was used to test blank samples, imported wet mortar admixture PC-1 and self-made chemical functional material PC-2 respectively. The hydration and exothermic behavior of
cement in 72 hours with 0.4% content which is shown in figure 1.

![Figure 1](image_url)

**Figure 1.** Hydration heat release curve of different admixtures

As shown in Figure 1, the main exothermic peak of the admixture for hydration exotherm is delayed: PC-2>PC-1> blank. Both admixtures increased the total amount of hydration heat release of 72h, and the total amount of hydration heat release at 72h was: PC-1>PC-2> blank. It could be seen that the chemical functional material PC-2 of wet-mixed mortar could delay the early hydration of cement, significantly increase the induction period, and slow down the hydration of C3A and the formation of AFt. Therefore, this was also the main reason why the chemical functional material of wet-mixed mortar could improve the plasticity of wet-mix mortar.

5. **The microstructure of hydration products**

The morphology of the 3d hydration products of the blank, PC-1 and PC-2 cement pastes are shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** The 3d morphology of Blank, PC-1 and PC-2 cement paste

As shown in Figure 2, when hydration was 3d, the blank structure was loose and the pores were more. There were more short columnar ettringite AFt and reticulated C-S-H gel\(^{[6,7]}\), indicating that the hydration product on the surface of cement particles had formed, but failed seeing the more obvious characteristic hydration products, it was concluded that the degree of hydration was lower. In addition, a large amount of C-S-H gel and Ettringite were formed in the hydrated products mixed with PC-1 and PC-2, and the slurry structure was relatively dense. The macroscopic performance showed that the strength of wet mixing mortar increased significantly. PC-1 could also clearly see the appearance of plate-like structure of Aluminum-Calcium Sulfate AFm, while PC-2 was less. This showed that PC-2 had more delaying effect on cement hydration than PC-1.
6. Engineering application research

At the client end, performance tests were performed on PC-1 and PC-2 (with 50% solids), including wet mix consistency, consistency loss, water retention, the tensile bond strength of 14d, the compressive strength of 7d and 28d, customer cooperation are shown in Table 5, the test results are shown in Table 6.

| Table 5 Customer cooperation |
|-------------------------------|
| Materials | C | F | S | W | A |
| Dosage(kg/m³) | 240 | 40 | 1250 | 210 | 7.4 |

| Table 6 Test results of wet mixed mortar |
|-----------------------------------------|
| Sample name | Consistency /mm | Water retention rate /% | The tensile bond strength of 14d /MPa | Compressive strength /MPa |
|-------------|-----------------|-------------------------|---------------------------------|------------------------|
| PC-1        | 92              | 85                      | 7.6                             | 90.0                   | 0.68                  | 7.5      | 10.2      |
| PC-2        | 88              | 82                      | 6.8                             | 91.2                   | 0.74                  | 8.1      | 11.8      |

As shown in Table 6, compared with PC-1, PC-2 could effectively reduce the consistency loss rate of wet mixed mortar, improved the water retention rate of wet mixed mortar, the tensile bond strength of 14d and the compressive strength of 7d and 28d. PC-2 could meet the requirements of pumping construction and performance indicators.

7. Conclusions

(1) The best preparation process of wet mixed mortar chemical functional material PC-2:n (acrylic acid):n (4-hydroxybutyl vinyl ether polyoxyethylene ether-4000) = 2.5:1. 4-vinylbenzene sulfonic acid, mono-2-(methacryloxy) ethyl succinate, potassium persulfate, sodium hypophosphite and Tert-dodecyl mercaptan accounted for 1.6%, 3%, 1.0%, 1.5% and 1.0% of the total mass of polyether macromonomers.

(2) Through the analysis of hydration heat and SEM morphology, it could be seen that PC-2 had more delaying effect on cement hydration than PC-1, and could improve the plasticity of wet-mixed mortar.

(3) Compared with PC-1, PC-2 could effectively reduce the consistency loss rate of wet mixed mortar, improved the water retention rate of wet mixed mortar, the tensile bond strength of 14d and the compressive strength of 7d and 28d. PC-2 has better performance in the process of pumping and spraying construction and can meet the requirement of continuous supply.

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