Preparation and characterization of early strength polycarboxylate superplasticizer

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Abstract. Through the adjustment of polyether monomer, polyether molecular weight and early strength functional monomer, the best process formula was determined, and its molecular weight was tested by gel permeation chromatography, as well as the product performance. The experimental results showed that the early strength polycarboxylate water reducer（ES-PCE）was prepared by solution polymerization using a vinyl polyoxyethylene ether with a molecular weight of 5000 and a 2-acrylamido-methylpropane sulfonic acid in the ammonium persulfate, hydrogen peroxide, and sodium bisulfite initiator system. Compared with similar products PC-1 and PC-2, the compressive strength of ES-PCE at 1d, 7d, and 28d was comparable to that of similar products PC-1, Compared to similar domestic products PC-2, it is about 2～3 MPa higher, indicating that ES-PCE can completely replace similar foreign products, to improve template turnover rate. Thereby it promotes the rapid development of prefabricated buildings.

Keywords: early strength type; early strong functional monomer; compressive strength; AMPS

1 Introduction

Prefabricated concrete technology, as an important way to achieve prefabricated buildings, has the characteristics of reducing construction pollution, improving construction efficiency and quality, and reflects the advantages of green construction [1]. It is an important way for the construction industry to achieve carbon peak and carbon neutrality. Modern precast concrete accelerates mold turnover and improves production efficiency by improving the early strength of concrete [2].

The research on early strength polycarboxylate water reducing agents began earlier abroad. Japanese catalyst companies, Swiss Sika companies, and German BASF companies all have mature products with excellent early strength performance and wide market applications[3]. A patent in the United States reported a method for preparing

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compressive results of incorporating the prepared water reducing agent into concrete showed that the addition of polycarboxylic acid water reducing agents with longer side chains can improve the early compressive strength of concrete. Compared with foreign countries, China started relatively late in the research and application of polycarboxylate superplasticizers. Kong [4] et al. also found that long side chains can promote cement hydration and improve early strength by studying the influence of different molecular structures of polycarboxylate based water reducing agents on the hydration performance of cement paste. Although the relevant research has been extensive, there are relatively few manufacturers that have truly synthesized and mass-produced early strength polycarboxylate water reducing agents [5-6]. Therefore, the development of key technologies and industrial research on early strength polycarboxylate water reducing agents has good technical and market prospects.

This article adopts a new type of high molecular weight polyether, 2-acrylamido-2-methylpropanesulfonic acid, and free radical polymerization reactions under the redox initiation system, which can greatly accelerate the early hydration of cement and is conducive to improving the early strength of cement-based materials. Solved the problems of low early strength and low formwork turnover rate, reduced concrete maintenance energy consumption, and facilitated the promotion and application of prefabricated concrete.

2 Experimental

2.1 Materials

(1) Raw materials for synthesis

Isobutene polyoxyethylene ether (HPEG), isopentenyl polyoxyethylene ether (TPEG), ethylene polyoxyethylene ether (EPEG); Acrylic acid (AA); Ammonium persulfate (AP),; 2-Acrylamido-2-methylpropane sulfonic acid (AMPS); Acrylamide(AM); Maleic anhydride monoamide (MAMA); N. N-dimethylacrylamide (NNDA); Hydrogen peroxide (H_2O_2); Sodium bisulfite (Sb); Thioglycolic acid (TGA); 30% sodium hydroxide solution (NaOH), all industrial grade.

(2) Materials for performance testing

Cement (C): Minfu P·O 42.5, the main performance indicators of cement is shown in Table 1; Fly ash (FA): Class F Class II fly ash from Houshi Power Plant; Mineral powder (SL): S95 grade, Fujian San'an Iron and Steel Plant; Sand (S): Machine-made sand with a fineness modulus of 2.6-2.9; Stone (G): continuously graded crushed stone (G1) with a particle size of 5-10 mm, and continuously graded crushed stone (G2) with a particle size of 16-31.5 mm; Water (W): tap water, in accordance with the requirements of JGJ 63-2006 "Concrete Water Standard"; Water reducing agent: PC-1 is an early strength polycarboxylate water reducing agent (with a solid content of 50%) from a well-known foreign manufacturer, while PC-2 is an early strength polycarboxylate water reducing agent (with a solid content of 50%) from a well-known domestic manufacturer, both of which are commercially available products.

Table 1. Main performance indicators of cement

Flexural Strength/MPa		Compressive strength /MPa		Requirement of normal consistency /%	Setting time /min		Stability	Fineness /%
3d	28d	3d	28d		Initial	Final		
7.1	10.3	30.3	54.0	28.8	135	280	qualified	1.0

2.2 Test methods

(1) Characterization by gel permeation chromatography

Waters 1515 Isostatic HPLP pump/Waters 2414 gel permeation chromatograph and Empower TM3 software acquisition and analysis system were used. The chromatographic column consists of Ultrahydragel^{TM} 250 and Ultrahydragel^{TM} 500 in series, with a mobile phase of 0.1mol/L sodium nitrate aqueous solution and a flow rate of 0.8mL/min.

(2) Determination of concrete properties

The testing method for concrete performance refers to GB 8076-2008 "Concrete Admixtures". Measure the slump of fresh concrete and the compressive strength of hardened concrete.

2.3 Synthesis method of water reducing agent

Firstly, add a certain amount of polyether and water to the reactor. After the polyether is completely dissolved, add hydrogen peroxide (H_2O_2) in one go. After 10 minutes, start dripping A, B, and C materials. A material is an aqueous solution of ammonium persulfate (AP); Material B is a mixed solution composed of acrylic acid (AA), early strength functional monomers, mercaptoacetic acid (TGA), and water, while Material C is an aqueous solution of sodium bisulfite (SHS). A and C materials should be dripped in 3 hours and 10 minutes, while B materials should be dripped in 3 hours. After all the drops are completed, react at constant temperature for 1 hour, and then add 32% sodium hydroxide solution to neutralize to a pH of 6-7 to obtain the early strength polycarboxylate water reducer ES-PCE.

3 Results and discussion

3.1 Effect of Polyether Monomer Types on the Performance of Early Strength Polycarboxylic Acid Water Reducing Agents

Other synthesis conditions remain unchanged. HPEG-2400, TPEG-2400, and EPEG-2400 were selected for copolymerization synthesis research, and the obtained products were compared for concrete performance to select the best macromonomer. By adjusting the amount of water reducing agent, the slump of the concrete is controlled at around (170 ± 10) mm, and the performance of the concrete is tested. The test results are shown in Table 2.

Table 2. Effect of Major Monomer Types on the Performance

Type	A/%	Slump/mm	Compressive strength /MPa		
			1d	7d	28d
HPEG-2400	0.53	165	16.8	33.9	50.0
TPEG-2400	0.48	170	17.0	33.6	51.7
EPEG-2400	0.43	170	18.2	35.6	52.2

From Table 2, it can be seen that the water reducing agent synthesized with EPEG monomer has the highest water reducing rate, with the highest compressive strength at 1 and 7 days. The water reduction rate of HPEG is relatively low, and the compressive strength at 1d, 7d, and 28d is equivalent to that of TPEG. EPEG has higher polymerization activity than TPEG and HPEG, and the synthesized water reducing agent has better performance. Therefore, the early strength polycarboxylic acid water reducing agent synthesized with EPEG was selected.

3.2 Effect of Polyether Molecular Weight on the Performance of Early Strength Polycarboxylic Acid Water Reducing Agents

Using EPEG with molecular weights of 2400, 3000, 4000, and 5000 for synthesis experiments, the main chain length was basically the same. By changing the molecular weight of the polyether macromonomer, a series of early strength polycarboxylate water reducing agents with different side chain lengths were synthesized. The effect of side chain length on the performance of early strength polycarboxylate water reducing agents was studied. The molecular weight is shown in Table 3, and the concrete test results are shown in Table 4.

Table 3. Molecular weight information

Molecular weight	Number average molecular weight(Mn)	Weighted average molecular weight(Mw)	Molecular weight distribution(PDI)
2400	21310	29711	1.695
3000	27714	44234	1.805
4000	34865	49860	1.768
5000	42142	64676	1.742

Table 4. Effect of Polyether Molecular Weight on the Performance

Molecular weight	A/%	Slump /mm	Compressive strength /MPa		
			1d	7d	28d
2400	0.43	180	17.7	35.4	51.2
3000	0.43	175	18.4	35.7	52.4
4000	0.42	175	19.2	36.9	52.6
5000	0.42	180	20.3	37.6	53.7

From Table 4, it can be seen that with the increase of polyether molecular weight, the water reduction rate of early strength polycarboxylate water reducing agent increases, resulting in an improvement in the dispersibility of concrete. As the length of the side chain increases, the charge density of the water reducing agent decreases, the surface adsorption amount of cement particles decreases, the coverage decreases, and the spatial repulsion increases. After the water reducing agent is adsorbed on the surface of cement particles, the adsorbed water reducing agent molecules repel each other and disperse due to steric hindrance and electrostatic effects, resulting in good dispersion effect. At the same age, with the increase of molecular weight, the compressive strength of concrete at 1 and 7 days is higher, while the improvement in compressive strength at 28 days is not significant. This is because polycarboxylic acids with different side chain lengths have different dispersion states on mineral phases, which in turn leads to different rates and crystal forms of ettringite formation. Increasing the side chain length of water reducing agents is beneficial for accelerating the hydration of cement to generate ettringite and promoting the development of early strength of concrete. Therefore, EPEG with a molecular weight of 5000 was selected to synthesize an early strength polycarboxylate water reducer.

3.3 Effect of Early Strength Functional Monomers on the Performance of Early Strength Polycarboxylic Acid Water Reducing Agents

Four early strength functional monomers were selected, including AM, AMPS, MAMA and NNDA, with dosages of 0.6% of the larger monomers, while maintaining other conditions unchanged. The effects of these four early strength functional monomers on the performance of early strength polycarboxylate water reducing agents were studied. The test results are shown in Table 5.

Table 5. Effect of Early Strength Functional Monomers on the Performance

Type	A/%	Slump /mm	Compressive strength /MPa		
			1d	7d	28d
blank	0.42	175	20.3	37.6	53.7
AM	0.42	170	21.5	38.1	53.6

AMPS	0.41	165	22.3	39.3	54.6
MAMA	0.43	165	19.9	38.9	54.7
NNDA	0.41	170	21.0	38.3	54.0

From Table 5, it can be seen that the addition of early strength functional monomers has a certain improvement in early strength compressive strength. Among them, the addition of 2-acrylamido-methylpropane sulfonic acid has the highest compressive strength after 1 day, mainly because the molecular structure of 2-acrylamido-methylpropane sulfonic acid contains amide and sulfonic groups, producing amphoteric polycarboxylic acid water reducing agents. The synergistic effect of anions and cations in the molecular structure is conducive to the generation of ettringite and increasing the amount of ettringite generated, Thus, it exhibits a superior early strength effect. The sulfonic acid group increases the density of anions in the molecular structure of polycarboxylic acid, and the sulfonic acid group can react with calcium hydroxide to accelerate the hydration rate, greatly increasing the number of acicular ettringite in the early stage, thereby improving the early strength of concrete.

3.4 Concrete application performance

Select similar early strength polycarboxylate water reducing agents with good quality in both domestic and foreign markets for comparison, control the initial slump to (170 ± 10) mm, and test the concrete slump, setting time, compressive strength, etc. The concrete mix is shown in Table 6, and the test results are shown in Table 7.

Table 6. Concrete Mix Proportions (kg/m^3)

C	F	K	S	G1	W	A
230	70	60	875	995	170	3.8

Table 7. Concrete Mix Ratio Table 7 Concrete Performance Test Results

Type	Dosage/%	Slump/mm	Compressive strength /MPa			Workability
			1d	7d	28d	
ES-PCE	1.9	180	21.7	38.2	56.5	good
PC-1	2.0	170	20.6	37.8	56.2	good
PC-2	2.1	175	17.9	36.2	53.1	good

From Table 7, it can be seen that under the same amount of cement content, the initial slump of ES-PCE is comparable to that of similar products both domestically and internationally; In terms of compressive strength, the 1d, 7d, and 28d compressive strength of ES-PCE is equivalent to that of similar foreign products PC-1, which is about 2-3 MPa higher than that of similar domestic products PC-2. The concrete mixed with three similar domestic and foreign products has good workability, indicating that ES-PCE can completely replace similar foreign products.

4 Conclusions

(1) The results showed that vinyl polyoxyethylene ether with a molecular weight of 5000 was used as the main monomer, and the early strength functional monomer was 2-acrylamide methylpropane sulfonic acid. The free radical solution polymerization was carried out in the system of ammonium persulfate hydrogen peroxide sodium bisulfite initiator. The prepared early strength polycarboxylate water reducer ES-PCE has the best performance, with a compressive strength of 21.7 MPa after 1 day.

(2) Compared with similar products PC-1 and PC-2 sold domestically and internationally, the compressive strength of ES-PCE at 1d, 7d, and 28d is equivalent to that of foreign similar products PC-1, which is about 2-3 MPa higher than that of domestic similar products PC-2. The concrete mixed with three domestic and foreign similar products has good workability, indicating that ES-PCE can completely replace foreign similar products. Improve the turnover rate of formwork in the prefabrication plant, reduce the energy consumption of concrete maintenance, and facilitate the promotion and application of pre mixed concrete, thereby promoting the rapid development of prefabricated buildings.

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