Preparation and characterization of EPEG-type viscosity reducing polycarboxylic superplasticizer

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Abstract. In order to solve the problems of high viscosity and slow flow rate of high-strength concrete. Using EPEG type low molecular weight large monomer as the main raw material, the effects of the acid to ether ratio, the amount of bottom liquid acrylic acid, the amount of chain transfer agent,and the amount of reducing agent on the flow properties of the viscosity reducing polycarboxylic superplasticizer were investigated. The results showed that the viscosity reduction effect of VR-PCE was the best when the acid to ether ratio is 3.5, the bottom liquid acrylic acid dosage is 6% of the total acrylic acid dosage, the chain transfer agent dosage is 0.30% of the EPEG dosage, and the reducing agent dosage is 0.25% of the EPEG dosage.

Keywords: EPEG, polycarboxylic superplasticizer, viscosity reducing performance, free water

1 Introduction

With the rapid development of the construction industry, the building materials industry has increasingly higher requirements for the performance of concrete, which promotes the development of concrete in the direction of high strength, high performance and high durability. Polycarboxylate superplasticizer (PCE) is one of the essential components of concrete because of its low dosage, high water reduction rate, good slump retention performance and environmental protection [1-3]. Due to the use of more cementitious materials and lower water-binder ratio, high-grade concrete is prone to the problems of slow dispersion, high viscosity, slow flow rate, poor workability and large pumping resistance.

In order to solve the viscosity problem of high-grade concrete, in recent years, the development of viscosity-reducing polycarboxylate superplasticizer (VR-PCE) by optimizing the molecular structure of superplasticizer has been a research hotspot in the field of concrete admixtures. Fang Yunhui [4] found that APEG-type PCE with long side chain and short main chain structure or XPEG-type PCE with short side chain and long main chain structure with low molecular weight can form a smaller water film thickness in concrete, thus releasing more free water and effectively reducing the viscosity of slurry. Qian Shanshan et al.[5] designed and synthesized a viscosity-reducing

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water reducer VR-PCE by using short side chain isopentenol polyoxyethylene polyoxypropylene ether macromonomer (IPEPPG) and maleic anhydride. VR-PCE has hydrophobic groups, short side chain and small molecular weight, which makes it easy to bend and move, reduces the generation of bound water, releases free water, and can effectively reduce the viscosity of the slurry.

Therefore, optimizing the structure of polycarboxylate superplasticizer, reducing the bound water in the slurry and releasing free water are effective ways to achieve viscosity reduction. At present, the research mainly focuses on the preparation of viscosity-reducing polycarboxylate superplasticizers by using low molecular weight macromonomers of APEG type[4], MPEG type [6], HPEG type [7], and TPEG type [8]. Ethylene glycol monovinyl polyoxyethylene ether (EPEG), as a new type of macromonomer in recent years, has high polymerization activity. It can copolymerize with acrylic acid and other monomers at lower temperature and in a short time to prepare polycarboxylate superplasticizer with excellent performance. However, there are few reports on the study of viscosity reducing agent with EPEG type low molecular weight monomer. It is of great guiding significance to prepare and study viscosity reducing agent with EPEG. Therefore, in this paper, ethylene glycol monovinyl polyoxyethylene ether (EPEG-1100) with a molecular weight of 1000 was used as a macromonomer, and investigate the effects of acid to ether ratio, the amount of acrylic acid in the base solution, the amount of chain transfer agent, and the amount of reducing agent on the performance of viscosity-reducing polycarboxylate superplasticizer.

2 Experimental

2.1 Synthetic raw materials

Industrial grade ethylene glycol monovinyl polyoxyethylene ether (EPEG-1100); industrial grade acrylic acid (AA); industrial grade hydrogen peroxide (H_2O_2); industrial grade ascorbic acid; industrial grade mercaptoethanol; 32% mass concentration industrial grade sodium hydroxide (NaOH); the synthesis water is deionized water, and the water for slurry and concrete verification is tap water.

2.2 Test materials

The manufactured sand (S) is medium sand, the fineness modulus is 2.7, and the mud content is 0.81 %. Stone (G) is gravel with particle size of 10mm ~ 25mm. Cement (C) is Runfeng P.O42.5 cement. The mineral composition of cement is shown in Table 1. Commercially available standard polycarboxylate superplasticizer PCE-1.

Table 1. Chemical composition of cement

sample	Fe2O3/%	Al2O3/%	SiO2/%	CaO /%	MgO/%	SO3/%	K2O/%	Na2O/%
cement	3.24	5.18	25.86	52.671	0.29	3.56	1.15	1.40

2.3 Synthesis

In a four-port flask containing a certain amount of EPEG-1100 solution, an appropriate amount of acrylic acid and a hydrogen peroxide solution were added. The temperature was kept at 15 °C, and then the acrylic acid solution and the mixed solution of ascorbic acid and mercaptoethanol were added dropwise to the four-necked flask. The dropping time was 60 min and the holding time was 60 min. After the reaction, the sodium hydroxide solution was added to adjust the pH value of the solution to neutral, and the EPEG type VR-PCE was obtained.

2.4 Performance Testing

The fluidity of cement paste was tested according to the method specified in GB/T 8077-2012 "Test method for homogeneity of concrete admixtures." 300 g of cement and 87 g of water were weighed. The mixing procedure was to mix slowly for 5 s and then quickly for 1 min. The amount of viscosity-reducing water reducer was adjusted to keep the expansion of cement paste between 220 mm and 230 mm. Keep the same amount of viscosity-reducing polycarboxylate superplasticizer r, reduce the water consumption to 75 g, test the expansion of the paste again, and record the value.

3 Results and discussion

3.1 Effect of acid to ether ratio on viscosity reducing performance

Keeping other factors unchanged, the effects of VR-PCE on the expansion of paste were investigated when the acid ether ratio was 2.0, 2.5, 3, 3.5 and 4.0 respectively. The results are shown in in Figure 1.

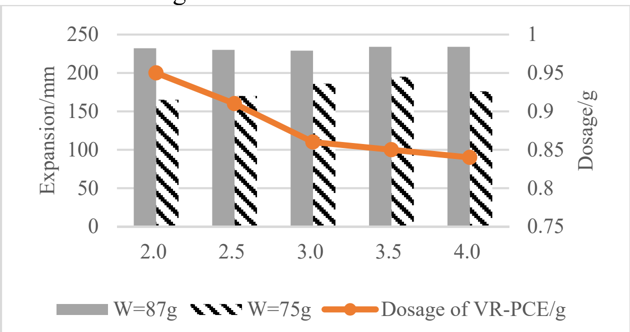

Fig. 1. Effect of acid to ether ratio on fluidity of clean pulp

The results show that when the water consumption is 87 g, the content of VR-PCE gradually decreases with the increase of the acid to ether ratio. This is because with the increase of the acid to ether ratio, the density of carboxyl groups on the molecular chain becomes larger, and the adsorption of VR-PCE is stronger and has higher dispersion effect. When the water consumption is reduced to 75 g, the expansion of the paste increases first and then decreases with the increase of the acid to ether ratio, indicating that the VR-PCE prepared by the low molecular weight macromonomer has a greater difference in adsorption and dispersion under the condition of low water consumption, affecting the water thickness on the surface of the cement particles. When the acid to ether ratio is 3.5, the expansion of the paste is the largest, indicating that it is most conducive to the release of free water under low water-binder ratio conditions.

3.2 Base liquid acrylic acid dosage on viscosity reducing performance

The ratio of acid to ether was fixed at 3.5, and the amount of total acrylic acid and other factors were kept unchanged. The amount of acrylic acid in the bottom liquid was adjusted to 4 %, 6 %, 8 %, 10 %, and 12 % of the total amount of acrylic acid, respectively. The effect of the prepared VR-PCE on the expansion of the paste was investigated. The results are shown in Figure 2.

The pH value of the initial solution has an important influence on the molecular structure assembly of the water reducer [9]. With the increase of the amount of AA in the bottom solution, the pH value of the bottom solution gradually increased. The test results showed that when the water consumption was 87 g, the amount of VR-PCE prepared was about 0.86 g, and the expansion of the paste was equivalent, indicating that the pH value of the bottom solution did not affect the dispersion effect.

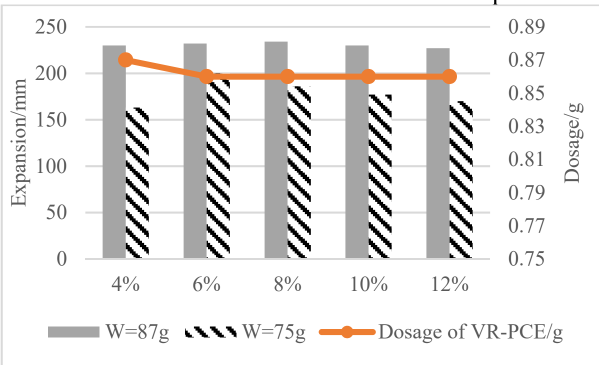

Fig. 2. Effect of the amount of bottom liquid AA on the fluidity of the clean slurry

When the water consumption was reduced to 75g, with the increase of the amount of AA in the bottom solution, the expansion of the paste showed a trend of increasing first and then decreasing, indicating that the pH value of the bottom solution was too high, which was not conducive to the adsorption and dispersion of VR-PCE at low water consumption, resulting in large viscosity. When the amount of AA in the bottom liquid is 6 % of the total amount of acrylic acid, the expansion degree of the paste is the largest and the dispersion viscosity reduction effect is the best.

3.3 Effect of mercaptoethanol dosage on viscosity reducing performance

Keeping other factors remained unchanged. The effect of VR-PCE on the expansion of paste was investigated when the amount of mercaptoethanol was 0.25%, 0.30%, 0.35%, 0.40% and 0.45% of the amount of EPEG, respectively. The results are shown in Figure 3.

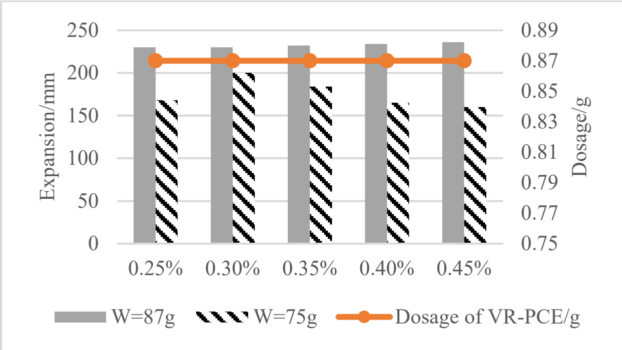

Fig. 3. Effect of mercaptoethanol dosage on fluidity of clean slurry

With the increase of the amount of chain transfer agent, the main chain length of the water reducer gradually becomes shorter. The test results show that when the water consumption is 87 g, the amount of VR-PCE is about 0.87 g, and the expansion degree is equivalent, indicating that the length of the VR-PCE main chain does not affect the water reduction rate of the viscosity reducer at high water-binder ratio. When the water consumption is reduced to 75g, with the increase of the amount of chain transfer agent, the expansion of the paste increases first and then decreases, indicating that the main chain is too short to be conducive to the dispersion adsorption effect of VR-PCE under low water consumption conditions, resulting in a large viscosity. When the amount of chain transfer agent is 0.30 % of the amount of EPEG, the expansion degree of the paste is the largest, the maximum free water can be released, and the dispersion viscosity reduction effect is the best.

3.4 Effect of reducing agent ascorbic acid dosage on viscosity reducing performance

Keeping other factors remained unchanged. The effect of VR-PCE on the expansion of paste was investigated When the amount of ascorbic acid is 0.10%, 0.15%, 0.20%, 0.25% and 0.30% of the amount of EPEG. The results are shown in Figure 4.

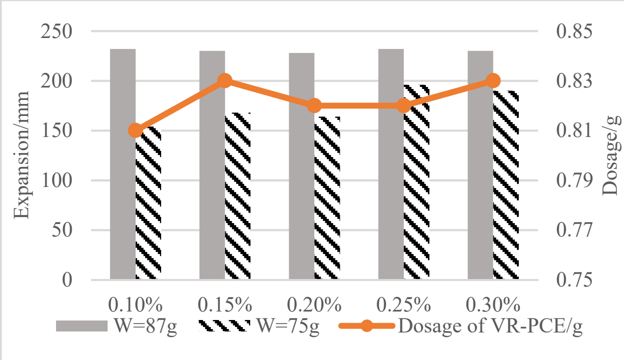

Fig. 4. Effect of reducing agent ascorbic acid dosage on fluidity of clean slurry

With the increase of the amount of reducing agent, more free radicals can initiate monomer polymerization in the same time, so that the polymerization efficiency of VR-PCE is higher, the number of molecules is more and the molecular weight is lower. The results show that when the water consumption is 87 g, the VR-PCE dosage reaches a considerable expansion when the dosage is about 0.81 g ~ 0.83 g, indicating that compared with other adjustment factors, the water reduction rate of the viscosity reducing agent prepared by adjusting the reducing agent is higher. When the water consumption is 75 g, with the increase of the amount of reducing agent, the expansion degree of the paste increases first and then decreases. When the amount of chain transfer agent is 0.25 % of the amount of EPEG, the expansion degree of the paste is the largest, indicating that the most free water can be released, and the dispersion viscosity reduction effect is the best.

3.5 Performance comparison betweenVR-PCE and standard polycarboxylate superplasticizer PCE-1

The performance of the VR-PCE prepared under the optimal conditions was compared with that of the commercially available standard polycarboxylate superplasticizer PCE-1. The test results are shown in Figure 5.

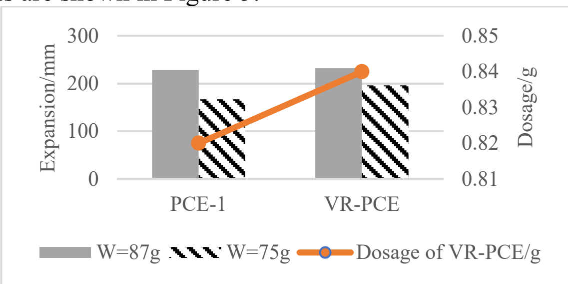

Fig. 5. Performance comparison betweenVR-PCE and PCE-1

The test results show that when the water consumption is 87 g, the EPEG type VR-PCE needs a higher amount of content to achieve a comparable paste expansion with PCE-1, indicating that the dispersion performance of-PCE is low, which is related to its lower side chain length and smaller steric hindrance effect.When the water consumption is 75 g, the paste expansion of VR-PCE is larger than that of PCE-1, indicating that VR-PCE has excellent dispersion and viscosity reduction performance under low water-binder ratio.

4 Conclusiong

The following conclusions were drawn:

(1) The optimal preparation conditions for VR-PCE are as follows: an acid to ether ratio is 3.5, a base solution AA dosage is 6% of the total AA dosage, a chain transfer agent dosage is 0.30% of the EPEG dosage, and a reducing agent dosage is 0.25% of the EPEG dosage.

(2) When the water consumption is 87g, i.e. the water cement ratio is 0.29, the adsorption and dispersion effect of VR-PCE is equivalent, and the viscosity reduction effect is not significantly reflected.

(3) When the water consumption is 75g, that is, the water-binder ratio is 0.25, VR-PCE has significantly better adsorption and dispersion effect and viscosity reduction effect than PCE-1, indicating that VR-PCE has a better application prospect in high strength and high performance concrete with low water-binder ratio, which is used to solve the problem of high viscosity.

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