Synthesis, characterization and mechanism of polycarboxylate superplasticizer with slump retention capability

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Abstract. Two kinds of slump-retaining polycarboxylate superplasticizer with different molecular structures were synthesized via maleic anhydride(MAH), polyethylene glycol monoallyl ether(APEG) and hydroxyethyl acrylate (HEA)/ethyl acrylate (EA) according to molecular structure design principle. The comprehensive performances of each slump-retaining polycarboxylate superplasticizer were analyzed and compared with that of different molecular structure. The Gel Permeation Chromatography (GPC), surface tension, zeta potential, adsorption behavior, cement paste fluidity and application performance in concrete were measured. And the slump retention mechanism was analyzed. The results show that the polycarboxylate superplaticizer with hydroxyethyl group prepared in this study has good dispersing performance and high slump retention capability for concrete.

Keywords: polycarboxylate superplaticizer, hydroxyethyl acrylate/ethyl acrylate, dispersing performance, slump retention

1. Introduction

Polycarboxylate superplaticizers have been increasingly widely used in concrete engineering because of their low admixing volume, high water reducing rate, good slump retention capability, adjustable molecular structure, and environmental protection. However, the large slump loss of concrete often appears in hot weather or during long-time and long-distance transportation due to the existence of large differences in concrete raw materials, especially in the hot summer, the slump loss is faster [1-2]. During the construction process, it is often to increase the amount of water reducing agent to restore good work performance of the concrete, making the concrete have good liquidity. However, the increase of the amount of water reducing agent in the initial stage of mixing will lead to the segregation and bleeding of concrete, which will destroy the uniformity of concrete and make the strength of each part of concrete quite different, reducing the compressive strength of the whole concrete. In practical engineering, it is generally to compound the retarders such as sodium citrate, sucrose, sodium citrate and so on [3-4]. But the problem of slump loss still remains unsolved with the additon of these retarders, and the retarders are easily to deteriorate in high temperature environment. Thus affecting the operational performance of the water reducing agent. To solve this problem, domestic and foreign researchers have begun to study the slow-release polycarboxylate superplaticizers [5]. The polycarboxylate superplaticizers with slump retention capability can be prepared through the optimal combination of different functional units to solve the problem of slump loss, as the molecular structure of polycarboxylate superplaticizers can be designed easily [6].

In this paper, two kinds of polycarboxylate superplaticizers PC-1 and PC-2 were synthesized through free radical polymerization of maleic anhydride (MAH) and polyethylene glycol monoallyl ether(APEG), using hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) as small molecule sustained-release monomers, respectively. The structure of hydroxyethyl ester/ethyl ester polycarboxylate superplasticizer was synthetically analyzed from the point of the synthesis of the polycarboxylate superplaticizers. The adsorption and dispersion mechanism of the two kinds of slump-retaining polycarboxylate superplaticizers PC-1 and PC-2 with the cement particle surface were studied by Gel Permeation Chromatography (GPC), surface tension test, Zeta potential, adsorption behavior, cement paste fluidity test and concrete test, which will provide a deep theoretical basis for the application of polycarboxylate superplaticizer in concrete.

2. Experiments

2.1. Main materials and instruments

Polyethylene glycol monoallyl ether(APEG), industrial grade, Zhejiang Huangma Chemical Group Co.Ltd .; small molecular ester monomers: hydroxyethyl acrylate (HEA) and ethyl acrylate (EA), analytical grade, Chinese Medicine Group Chemical Reagent Co.Ltd.; sodium methyl methacrylate (SMAS), industrial grade, Nanjing All-plus Chemical Co.Ltd.; maleic anhydride(MAH), ammonium persulfate (APS), sodium hydroxide, all of analytical grade, Nanjing Wanqing Chemical Classware Istrument Co.Ltd.; vitamin C, commercially available.

Cement: P•O42.5 benchmark cement; sand: medium sand in area Ⅱ, fineness modulus of 2.6 to 2.9, mud content <1%.

2.2. Synthesis of the polycarboxylate superplaticizers

Ammonium persulfate (APS) and H_2O were weighed and added into a three-necked flask containing polyethylene glycol monoallyl ether(APEG) and stirred and heated in water bath. Component A and component B were weigned at the same time, component A: maleic anhydride (MAH)+small molecule ester monomers+H_2O; component B: Vc+sodium methyl methacrylate (SMAS). Component A and component B were dropwise added at the same time, finished within 3h and 3.5h respectively, and then the reaction was incubated for 1h. After cooling, the pH value of the reactant was adjusted to 6 ~7 with NaOH solution with concentration of 40% to obtain the desired the polycarboxylate superplaticizer with slump retention capability.

In this experiment, the slump-retaining polycarboxylate superplaticizer PC-1 and PC-2 were prepared by using hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) as monomers, respectively.

2.3. Performance testing and characterization

2.3.1. Gel Permeation Chromatography (GPC). Gel permeation chromatography (GPC) separates the polymer molecules based on the principle that their hydrodynamic volume of the polymer molecular is different. The mobile phase was 0.10mol/L sodium nitrate solution with the flow rate of 0.5mL/min, and the stationary phase was gelatinous porous filler. 1.1mL of superplasticizer sample with solid content of 40% was dissolved into 6.0 mL of 0.10 mol /L sodium nitrate solution to make a gel chromatogram.

2.3.2. Surface tension test. The surface tension of the superplasticizer solutions, of which the concentrations were 0.2%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3.0% respectively, was determined by Wilhelmy method. The superplasticizer solutions were prepared by superplasticizer and deionized water. The same group of solutions was measured continuously for three times and took the average.

2.3.3. Zeta potential. The Zeta potential of the cement paste was determined by the microscopic (cell) electrophoresis meter. Weighed 0.5g of cement, 0.1g of superplaticizer and 150mL of deionized water were weighed. After mixing well, the mixture was allowed to stand for about 5 minutes. The upper layer solution was taken at regular intervals to measure the Zeta potential. The voltage was 100V. 10 cement particles were taken as a group and took the average.

2.3.4. Adsorption behavior(TOC). 30g of superplasticizer solutions with different concentrations were prepared using the superplasticizer and deionized water, the concentrations of the solutions (%) were 0.2g/L, 0.4 g/L, 0.8 g/L, and 1.6 g/L. Then 5g of reference cement was added into the prepared solutions respectively, stirred evenly, and filtered centrifugally after standing. The adsorption capacity was tested at 10min and 1h respectively.

2.3.5. Cement paste fluidity. Cement paste fluidity was tested with reference to GB 8077-2012 "test methods of concrete admixture homogeneity", the admixture solid content of the polycarboxylate superplaticizer was 0.2% of cement quality, water-cement ratio of 0.29.

2.3.6. Concrete test. Concrete test was carried out with reference to GB8076-2008 "concrete admixtures".

3. Results and discussion

3.1. Gel Permeation Chromatography (GPC)

Molecular weight and molecular weight distribution is one of the most basic structural parameters of water reducing agent. If the molecular weight is too small, the molecular chain will be too short, which influences the water-retaining property and has the defect of easy bleeding; If the molecular weight is too large, bypass effect and flocculation will happen, influencing the disperse effect. Therefore, the molecular weight and molecular weight distribution have great influence on the performance of water reducing agent. The synthesized slump-retaining polycarboxylate superplasticizers PC-1 and PC-2 were analyzed by GPC, as shown in figure 1.

After the polycarboxylic acid molecules were injected into the column, the large molecules first came out through the eluent, and the small molecules occur later. It's known that the former larger peak is the molecule with lager molecular weight polycarboxylate superplasticizer, of which the peak area is larger, the peak height is also high, and the peak area ratio is about 95%. However, the shoulder peak is clearly observed in PC-2, while the smaller peak is probably the self-polymer of maleic anhydride monomer or the macro monomer not participating in reaction after analyzing. The peak area is smaller, the peak height is also lower, and the peak area ratio is 3.5%. Comparison of the two spectral lines shows that there is little difference between the GPC diagrams of the synthesized two kinds of polycarboxylate superplasticizers. GPC results show that the monomer conversion rate is higher in the polymerization of PC-1.

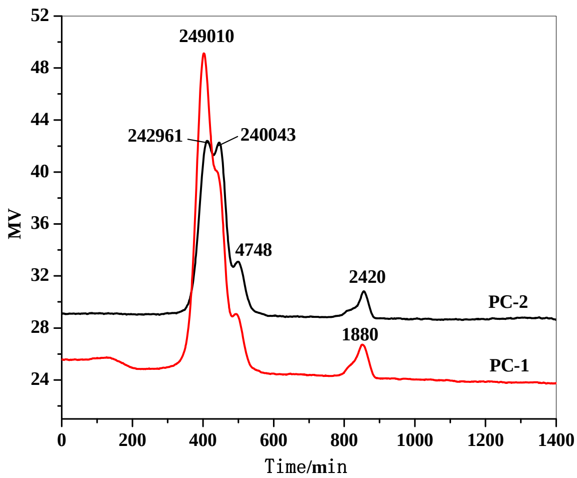

Figure 1. Gel Permeation Chromatography (GPC).

3.2. Surface tension test

The surface tension of the superplaticizer has a great influence on the dispersion of cement particles and the hydration process of cement. Hydroxyethyl acrylate-type / ethyl acrylate-type polycarboxylate superplaticizer can be arranged oriented on the solution surface as a surface active agent with carboxyl and hydroxyl hydrophilic groups, making the surface tension decrease significantly.

In this study, the synthesized two kinds of polycarboxylate superplasticizers were compared in the concentration gradient of 0.2% to 3%, and their influence variety on the surface tension of the solution is shown in Figure 2. From figure 2, it can be seen that the surface tension of the synthesized two kinds of polycarboxylate superplasticizers show the same trend, that is, the surface tension of the solution gradually decreased with the increase of the concentration, which significantly reduced compared with the surface tension of pure water. When the concentration of admixture was 1.0%, the difference of the surface tension reduction rate between PC-1 and PC-2 was little, about 12%. But when the concentration was from 1.0% to 3%, the surface tension reduction rate was up to 20%.The results showed that the hydroxyethyl acrylate-type polycarboxylate superplaticizer PC-1 was more effective than ethyl acrylate-type polycarboxylate superplaticizer PC-2 in obviously decreasing the surface tension of water, which indicated that PC-1 could increase the trendency of the superplaticizer molecule to wet, penetrate and adsorb the cement surface due to its strong adsorption ability of cement particles and the formation of strong electric field.The structure of the hydroxyethyl ester in the molecular chain can effectively increase the adsorption and alignment of the molecular chain to the polar surface, reduce the solid-liquid interface energy on the cement particles and increase the wetting effect between the water and the cement, so as to improve the thermodynamic stability of the dispersion system, and ultimately to achieve the purpose of improving the dispersion of cement particles.

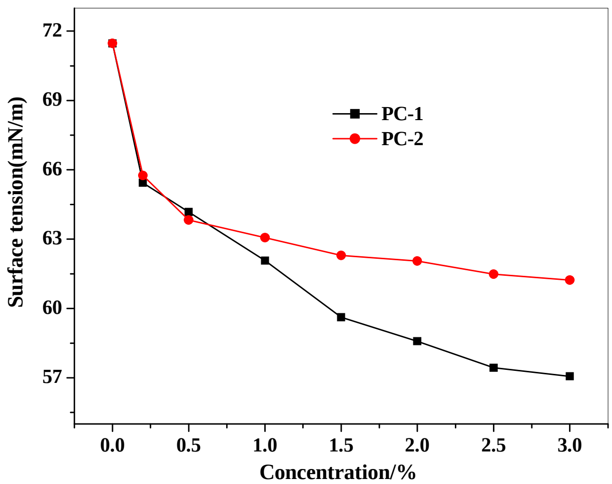

Figure 2. Effect of admixture concentration on the surface tension of the solution.

3.3. Zeta potential

In order to further understand the effect of the prepared polycarboxylate superplaticizer on the cement particles, two kinds of polycarboxylate superplasticizers PC-1 and PC-2 synthesized in this experiment were tested for the surface ζ-potential of the cement particle. The results are shown in figure 3.

It can be seen from figure 3, the surface ζ-potential of the cement particle without admixtures is positive. It gradually transits from positive to negative with the concentration of admixtures increasing, while the absolute value gradually increases to flatten. This phenomenon may be due to: pure cement particles have positive charge on the surface, so ζ-potential is positive, whereas the superplasticizer molecules are generally anionic surfactants, making the cement particles have negative charge after adsorption on the surface under the joint influence of electrostatic interaction and complex effect.Therefore, the electrostatic repulsion occurs between the particles, which makes the particles disperse from each other. As the amount of admixture increases, the amount of superplaticizer adsorbed on the surface of cement particles continuously increases, so that the negative charge on the surface of cement particles increases and the absolute value of ζ-potential increases. The traditional electrostatic repulsion theory holds that the higher the Zeta potential, the greater the electrostatic repulsion between the cement particles and the more dispersed the cement particles, which can explain the mechanism of high efficiency superplaticizer to a certain extent. From figure 3, it can be seen that the dispersion property of the polycarboxylate superplaticizer PC-1 is better than that of PC-2. This may be related to the molecular structure of PC-1. The structure of ethyl hydroxyl in the molecular chain of PC-1 can increase the wetting and adsorption trend of the superplaticizer molecules on the cement surface. The greater the adsorption capacity of cement particle surface, the stronger the electrostatic repulsion caused by the same charge between particles, which effectively increases the adsorption of the molecular chain to polar surface, thus improving the dispersion of cement particles.

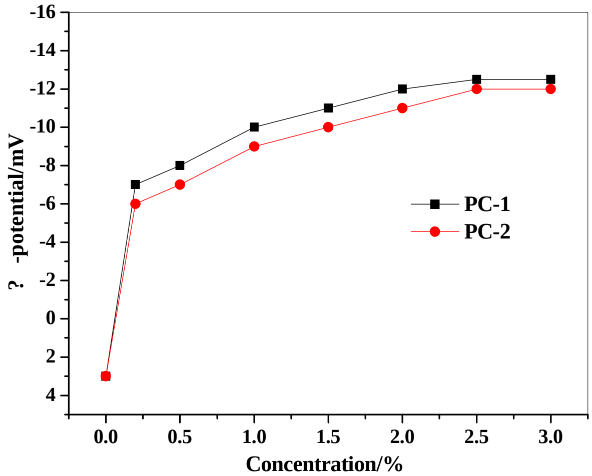

Figure 3. Effect of admixture concentration on the surface ζ -potential of cement particles.

3.4. Adsorption behavior

In order to further study the relationship between the molecular structure and the adsorption performance of the synthesized polycarboxylate superplaticizer, the adsorption capacity of the two kinds of slump-retaining polycarboxylate superplasticizers at different concentrations on the surface of cement particles was studied. The adsorption curve is shown in figure 4.

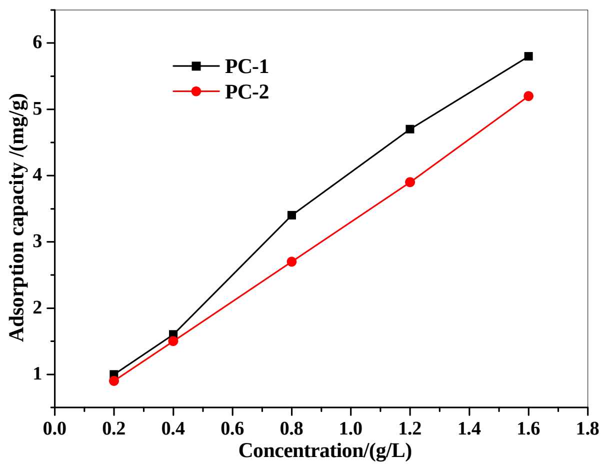

Figure 4. Adsorption curve of the admixtures on cement particles.

It can be seen from figure 4, with the increase of the concentration of the superplaticizer, the adsorption capacity of cement to superplasticizer is gradually increasing. The adsorption capacity of cement to the synthesized polycarboxylate superplaticizer PC-1 is higher than that of PC-2, Which also reflects the flowability and slump retention capability of the concrete mixture with polycarboxylate superplasticizer PC-1 is better than PC-2. This is consistent with the ζ-potential testing result that the synthesized polycarboxylate superplaticizer PC-1 has better dispersion retention capability than PC-2.

3.5. Cement paste fluidity

Cement paste fluidity test is the most direct way to characterize the ability of admixtures to disperse cement. Figure 5 is the cement paste fluidity and flow retention curve over time of the prepared two kinds of polycarboxylate superplasticizer, with the admixture solid content of 0.2% of cement quality, water-cement ratio of 0.29.

From figure 5, it can be seen that the initial cement paste fluidity of the prepared two kinds of polycarboxylate superplaticizers is very small, but gradually increases with time. The fluidity value reaches the maximum at 90min, and gradually decreases after 90min. And the synthesized polycarboxylate superplasticizer PC-1 has better dispersibility and retention than PC-2. This is because the hydroxy group of the hydrophilic hydroxyethyl ester of the superplaticizer PC-1 with a low surface tension is more likely to adsorb on the surface of the hydrophilic cement particles to enhance the steric hindrance effect, thereby making it possible to obtain a larger initial cement paste fluidity. At the same time, the hydroxy groups in the hydrophilic hydroxyethyl groups are easily associated with polar water molecules in the form of hydrogen bonds, forming a stable layer of solvated hydration membrane with a certain mechanical strength on the surface of the cement particles. The formation of the hydration membrane makes the cement particles wet and easy to slip, which prevents mutual coalescence of the cement particles, therby maintaining better cement paste fluidity.

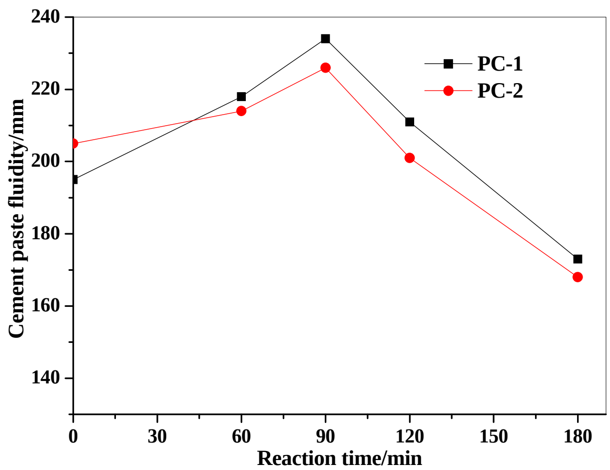

Figure 5. Cement paste fluidity and flow retention curve over time.

3.6. Concrete test

The properties of the concretes mixed with the synthesized two kinds of polycarboxylate superplasticizers PC-1 and PC-2 respectively were compared. Concrete mix ratio and test requirements are tested according to GB / T 8076-2008 "Concrete admixtures", the test results are shown in table 1.

It can be seen from Table 1 that under the same test conditions and the same admixture dosage, the synthesized polycarboxylate superplasticizer PC-1 has smaller slump loss than PC-2. The slump loss of the concrete is small at 2h, and the slump retention capability of PC-1 is better than that of PC-2.

The alkyl structure of the alkyl ester in PC-2, with smaller HLB value than that of the hydroxyl of hydroxyl ester in PC-1, has strong air-entraining performance, which is also confirmed from its concrete compressive strength values.The compressive strength ratio of PC-1 reached 150% at 28d. The higher gas content of PC-2 also affected the compactness of cement stone, which reduced the strength of concrete.

Table 1. Test results of concretes with different slump-retaining polycarboxylate superplasticizers.

Type of polycarboxylate superplasticizer	Slump/Divergence (mm)			Gas content /%	Compressive strength ratio/%		
	Initial	1h	2h		3d	7d	28d
PC-1	210/460	195/440	190/430	4.6	180	161	150
PC-2	210/430	180/400	170/370	7.0	174	154	144

3.7. The mechanism of superplaticizer with hydroxy ester structure

In the cement-water system, the polycarboxylate superplaticizer has the main functions of electrostatic repulsion, steric hindrance, complexation, hydration membrane lubrication and wetting [7-8]. Based on the existing theory and performance results, the mechanism of the effect of the polycarboxylate superplaticizer with hydroxy ester structure was discussed.

1) Electrostatic repulsion effect. According to the electrostatic repulsion theory of the polycarboxylate superplasticizer [9-10], when the polycarboxylate superplaticizer with hydroxy ester structure adsorbed to the surface of cement particles, the electrostatic repulsion is generated on the surface of the cement particles with the same charge due to the electrolysis of hydrophilic polar groups ,making the cement - water system in a relatively stable state of suspension, thereby improving the cement paste fluidity. The results showed that the hydrophilic hydroxylethyl ester of PC-1, the superplaticizer with low surface tension, more easily adsorbed on the hydrophilic surface of cement particles by generating electrostatic repulsion as well as reducing surface tension, and the steric hindrance was enhanced. This achieved a lower surface tension and a stable electrostatic repulsion of the superplaticizer, which is conducive to the realization of cement particles dispersion.

2) Steric hindrance effect. The main chain of the superplaticizer with hydroxy ester structure adsorbed on the surface of cement particles, and the hydrophilic side chain stretched to form thicker polymer molecular adsorbent layer in the liquid phase, thus forming a huge three-dimensional adsorption structure, resulting in steric hindrance effect [11], so that the cement particles repel each other and disperse. With the results of this study, the hydroxyl group of hydrophilic hydroxyethyl ester on the synthesized main chain with comb structure was easily associated with the polar water molecules in the form of hydrogen bonds,and the introduction of hydroxyl ester structure could also form strong hydrogen bonds with the polyether side chain, forming a stable layer of solvated hydration membrane with a certain mechanical strength on the surface of the cement particles,thus playing a role in strengthening the steric hindrance.

3) Complexation. The Ca^{2+} released from cement hydration process can form complexes with carboxyl groups hydrolyzed by hydroxyl ester [12]. The concentration of Ca^{2+} was reduced to delay the formation of $Ca(OH)_2$ and reduce the formation of C-S-H gel, thus delaying the cement hydration process. The incorporation of superplaticizer with hydroxy ester structure can delay the hydration process obviously.

4) lubrication. The hydrophilicity of the hydroxy ester is favorable to the adsorption of the superplaticizer with hydroxy ester structure on the cement particles, and the bonding with the surface charge of the cement, which plays the anchoring effect, is beneficial to the wetting and lubricating effect and the relative lubrication among the aggregate particles of the superplaticizer aqueous solution. According to the theory of Kim [13], the surface of the particles can be stabilized to form a solvated hydration membrane with a certain mechanical strength, generating the lubrication which can destroy the flocculation structure of cement particles and improve the slurry flow performance.

4. Conclusion

Two kinds of functional polycarboxylate superplaticizers PC-1 and PC-2 were synthesized through introducing hydroxyethyl acrylate / ethyl acrylate into the molecular structure respectively by free radical copolymerization. The molecular weight and distribution of the molecular structure were determined by GPC. The surface tension, Zeta potential and adsorption capacity testing results show that the polycarboxylate superplasticizer PC-1 can not only reduce the surface tension of the solution, but also increase the wetting, permeation and adsorption of the cement surface with good dispersion retention performance.

The cement paste fluidity and concrete performance of the synthesized two kinds of polycarboxylate superplasticizers PC-1 and PC-2 have been studied. The results show that under the same test conditions and the same dosage, the synthesized polycarboxylate superplasticizer PC-1 has better slump retention capability and compressive strength than PC-2.

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