Effect of side chain molecular weight on properties of slump retaining poly carboxylic acid water reducer

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Abstract. Slump retaining polycarboxylic acid superplasticizers with different side chain molecular weight were synthesized by using ethylene glycol vinyl polyoxyethylene ether monomers with different molecular weight by different ester to ether ratio and the same ester to ether ratio. Gel permeation chromatography and total organic carbon analyzer were used for structural characterization and adsorption tests to investigate the effects of slump retaining properties of concrete. The results showed that different ester to ether ratio and side chain molecular weight had different effects on PCE molecular weight and molecular weight distribution. At the initial stage of adsorption, the adsorption capacity first increases and then decreases with the increase of side chain molecular weight. In the later stage of adsorption, the adsorption capacity increases first and then decreases with the increase of ester to ether ratio. When the ratio of ester to ether and the molecular weight of side chain increase, the slump retention performance increases first and then decreases. With the increase of side chain molecular weight, the slump retention performance of the same ester to ether ratio increases first and then decreases.

Keywords: side chain molecular weight, slump retention, adsorption, concrete

1 Introduction

Polycarboxylic acid superplasticizer (PCE) is generally composed of polyether monomer, acrylic acid and unsaturated monomer, among which the unsaturated monomer includes ester monomer. Although the amount of ester monomer is not large, accounting for about 4% of the total, it is very important for the slump retention performance of concrete. There have been numerous studies on slump retaining polycarboxylic acid water reducing agents. Guo Yuanqiang [1] et al., by introducing groups with slump retaining and viscosity reducing properties, synthesized high slump retaining and viscosity reducing PCE, explored the influence of polymeric monomer on the performance of PCE, and finally determined the synthesis process to achieve slump retaining and viscosity reducing of high-strength grade concrete. Shi Huizhou [2] et al. synthesized high-slump type PCE by polyether, acrylic acid and other monomers, explored the optimal synthesis process and its influence on concrete performance, and finally determined

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that the acid-ether ratio of 4 and the reaction temperature of 60°C were the best conditions for concrete performance. Zhao Yue [3] et al. analyzed and studied the isothermal adsorption characteristics of slump retaining PCE and the intercalation behavior of hydration products, and the results showed that the main mechanism of action of slump retaining PCE was to promote the formation of hydrated calcium sulfoaluminate and increase the equilibrium concentration of solution in time.

Adsorption is the basis of interaction between superplasticizer and cement particles, and for different microstructures of superplasticizer, their adsorption behavior to cement particles is also different. The increase of carboxyl group density can increase the adsorption capacity to a certain extent, while the main chain polymerization degree has little influence on the adsorption, and the introduction of different groups will also affect the adsorption [4-7].

In this paper, two series of polycarboxylic acid superplasticizers with different ester to ether ratio and fixed ester to ether ratio were designed and synthesized by using polyether monomer with different molecular weight. Their molecular weight, molecular weight distribution and adsorption capacity were studied by gel permeation chromatography and total organic carbon analyzer. Finally, the influence on concrete performance is explored.

2 Experimental

2.1 Material

Cement.

This paper uses P.O 42.5 Run Feng cement from China Resources Cement Co., LTD. (CUCC).

Water.

This paper uses tap water, which meets the requirements of mixing water specified in JGJ 62-2006 "Concrete Water Standard".

Synthetic material.

The synthetic raw materials used in this paper: ethylene glycol polyoxyethylene ether (EPEG) : the relative molecular weights are 1 200, 2 400, 3 000, 4 000, 6 000, respectively, industrial grade; Hydrogen peroxide (H2O2), acrylic acid (AA), hydroxyethyl acrylate (HEA), sodium hydroxide (NaOH), mercaptoethanol (ME), ferrous sulfate (FeSO4), are all industrial grade. Water: Deionized water (W).

Instrument and equipment.

The instruments and equipment used in this paper are shown in Table 1.

Table 1. Main instruments and equipment of the experiment

Instrument name	specifica-tion	manufacturer
Peristaltic pump	BT100-01	Baoding Qili constant flow pump Co., LTD
Electronic balance	JJ1000	Fuzhou Kedi Electronic Technology Co., LTD
Digital display thermostatic water bath	Type HH-4	Changzhou Guohua Electric Appli-ance Co., LTD
Automatic drip device	ZD2000	Wuhan Benheng Technology Co., LTD
Forced single horizontal shaft concrete mixer	SJD60	Shaoxing Dongxin instrument equip-ment manufacturing Co., LTD
agitator	GZ120-S	Yancheng Leigu Technology Co., LTD

2.2 Sample preparation

The main synthetic steps of PCE with different side chain molecular weight are as follows: First, EPEG, AA, $FeSO_4$ and W are added into the four-hole flask and stirred until dissolved by an electric stirring device, then ME and W are mixed into liquid A, AA, HEA and W are mixed into liquid B, and liquid A and B are dropped into the four-hole flask by a dropping device for reaction, and finally NaOH is added to adjust the pH to neutral. This gives you PCE-1~PCE-10. The synthesis process is shown in Figure 1, and the specific molar ratio is shown in Table 2.

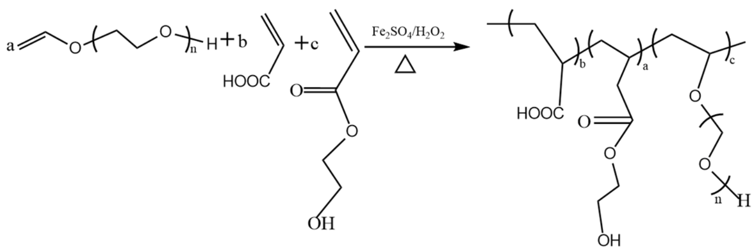

Fig. 1. Synthesis equation

Table 2. Resultant molar mix ratio

Sample number	n（HEA）/n（EPEG）	n（AA）/mol	n（ME）/mol
PCE-1	1.32	0.111	0.0083
PCE-2	2.64	0.111	0.0083
PCE-3	3.30	0.111	0.0083
PCE-4	4.40	0.111	0.0083
PCE-5	5.50	0.111	0.0083
PCE-6	3.30	0.111	0.0083

PCE-7	3.30	0.111	0.0083
PCE-8	3.30	0.111	0.0083
PCE-9	3.30	0.111	0.0083
PCE-10	3.30	0.111	0.0083

2.3 Experimental method

Adsorption capacity.

The adsorption capacity was tested using the German Elementar Vario-TOC instrument. First, PCE solution with a concentration of 4 g/L was configured. Then, 10 g of CR cement was added into 20 mL PCE solution. Then, stir for 1 min and pour appropriate amount of liquid into the centrifugal tube, centrifuge is used to separate filtrate (rotational speed is 7 000 r/min, centrifuge separation is 10 min), and the supernatant is collected as the solution to be measured. Finally, the TOC test was carried out by diluting the solution to be tested by 50 times, and the adsorption amount of PCE on cement particles was calculated according to the following formula.

$$\mathrm{r} = \frac{(C_0 \times V_1 - C_1 \times V_1)}{m \times 1000}$$

In the formula: *r*-Adsorption capacity of PCE in cement paste, mg/g; C_0-TOC content of PCE solution, mg/L; V_1-Add the volume of PCE solution, mL; C_1-TOC content in the solution after mixing PCE with cement paste, mg/L; *m*-Cement sample quality, g

Gel permeation chromatography.

Using the American Waters1515IsocraticHPLCpump/Waters2414 differential detector and Omnisec software acquisition and analysis system. The chromatographic column was composed of UltrahydragelTM250 and UltrahydragelTM500 in series, the mobile phase was 0.1 mol/L sodium nitrate aqueous solution (containing 0.05% sodium azide), and the flow rate was 1.0 mL/min.

Concrete.

The test was carried out according to GB/T 50080-2016 "Standard for Performance Test Method of Ordinary Concrete Mix", and the concrete mix ratio was shown in Table 3.

Table 3. Concrete mix unit: kg/m^3

Cement	Machine-made sand	Stone	Water
360	840	1020	175

3 Results and discussion

3.1 GPC

The structural characteristics of PCE with different side chain molecular weights were investigated and tested with GPC. The results are shown in Table 4.

Table 4. GPC data of PCE with different side chain molecular weights

Sample number	Mn/(g/mol)	Mw/(g/mol)	α/%	PDI
PCE-1	19272	37465	90.53	1.944
PCE-2	22110	39128	89.37	1.769
PCE-3	28747	47059	84.84	1.637
PCE-4	27942	44723	79.78	1.600
PCE-5	44463	61536	68.61	1.384
PCE-6	28747	47059	84.84	1.637
PCE-7	18979	36693	85.21	1.933
PCE-8	26911	46832	88.48	1.740
PCE-9	27220	43599	82.47	1.602
PCE-10	44579	63099	78.92	1.415

As can be seen from Table 4, when the ester ether ratio is fixed, the number average molecular weight (Mn) and weight average molecular weight (Mw) increase with the increase of side chain molecular weight, while the monomer conversion (α) and polydispersion coefficient (PDI) decrease. When the ester to ether ratio and side chain molecular weight increase at the same time, Mn and Mw decrease first and then increase, while α and PDI increase first and then decrease。

3.2 Adsorption capacity

In order to study the adsorption capacity of PCE with different side chain molecular weight, TOC was used for testing, and the results were shown in Figure 2.

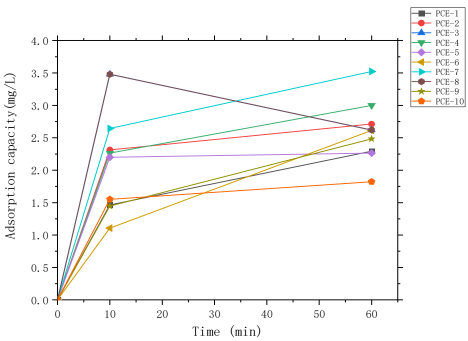

Fig. 2. Adsorption capacity data of PCE with different side chain molecular weight

As can be seen from Figure 2, in the initial stage of adsorption, the adsorption capacities of PCE-1 ~ PCE-5 and PCE-6 ~ PCE-10 both increased first and then decreased. It is shown that the adsorption capacity increases first and then decreases when the side chain molecular weight increases, while the ester to ether ratio has little effect on the adsorption capacity. At the later stage of adsorption, the adsorption capacity of PCE-1 ~ PCE-5 was not different, while the adsorption capacity of PCE-6 ~ PCE-10 increased first and then decreased. The results showed that with the same ester to ether ratio, the increasing of side chain molecular weight had little effect on the adsorption capacity. When the ester to ether ratio increases, the adsorption capacity first increases and then decreases.

It may be that at the initial stage of adsorption, when the ester to ether ratio is the same, the adsorption dispersion is related to the length of the side chain. When the length of side chain is moderate, the adsorption and dispersion effect is better. When the side chain length is too small, the spatial effect can not be generated. When the length of the side chain is too large, it will curl and tangle with each other, which will affect the adsorption. At the later stage of adsorption, the ester to ether ratio affects the side chain density. When the ester ether is relatively large or small, the side chain density changes accordingly, which affects the adsorption.

3.3 Concrete performance

In order to understand the effects of the same ester to ether ratio and different ester to ether ratio and different side chain molecular weight PCE on the slump retention performance of concrete, concrete experiments were conducted, in which S10 was general slump retention type PCE, and PCE-1 ~ PCE-10 was different side chain molecular weight PCE. The initial concrete expansion degree and the concrete expansion degree lost after 60 minutes were shown in Table 5.

Table 5. PCE time expansion of different side chain molecular weights

Sample number	Initial concrete spread /mm	60min Concrete expansion /mm
S10	570	450
PCE-1	555	300
PCE-2	550	375
PCE-3	545	375
PCE-4	560	490
PCE-5	545	425
PCE-6	570	405
PCE-7	560	490
PCE-8	560	455
PCE-9	560	475
PCE-10	570	455

As can be seen from Table 5, compared with S10, the initial expansion degree of PCE-1 to PCE-5 is smaller, while that of PCE-6 to PCE-10 is not much different. The slump retention performance of PCE-4, PCE-7 and PCE-9 was better, followed by PCE-8 and PCE-10, while the slump retention performance of PCE-1 was the worst. The results show that under the same ester to ether ratio, the slump retention performance of PCE increases first and then decreases with the increase of side chain molecular weight, and the slump retention performance is the best when the side chain molecular weight is 4000. With the increasing of side chain molecular weight, the slump retention performance of PCE increases first, then decreases and then becomes stable.

4 Conclusions

By synthesizing different slump retaining PCE with different molecular weight EPEG, the adsorption of PCE and its influence on concrete properties were investigated. The conclusions were as follows:

(1) With the increase of ester to ether ratio and side chain molecular weight, the molecular weight of different PCE increases and the molecular weight distribution Narrows; With the same ester to ether ratio, the molecular weight of different PCE decreases first and then increases with the increase of side chain molecular weight, and the molecular weight distribution first widens and then Narrows.

(2) At the initial stage of adsorption, the side chain molecular weight increases, the adsorption capacity of different PCE increases first and then decreases, and the ester to ether ratio has little effect on the adsorption capacity. At the later stage of adsorption, when the ester to ether ratio was the same, the increasing of side chain molecular weight had little effect on the adsorption capacity of different PCE. When the ester to ether ratio increases, the adsorption capacity first increases and then decreases.

(3) Compared with S10, the slump retention performance of PCE with different side chain molecular weight was different. When the ester to ether ratio and the molecular weight of side chain increase, the slump retention performance increases first and then decreases, and the molecular weight of side chain 2400 is the best performance. For the same ester to ether ratio, the slump retention performance increases first and then decreases with the increase of side chain molecular weight, and the best performance is 4000 side chain molecular weight.

Reference

1. GUO Y Q. Synthesis of polycarboxylic acid superplasticizers with high slump retention and viscosity reduction [J]. New Building Materials,2022,49(02):45-48. (in Chinese)
2. Shi Huizhou, Wang Hui. Synthesis of polycarboxylic acid superplasticizer with high slump retention and its effect on concrete properties [J]. Journal of Functional Materials, 2019,53(08):8196-8201.
3. Zhao Yue, Jiang Yaqing, Zhang Minjie. Adsorption and dispersion mechanism of slump retaining polycarboxylic acid water reducer [J]. New Building Materials, 2016, 43(06): 57-59+74. (in Chinese)
4. Y.H. Fang, Z.J. Lin, D.M. Yan, et al. Study on the Effect of Polycarboxylate Ether Molecular Structure on Slurry Dispersion, Adsorption, and Microstructure. Polymers, 2023,15,2496.

5. Y.H. Fang, X.F. Xiao, D.M. Yan, et al. Study on Dispersion, Adsorption, and Hydration Effects of Polycarboxylate Superplasticizers with Different Side Chain Structures in Reference Cement and Belite Cement. Materials, 2023,16,4168.
6. Y.H. Fang, Z.H. Chen, D.M. Yan, et al. Study on the Effect of Main Chain Molecular Structure on Adsorption, Dispersion, and Hydration of Polycarboxylate Superplasticizers. Materials, 2023,16,4823.
7. Matsuzawa, K; Miyauchi, M; Sakai, E. Relationship between Fluidity of Cement Paste with Fluoride Ion and Type of Superplasticizer [J]. Journal of Advanced Concrete Technology,2018,16(11):577-586.