

Development of the poly-carboxylate slump retaining admixture

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ABSTRACT

In recent years, the related researches on admixtures have progressed towards high performance, green and no pollution. In order to meet the requirements of high-performance concrete, most of the concrete are primarily mixed with poly-carboxylate superplasticizer. With the advantages of low dosage, high water reduction and high security, it has high degree of freedom in molecular structure design, but it still requires heating during the synthesis, and the synthesis process must be strictly controlled, which may not only cause energy consumption, but also increase the energy consumption as well as equipment costs.

After understanding the reaction mechanism between the raw materials and the molecular design method, the research and development of extended-release superplasticizer by dropping method at ordinary-temperature and slump-retaining superplasticizer by disposable input method at ordinary-temperature, were proposed and tested for their flow expansion and flow retention to find the optimum formula; separately tested for saturation, and tested for 0, 30, 60, 90, and 120 minutes of paste flow. The test results showed that the effects of the two are not significant in single use, so use them together, then use the experimental design to find the best mixing ratio, and test its effect on the cement mortar. The test results showed that the water ratio of the two cement control groups was 82% and the strength ratio of the control group meet the standard of the chemical admixture G type high-performance water-reducing retarder of concrete (CNS12283,2017).

1. INTRODUCTION

Concrete is one of the popular building materials in the world at present, and the application of admixtures is one of the major approaches to the progress of concrete technology. In recent years, the related researches on admixtures have also progressed towards high performance and green pollution. In order to satisfy the

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requirements of high-performance concrete, most of the concrete is currently mixed with poly-carboxylate superplasticizer. Because of its low content and high water-reducing effect, construction performance can be significantly improved, and the greatest advantage lies in the high freedom of molecular structure design. It can be prepared through different monomer species into different performance products. However, the disadvantages are that the traditional preparation procedure requires strict control of the dropping time of each raw material synthesis, and the preparation needs to be heated to 60°C-90°C so that the initiator undergoes thermal decomposition to provide the required free radical copolymerization, achieving its typical comb-type structure. Such traditional preparation procedures not only make the program complicated, but also cause energy consumption.

In order to meet the goal of high performance and green pollution, this study was based on the preparation and application of poly-carboxylate slump-retaining admixture (Chen Y. 2017). Followed by synthesizing the extended-release superplasticizer by the ordinary-temperature dropping method, the slump-retaining superplasticizer by the ordinary-temperature disposal input method was also synthesized to replace traditional synthesis methods and heating principles, and to develop high-precision, low-energy-consumption, and high-performance water-reducing retarding admixture with good adaptability to cement paste. The purposes of this study are collated as follows:

- Synthesis at ordinary-temperature ($25\pm 5^{\circ}\text{C}$) without heating, instead of normal heating synthetic method to synthesize poly-carboxylate superplasticizer.
- Synthesis of the poly-carboxylate superplasticizer by disposal input method instead of dropping method.
- The synthesized superplasticizer must meet the water ratio and meet the compressive strength requirement at the ages of 3-day and 7-day in accordance with (CNS 12283,2017).

2. LITERATURE SURVEY

High-performance poly-carboxylate superplasticizer, the structure of which is a comb-type copolymer having carboxyl functional groups in a linear main chain and connecting a plurality of branches, and is generally obtained by radical polymerization through different monomers, with the advantage of low dosage as well as high water-reducing effect and high design freedom of the molecular structure (Wang Z. 2011).

The esterified carboxylate monomer and water were stirred in the reactor and heated to 80°C., and the prepared liquids A and B were respectively added dropwise for 2 hours and 2.5 hours, and the polymerization was aging for 1 hour. Finally, followed by the lye added for liquid neutralization, poly-carboxylate superplasticizer could be prepared (Wang P. 2015).

The base liquid consisting of monomer, initiator and water was heated to 30°C-35°C in water bath, stirred until the materials within base liquid were completely dissolved, and then the oxidant was added continuously to stir, and then the prepared A liquid and B liquid were respectively prepared. After 3 hours and 3.5 hours of dropwise addition, the addition of A and B was completed. After standing and aging for 1.5 hours, the lye was added to neutralize for obtaining high-performance poly-carboxylate superplasticizer (Huang Y. 2016).

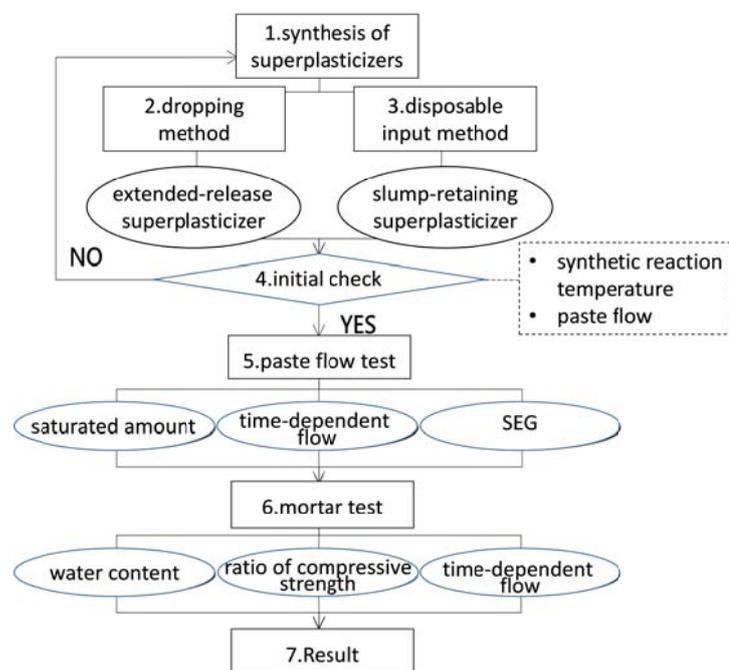
The macro-monomer and water were added to the reaction vessel and stirred, and the temperature was raised to 60°C to completely dissolve the macro-monomer. After the macro-monomer was completely dissolved, pH of the base liquid was adjusted to 4 to 6 using the unsaturated carboxylate monomer. After the adjustment, the oxidant was put into the reactor and stirred for 20 minutes to fully dissolve. The remaining unsaturated carboxylate monomer, chain-transfer agent and reducing agent were dissolved in water and added dropwise to the reaction within 3 hours. In the reactor, after standing and aging for 1 to 2 hours, followed by adjustment to pH of 6 to 7 using neutralizing agent, the slump-retaining admixture could be prepared (Chen Y. *et al.* 2017)

As aforementioned, the advantages of poly-carboxylate superplasticizers as well as the complexity of the general poly-carboxylate superplasticizers can be well understood. In the preparation, for the conventional methods, it needs to be heated to 60°C-90°C while some other processes referred to the normal temperature between 30°C-35°C need slightly warming. If the method of synthesis of poly-carboxylate superplasticizer can be changed without heating, the advantages of the original poly-carboxylate superplasticizer can be retained. In this study, it is hopefully to develop and prepare simple, low-energy and high-performance water-reducing retarding admixture with good adaptability to cement paste.

3. EXPERIMENTAL PROGRAM

With the help of economical and environmentally friendly raw materials, the non-heating method to prepare poly-carboxylate superplasticizers suited for cement was adopted in this study. The test program started with the synthesis of superplasticizer. After the synthesis, the temperature profile of the reaction and the dispersity of the superplasticizer in the cement paste were checked. Then, the saturation dosage, time-dependent flow and the best addition proportions of the prepared superplasticizers for cement paste were tested separately. Subsequently, the water content, the strength ratio, and the time-dependent flow for cement mortar were carried out.

The flow process of the experiment program is shown in **Fig.1**.



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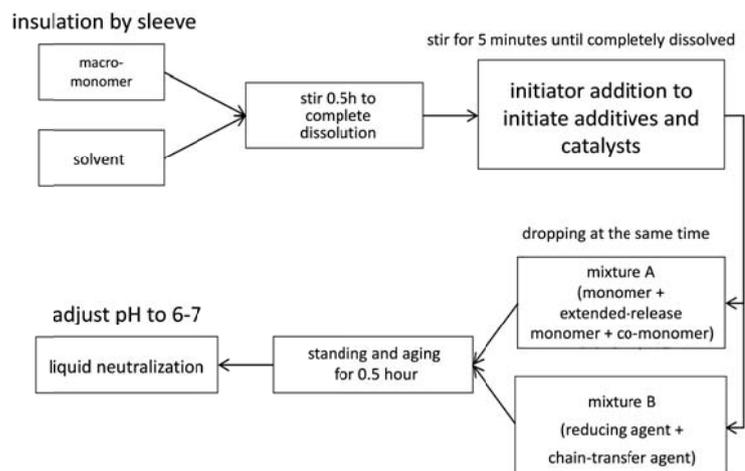
3.1 Test material

The materials used in this study are mainly based on the sources of stability, convenience, and no environmental impact. The raw materials are briefly described as follows:

- Extended-release superplasticizer : in order to extend the release effect of superplasticizer, extended-release monomer was introduced during the synthesis and the amount of monomers was reduced, and for the purpose of strengthening the oxidation reaction, initiator supplement and catalyst for the extended-release of monomers were added while the test materials included macro-monomer, deionized water, initiator, initiator supplement, catalyst, monomer, extended-release monomer, co-monomer, reducing agent, chain-transfer agent and neutralizer.
- Slump-retaining superplasticizer : in order to simplify the disposal input method, raw materials were reduced and the amount of monomer was increased to ensure that the superplasticizer has the effect of slump-retaining while the test materials included macro-monomer, monomer, chain-transfer agent, initiator, reducing agent and neutralizer.

3.2 Synthesis method

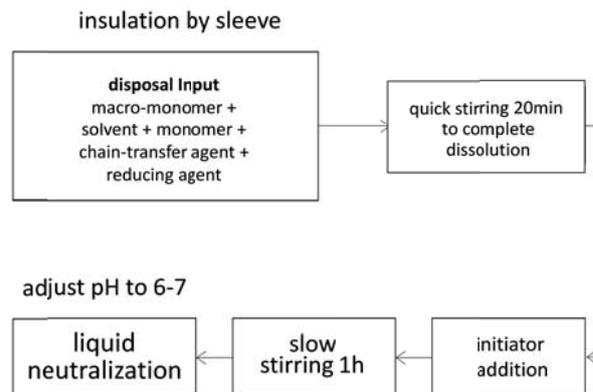
● extended-release superplasticizer (dropping method) : The reaction vessel was insulated by sleeve in the non-heating state, and the solvent and macro-monomer were put into the reaction vessel, which were the constituents of the base liquid. After stirring for 0.5 hour until completely dissolved, the initiator and catalyst were added to the base



liquid, stirred for 5 minutes to completely dissolve, and the mixed liquids A and B were added at the same time within 1 hr. The liquid A consists of monomer, extended-release monomer, co-monomer and deionized water while liquid B composed of the chain-transfer agent and reducing agent. After standing and aging for 0.5 hour, neutralizing agent was added to adjust pH value between 6 and 7. This resulted in extended-release (abbr. as **ER**) superplasticizer, and the mixing process is shown in **Fig.2**.

● **slump-retaining superplasticizer**

(disposable input method) : The reaction vessel was insulated by sleeve in the non-heating state, and the macro-monomer, the solvent, the monomer, the chain-transfer agent, and the reducing agent were thrown in once, which were the constituents of the base liquid, and the base liquid was rapidly stirred. As the macro-monomer and the reducing agent were solid, the direct addition of the initiator might affect the reaction, and the raw materials in the base liquid were stirred until completely dissolved, and then were directly put into the base liquid after about 20 minutes, and then the slow stirring lasted for 1 hour. After 1 hour, followed by the addition of the neutralization agent to adjust pH between 6 and 7, the slump-retaining (abbr. as **SR**) superplasticizer could be prepared. The mixing process is shown in **Fig.3**.



4. RESULTS AND DISCUSSION

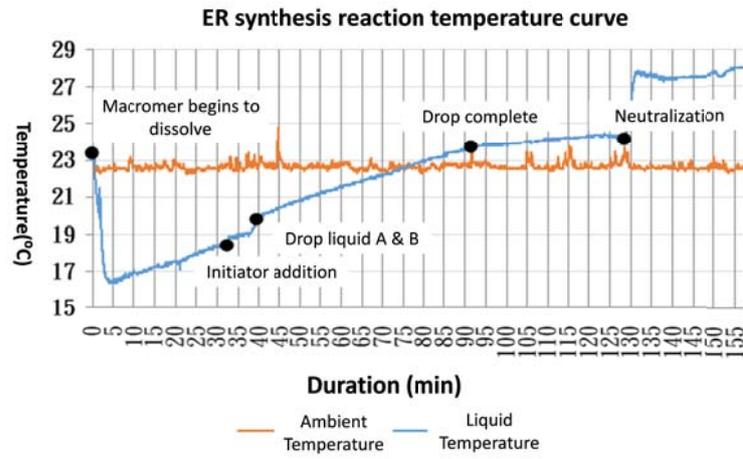
In this study, using the oxidation-reduction principle, ER superplasticizer and SR superplasticizer were prepared. The synthesis reaction temperature curves were shown in **Fig. 4&6**. Based on the standard of CNS12283, the basic physical properties including solid content and pH etc., were tested, as shown in **Table 1**. Extended-release time-dependent features of ER synthesis reaction was shown in **Fig.5** while slump-retaining time-dependent features of SR synthesis reaction was shown in **Fig.5**

From ER and SR synthesis reaction temperature profiles, it could be seen that the temperature of the solution from 60 minutes to 90 minutes exceeded the ambient temperature ($25\pm 5^{\circ}\text{C}$), and there was indeed oxidation reaction, and the reaction was completed before the addition of the neutralizing agent. The slightly lower temperature of the solution indicated that there was indeed reduction reaction.

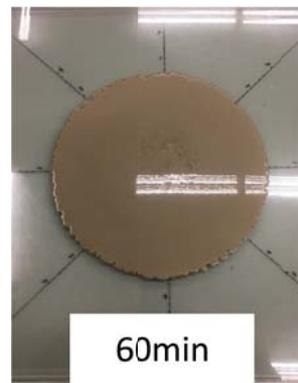
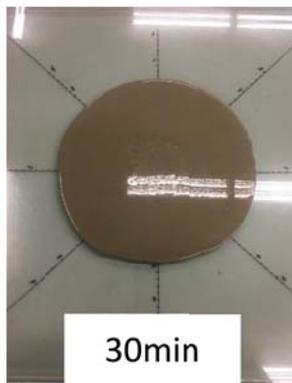
The colour of the ER superplasticizer after synthesis was yellowish as shown in **Fig.8** on the left with pH = 6.00 and solid content = 42.8% while the colour of the SR superplasticizer after synthesis was transparent and colourless as shown in **Fig.8** on the right with pH = 6.00 and solid content = 44.4%. Both synthesis processes had to be diluted to solid content of 40.0% before testing.

4.1 Test of cement paste

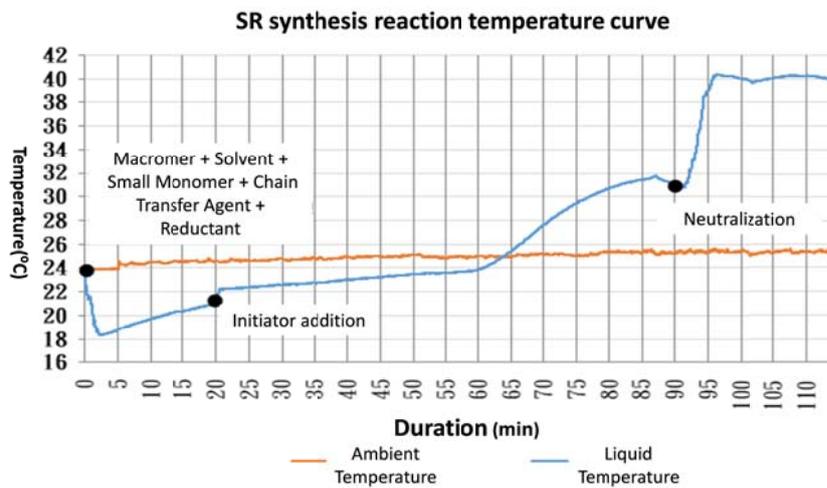
In this study, with reference to the specification (GB/T8077, 2012), the saturation dosage and the time-dependent flow of the superplasticizer in the cement paste were tested to determine the amount of cement, water and superplasticizer, as shown in **Table 2**.

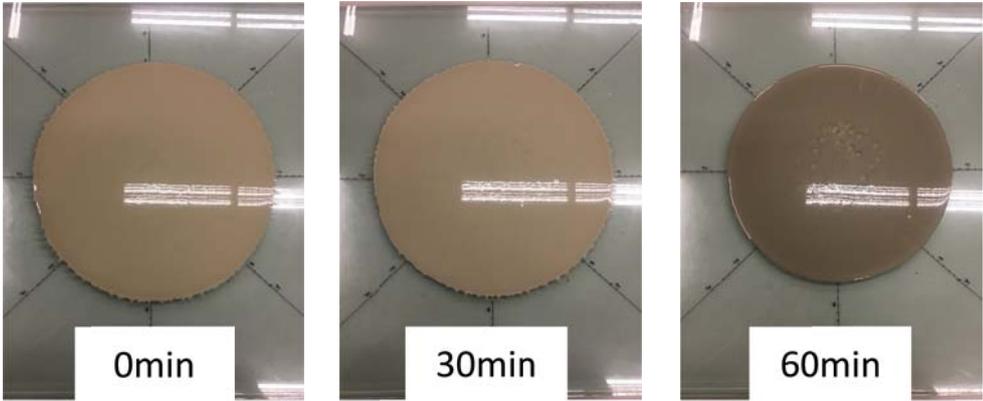


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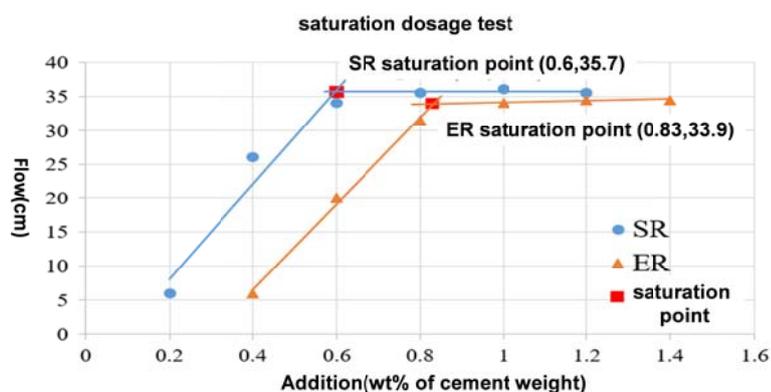
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specimen	cement (g)	w/c
saturation dosage	300	0.29
time-dependent flow	300	0.29



- Saturation dosage** : because poly-carboxylate superplasticizers were highly sensitive to water; that is, they were sensitive to changes in the addition amount, in order to investigate the influence of the saturation dosage of the superplasticizers, the corresponding tests of flow were carried out with the added amount 0.4, 0.6, 0.8, 1.0, 1.2, 1.4% of the cement weight. The test duration for ER superplasticizer was set at 60 minutes due to the initial no-flow while the measurement of the flow for SR since initial flow would be terminated if the flow no longer rises since, as shown in **Table 3**. The test results were plotted as **Fig.9**. It could be seen that, there is a section of rise in the front section and flat section in the end section, the saturation dosage of SR is 0.6% and that of ER is 0.8%; if the amount is changed to the amount of solid content of the cement weight, solid content of SR was 0.24% while solid content of ER were 0.32%.



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specimen	saturation dosage (cm)					
	0.2%	0.4%	0.6%	0.8%	1.0%	1.2%
SR	6	26	34	35.5	36	35.5
ER	-	6	20	31.5	34	34.5

specimen	cement	Time-dependent flow of paste (cm)				
		0min	30min	60min	90min	120min
SR	A	33	31.5	26	21	18.5
	B	10	9	11.5	13	13
ER	A	6	8	13	12	8
	B	6	20	25.5	25.5	22

- Time-dependent flow of paste** : In order to understand the flow expansion and fluidity retention of the superplasticizers, based on the results of saturation dosage tests, the time-dependent flow of paste were tests on two different brands of cement A&B, according to the specification (JC/T1083, 2008). The test results were shown in

Table 4. It could be seen from the test results that the dispersion effect of SR on B cement was poor. It might be that the side chains grafted at ambient temperature were shorter and denser, resulting in retarding effect, but the fluidity of the paste was not good while, for the extended-release of monomer added to ER, due to the reduction in the amount of monomer, there were no flow at 0 minutes, slow-release start at 30 minutes, the maximum flow at 60 minutes, remaining flow at 120 minutes, but its poor dispersion of cement A.

- **SR and ER Blending** : Due to the inconsistent performance and poor fluidity retention of SR and ER on different cements, the use of composite superplasticizers (by blending SR and ER) was adopted in the following experiment. In addition, a retarder (sodium gluconate) was also added as well as the use of composite superplasticizers. In this study, an experimental design method was used to set the lower limit of the test according to the test results of the cement paste fluidity test, and the extended-release and slump-retaining superplasticizer (denoted as SEG) was prepared for the tests of cement mortar.

4.2 Test of cement mortar

- **Strength ratio of cement mortar** : strength ratio of cement mortar was determined according to (CNS1010,1993). The amount of water mixed in cement mortar with superplasticizer was determined as the fluidity difference between the control group and the cement mortar without addition of superplasticizer within ± 5 mm, the amount of SEG added was 0.5% solid content of the cement weight, the test results were shown in **Table 5**, and the results of strength test of the cement mortar were shown in **Table 6**. According to the results of test water mixing, the ratio of water consumption of SEG group to that of control group could be roughly calculated to be 82%; according to the test results of strength ratio, it could be found that the compressive strength ratio of SEG to A cement for 3 days was 166%, and 7 days was 149%, the compressive strength ratio of B cement for 3 days was 157% and that for 7 days was 141%. All of these were in compliance with the requirements of (CNS 12283, 2017).

Table 5 specimen mixing water

specimen	W/C	flow(mm)
A	0.485	128
B	0.485	128
A(SEG)	0.4	124
B(SEG)	0.4	124

Table 6 strength ratio (to the compressive strength of the control group)

specimen	strength ratio (%)	
	3day	7day
A(SEG)	166	149
B(SEG)	157	141

- **Flow of the cement mortar** : in order to understand the workability of cement mortar, the proportion of cement and standard sand ratio were determined according to the related standard (CNS1010, 1993) while the amount of water consumption and

superplasticizer were decided according to the test results of strength ratio, which followed the specification (GB50119, 2013). The test results of cement mortar flow were shown in **Table 7**. It could be seen from the test results that SEG was not good for both cements, but both have fluidity at 120 minutes.

Table 7 Time-dependent flow of cement mortar

cement	Time-dependent flow of cement mortar (cm)				
	0min	30min	60min	90min	120min
A	25.5	23	20	17.5	14
B	27.5	17.5	18	17	15.5

5. CONCLUDING REMARK

- From the results of synthesis and test results, it was found that the synthesized extended-release superplasticizer was added dropwise at ordinary-temperature ($25\pm 5^{\circ}\text{C}$) without warming, and the initial fluidity of the cement paste was 6cm, and the fluidity begins to have flow of 20cm in 30 minutes. The maximum fluidity was at 25.5cm in 60 minutes and the fluidity could be maintained at 22cm for 120 minutes.
- In this study, based on the normal-temperature dropping method, the disposal-input method for synthesizing slump-retaining superplasticizer at ordinary-temperature was proposed. The features of the reaction temperature indicated the reactions to take place and the test results can be found to have disperse effect on the cement paste.
- To understand whether the superplasticizers developed in this study affect the workability and strength development of concrete, the test results showed that both the water consumption ratio and the compressive strength ratio conform to CNS12283 type G high-performance water-reducing retarder, and the slump of the cement mortar was still verified to have fluidity after 120 minutes.

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