Synthesis and sustained release mechanism of slow release polycarboxylate superplasticizer

Jian Sun, Xueyu Yin, Bo Cui, Chunyu Zhao, Guikun Miao
Shandong Lubi Building Materials Corporation Limited, Jinan, Shandong; 271103, China

Abstract. Based on the research and experiment on the mechanism of carboxylate ion protection and release, based on this system, it is determined that dimethyl carboxylic acid is the main sustained-release component, and then the sustained-release system is optimized to obtain excellent performance. A slow release polycarboxylate superplasticizer. Through the experiment of different cement compatibility, water-reducing agent saturation, concrete slump retention and mechanical properties, the dosage, working performance and strength of the target slow-release polycarboxylate superplasticizer were clarified. It is proved that the experimentally prepared sustained-release polycarboxylic acid superplasticizer has a good sustained release effect in application.

1. Introduction
With the development of the construction industry, the requirements for water reducing agents in engineering applications have been gradually improved, and polycarboxylate water reducing agents that meet different construction requirements and application characteristics have been successively developed. The slow-release polycarboxylic acid superplasticizer has the characteristics of slowly releasing its dispersion, and can achieve the effect of gradually increasing the fluidity of the concrete, thereby preventing the bleeding of the fresh concrete and ensuring good concrete construction. The work performance, and can avoid the excessive slump loss caused by high temperature transportation, ensure the work performance, mechanical properties and good durability of concrete, and is a new type of polycarboxylate water reducer that meets the special construction requirements.

2. Choice of sustained release method
The sustained-release type water reducing agent can be classified into two types: physical sustained release and chemical sustained release according to its release mechanism. The physical sustained release is mainly achieved by diffusion and osmosis. Usually, the water reducing agent is mixed with the filler to form a granule, and the slow dissolution of the granules releases the water reducing agent component during use to achieve a slow release. The physical slow release effect is affected by factors such as particle distribution and agitation, temperature, concrete mix ratio, etc., and there are certain difficulties in practical use. The chemical sustained release is achieved by breaking the chemical bond to achieve a sustained release effect.

In this study, the slow dispersion of the water reducing agent was achieved by chemical slow release method. The chemical slow release type water reducing agent can be further divided into an intramolecular reaction type and a crosslinked type. The molecule of the intramolecular reaction type
slow release water reducing agent generally contains an amide group, an acyl anhydride, an ester, and the like, which can be hydrolysed into a hydrophilic group such as a carboxylic acid in an alkaline environment, and these pros are in a gradual hydrolysis reaction. The water group continuously adsorbs and disperses the cement particles. The cross-linked slow-release type water reducing agent can directly cross-link the monomer of the double bond or the micro-crosslinking of the polymerized macromolecule through the polymerization reaction, or can also pass the coordination bond formed between the oxygen on the carboxyl group and the metal element. Ion cross-linking is the same as intramolecular reaction type. Cross-linking and slow-release also release a macromolecule with a dispersing effect by hydrolysis of the molecule in an alkaline environment, thereby achieving a sustained release effect.

3. Research and Preparation of Crosslinked Polycarboxylate Superplasticizer
Since a compound containing a lone pair of electrons can form a complex with an empty electron orbital of some cations, or an unstable covalent bond can be formed between the compounds, if the complex or covalent bond is in a strong alkaline environment of the cement slurry The lowering agent can be broken and the effective group of the water reducing agent can be released again, so that the effect of the water reducing agent slowly working can be achieved. The sample of the synthesized water reducing agent was treated with three reagents: ethylene diamine, Ca (OH)2 and Al2(SO4)3.

The experimental results show that the results of the slurry of the water-reducing agent treated with ethylene diamine, Ca (OH)2 and Al2(SO4)3 do not gradually increase, and the results of the slurry are better than those before treatment. The net pulp result is reduced, and the water reducing agent which does not obtain the sustained release effect in the experiments that have been carried out may be that the formed complex or the covalent bond does not gradually break in the alkaline environment of the cement slurry, or the third The reagent has no good complexing effect with the water reducing agent sample.

4. Effect of different carboxylic acid esters
The hydrolysis rate of the lower carboxylic acid ester is higher than that of the higher ester. The methyl carboxylate can be hydrolysed under normal temperature alkaline or acidic environment. The higher ester needs to be hydrolysed in an alkaline or acidic environment at a higher temperature. In the hydrolysis environment of the ester, the lower ester is harsh, so the carboxylate is first selected for the experiment.

4.1. Monomethyl carboxylic acid
The carboxylic acid monomethyl ester is similar to the corresponding carboxylic acid polymerization activity, so the reaction conditions are initially carried out using the corresponding optimized basic system. Therefore, the methyl propyl carboxylate and the ethyl propylene carboxylate are reacted in a single-time feeding method at 70°C for 3.0 hours; the methyl methacrylate carboxylic acid is added by adding the active monomer and APS. Adding dropwise at 70°C for 2 hours and holding for 2 hours, the effect curve of methyl methacrylate is shown in Figure 1:

![Figure 1. Effect of methyl methacrylate](image-url)
It can be seen from Fig. 1 that the addition of methyl acrylate does affect the fluidity of the cement, and the effect is most significant at a concentration of 0.12 mol, achieving a good effect.

4.2. Dimethyl carboxylic acid

Compared with the monomethyl carboxylic acid, the carboxylic acid dimethyl ester has a high ester group ratio, and the sustained release ability should be stronger. In this study, dimethyl cis-vinyl carboxylate, dimethyl trans-vinyl carboxylate and propylene-based dimethyl ester were selected for preliminary exploration experiments. The experimental ratio is TPEG: (acrylic acid + cis / trans carboxylic acid dimethyl ester / propylene carboxylic acid dimethyl ester): SMAS = 1: 3.25: 0.25, APS mass of TPEG with acrylic acid, ester and 1.5 %, the reaction temperature was 70 °C in one feeding mode, and the reaction was carried out for 3.0 hours. The dropping method was to simultaneously add a mixed aqueous solution of acrylic acid, ester, and SMAS and APS aqueous solution, and add dropwise at 70°C for 2 hours for 2 hours.

The experimental results show that dimethyl cis-vinyl carboxylate has a better sustained-release effect in the range of ester ratio of 2.0:1 to 1.0:1, and is slower than methyl propyl carboxylate and ethyl propylene carboxylate. The release ability is improved, and the trans-vinyl carboxylic acid dimethyl ester has a slower release ability than the cis-vinyl carboxylic acid dimethyl ester. The experiment also investigated the dropwise addition of cis/trans dimethyl carboxylic acid dimethyl ester, but the results were not satisfactory, indicating that the cis/trans carboxylic acid dimethyl ester was not particularly reactive.

The experimental results show that the ratio of acrylic acid to propylene dimethyl ester can reach a significant sustained release effect under the condition of 3.0-2.5, and its 2-hour flow performance is also relatively large, especially when the acid-acid ratio is 3.0. The dispersion performance has reached a relatively good level.

Compared with monomethyl carboxylic acid, the dimethyl ester of carboxylic acid contains twice as many ester groups as monomethyl carboxylic acid.

And experiments have shown that the carboxylic acid ester has the same slow release dispersion effect on the cement particles, and the effect of optimizing the sustained release of the carboxylic acid dimethyl ester by experiments should be better. Among the carboxylic acid dimethyl esters, the propylene dimethyl ester of dimethyl carboxylic acid achieves a good effect in a small proportion, and the better sustained release effect of the dimethyl carboxylic acid dimethyl ester is in the ester ratio of 2.0~ In the range of 1.0, the dimethyl propylene carboxylate can obtain a better sustained release effect at a lower acid ester ratio of 3.0 to 2.5, and the dispersion effect is good. Therefore, the propylene carboxylic acid is used in this study. The ester is optimally adjusted as a target sustained release component.

5. Research and preparation of intramolecular reaction type polycarboxylate water reducer

The carboxylic acid derivative can release the carboxylate ion by its hydrolysis in an alkaline environment, thereby gradually releasing the anchoring group of the water reducing agent to achieve a sustained release effect. Since the methyl carboxylate is similar in activity to the corresponding carboxylic acid and slightly lower than the corresponding carboxylic acid, the experiment was carried out by replacing the partial carboxylic acid with a carboxylic acid ester under the premise of an optimized basic system using the reaction conditions of the corresponding acrylic acid system.

In the mechanism study of the adsorption of polycarboxylate superplasticizer on cement particles, the carboxylate anion is an anchoring group, which is adsorbed on the cement hydrate showing positive electrochemistry, and then exerts the steric effect of the long side chain of the alkoxy group. The two synergistically achieve the role of dispersing cement particles. In the process of cement hydration, the initially adsorbed polycarboxylic acid molecules will be covered by cement particles which are gradually hydrated, and the dispersion effect will be gradually weakened. If a monomer containing a carboxylic acid ester is selected instead of a carboxylic acid monomer for copolymerization, the carboxylic acid ester on the polycarboxylic acid-based water reducing agent is gradually hydrolysed to
a carboxylic acid group to supplement the dispersed anchoring group in the polymer. Improve the purpose of reducing slump loss. The following are studies on carboxylic acid derivatives and their reaction mechanisms.

Since the applicable environment of the water reducing agent in concrete is an alkaline environment, only the alkaline hydrolysis of the carboxylic acid derivative is studied in the text. The first step of hydrolysis of the carboxylic acid derivative is the attack of the carbonyl group by the nucleophile. Therefore, the more positively the carbonyl carbon is, the smaller the steric hindrance of the attached group is, and the easier the reaction is. The second step is to eliminate the reaction. The more easily the leaving group is, the easier it is to carry out the reaction. The substitution of different electronegativity and steric hindrance effects for the carbonyl hydroxyl group causes a large change in the physicochemical properties of the carboxylic acid derivative, and the conditions and ease of hydrolysis are also different depending on the substituent group.

The specific hydrolysis conditions of the carboxylic acid derivative are as follows:

5.1. Hydrolysis of acid halide
The halide ion is a good leaving group, so the acid halide is very active and easily hydrolysed. The hydrolysis of low molecular acid halides is very violent, so most simple acid halides must be stored under anhydrous conditions, otherwise they will react with water in the air, such as acetyl chloride, which will emit smoke in humid air. The water in this hydrolysis reaction is a sufficiently strong nucleophile, so the hydrolysis of the acid halide is generally not acid catalysed.

5.2. Hydrolysis of anhydride
The anhydride can be hydrolysed in a neutral, acidic, alkaline solution. For anhydrides, water is already a strong enough nucleophile. Monohydride is insoluble in water, making it slow to hydrolyze at room temperature. If a suitable solvent is chosen to make it homogeneous, or heated to a homogeneous phase, no acid-base catalysis is required. Hydrolysis can also be carried out. The hydrolysis of the acid anhydride is slower than that of the acid halide. However, in the concrete construction, the slow release effect of the water reducing agent is required to be gradually exerted at least half an hour later, so the hydrolysis rate of the acid anhydride is still relatively fast in the application of concrete. In the actual production, a polycarboxylate water-reducing agent having high retention properties has been prepared by copolymerizing maleic anhydride with acrylic acid.

5.3. Hydrolysis of ester
The hydrolysis of the ester is usually carried out in an acid and a base. Since the ability of OR to leave is much worse than that of halogen atoms and OCOR, most of the esters cannot undergo hydrolysis when water is present. The reaction conditions of the higher ester are harsher than the lower ester, and the methyl ester can be removed by dilute base hydrolysis at room temperature.

5.4. Hydrolysis of amide
The hydrolysis conditions of the amide are much more severe than the above carboxylic acid derivatives, which require a strong acid or strong base environment and a longer heating and reflux. The hydrolysis conditions of the amide are of little value for concrete construction applications.

The ester hydrolysis reaction is better with a base as a catalyst because the base is a stronger nucleophilic reagent and easily undergoes a nucleophilic reaction with the carbonyl carbon, and the resulting carboxylic acid reacts with a base to form a salt, thereby completing the reaction. Many experiments have demonstrated that alkaline hydrolysis of esters is carried out in accordance with acyloxy bond cleavage, as evidenced by stereochmistry and tracer atomic studies. Further, when the ester formed of the carboxylic acid and the optically active alcohol is hydrolyzed, the obtained alcohol maintains the original configuration, and if alkoxide cleavage occurs during the hydrolysis, the obtained alcohol configuration completely reverses or causes racemization. Further, the ester was hydrolyzed
under basic conditions with H$_2^{18}$O. If the obtained carboxylic acid anion was found to contain $^{18}$O and the alcohol contained no $^{18}$O, it was confirmed that the acyloxy bond was broken during the hydrolysis.

6. Determination of adsorption amount
In the initial stage of hydration, a small amount of water-reducing agent molecules adsorbed on the cement particles, resulting in a small initial slump of the concrete. However, with the hydration of the cement, the adsorbed water-reducing agent molecules are gradually covered by the hydrate and lose its dispersion. At this time, the water reducing agent that has not been adsorbed to the cement particles can continue to adsorb, and the covered water reducing agent is supplemented to exert a dispersion effect, and the composition of the water reducing agent that can be adsorbed continuously increases with time, and can continue to exert its effect. The dispersion makes the dispersibility of the water-reducing agent to the cement particles gradually increase in a certain time range, which has been explained in the cement paste results.

The experiment shows that the slow-release type water reducing agent achieves the sustained release effect by the slow adsorption mechanism, and also shows that the carboxylic acid ester is continuously hydrolysed to carboxylate in this time range, so that the adsorbable water reducing dose continues to increase, and the water reducing agent the dispersion of cement particles is enhanced.

7. Determination of cement hydration heat
Cement hydration heat and its hydration rate reflect the progress of cement hydration. In general, most of the heat of cement hydration is concentrated within 3 days. Studying the performance of cement hydration heat can not only obtain important information on the hydration process of cement minerals, but also provide a scientific theoretical basis for cement concrete engineering. The hydration heat image of this experiment is shown in Figure 2.

As shown in Figure 2, the hydration heat curve of the first black line normal cement, the latter three added water reducing agent, it can be seen that the exothermic peak of muddy water was successfully delayed and the water reducing agent succeeded.

8. Conclusion
By measuring the infrared functional group of the synthetic target water reducing agent, the light scattering molecular weight measurement, the Zeta potential and the TOC total organic carbon adsorption amount, the partial microscopic properties of the water reducing agent molecules were obtained and the ratio of the raw materials to the raw materials and the reaction conditions were obtained. An analysis of the effects of molecular structure was made. In addition, the hydration process was
delayed with the increase of the amount of polycarboxylate water-reducing agent, but the degree of hydration heat release was not significantly reduced. U4, U7, PC-1, and PC-2 the effect of the carboxylic acid water reducer on cement hydration in 3 days of cement hydration is generally comparable.

References
[1] J. Plank. Synthesis and performance of methacrylic ester based poly carboxylate super plasticizers possessing hydroxy terminated poly (ethylene glycol) side chains. Cement and Concrete Research. 2017 (1): 1 - 7.
[2] Chong-Zhi Li, Nai-Qian Feng, Yong-De Li. Effects of polyethlene oxide chains on the performance of polycarboxylate-type water-reducers. Cement and Concrete Research. 2015 (35): 867 - 873.
[3] S. Chandra. Influence of superplasticizer type and dosage on the slump loss of Portland cement mortars—Part II. Cement and Concrete Research. 2015 (32): 1613 - 1619.
[4] E. Wirquin, M. Broda, B. Duthoit. Determination of the apparent activation energy of one concrete by calorimetric and mechanical means Influence of super plasticizer. Cement and Concrete Research. 2016 (32): 1207 - 1213.
[5] W. Prince, M.Espagne, Ettringite formation:A crucial step in cement superplasticizer compatibility.Cement and Concrete Research. 2016 (33): 635 - 641.