IOP Conf. Series: Materials Science and Engineering **392** (2018) 052001 doi:10.1088/1757-899X/392/5/052001

Study on Preparation of Low Hydration Thermal Polycarboxylate Superplasticizer by Low Temperature Esterification

Xingqi Guo

KZJ New Materials Group Co., Ltd. Xiamen 361101, Fujian, China

E-mail: gxq00008@163.com

Abstract: A low hydration thermal polycarboxylate superplasticizer (P-DR) is obtained by unsaturated monomer (P1) with isoprenol polyoxyethylene ether. P1 is obtained by esterification of acrylic acid with (2-Hydroxyphenyl)phosphoric acid at 70°C, having a benzene ring and a phosphate group. The experimental results show that the prepared P-DR has a higher water reduction rate and can significantly reduce the 1d hydration heat of cement.

1. Introduction

With the gradual rise of high-rise and super high-rise buildings, long-span bridge structures and industrial buildings, the dosage of mass concrete increases year by year. Hydration of cement minerals is an exothermic reaction, and the thermal conductivity of concrete is low. Mass concrete that generated heat of hydration causes the internal temperature of the concrete to rise rapidly. Due to the heat dissipation from the exterior of the concrete, a temperature gradient forms between the inside and the outside of the concrete, resulting in a large temperature stress and temperature cracks[1].

At present, retarder is mainly used to extend the heat release process of cement to reduce the heat of cement hydration. There are also slump retention agents used to achieve the reduction of cement hydration heat. [2,3]。However, the use of retarder and slump retention agent in concrete is small, and the resulting effect is limited. There is a need to develop a polycarboxylate superplasticizer with a dual function of water reduction and hydration heat reduction to prevent excessive heat concentration of concrete hydration, reduce the temperature stress of concrete, reduce cracks in concrete, and extend the service life of concrete.

2. Experimental

2.1. The main experimental raw materials

Acrylic acid(AA),Industrial grade. (2-Hydroxyphenyl) phosphoric acid(HPP),Industrial grade. Periodic acid,Industrial grade. Hydroquinone(HQ),Industrial grade. Isoprenol polyoxyethylene ether(TPEG), Molecular mass 2400,Industrial grade. Cement(C): Min Fu P.O 42.5 Cement. Commercial polycarboxylate superplasticizer(PCE): Solid content is 40%.

2.2. Esterification

Add metered amounts of acrylic acid, (2-Hydroxyphenyl) phosphoric acid, and hydroquinone to a four-neck bottle, open nitrogen gas device, raise the temperature to 50°C, add measured periodic acid,

IOP Conf. Series: Materials Science and Engineering **392** (2018) 052001 doi:10.1088/1757-899X/392/5/052001

slowly warm to reaction temperature, keep constant temperature for a certain time, cool down and pour the materials which is brought out of the bottle by nitrogen into the bottle to get P1.

2.3. Performance test method

2.3.1. Cement paste fluidity determination

Cement paste fluidity according to GB/T8077-2012 "Concrete admixture homogeneity test method" was carried out, W/C was 0.29, polycarboxylate superplasticizer solid dosage 0.12%.

2.3.2. Gel chromatography test

Use US Waters 1515 Isocratic HPLP pump/Waters 2414 differential detector and Breeze software acquisition and analysis system. The column was connected in series with UltrahydragelTM250 and UltrahydragelTM500. The mobile phase was a 0.1 mol/L aqueous solution of sodium nitrate (containing 0.05% sodium azide), degassed in advance through a 0.22 μm microporous membrane, and degassed by sonication. The mobile phase flow rate was 0.8 mL/min. Injection volume was 200 μL. Column temperature was 40°C. Deutererator internal temperature was 40°C.

2.3.3. Esterification rate test

The acid value before and after the esterification was measured by acid-base titration, and the esterification rate was calculated based on the change in the acid value.

2.3.4. Double bond retention test

Weigh a suitable amount of sample in a 250 mL iodine flask, add 20 g of deionized water as a solvent, add 5 mL of methanol, shake and dissolve. Continue to add 10mL potassium bromide-potassium bromate solution with a potassium bromide concentration of 0.09mol/L and 5mlL 1+1 hydrochloric acid solution, cover the ground stopper, place in a dark place for 5min, shake the iodine bottle constantly, and then add 10ml 10 % Potassium iodide solution, close the stopper and place it for 20 minutes. At the same time blank test. Titrate with 0.1 mol/L sodium thiosulfate standard solution to pale yellow, add 2~3 drops of 1% starch indicator (the solution turns dark tan), titrate to colorless to the end point. The double-key value is calculated as follows:

$$x = \frac{cV_0 - cV}{2m}$$

In the formula:x–The double bond value per gram of sample,mmol/g.

c–The concentration of $Na_2S_2O_3$,mol/L.

V–Titrate the amount of $Na_2S_2O_3$ required for a given amount of sample, mL.

V_0–Titrate the amount of $Na_2S_2O_3$ required for the blank sample, mL.

m–The amount of sample taken,g.

The double bond retention rate of the esterified sample is calculated as follows:

$$r = \frac{x_1}{x_0} \times 100\%$$

In the formula:r–Sample double bond retention,%.

x_0–The double bond value per gram of sample before esterification, mmol/g.

x_1–The double bond value per gram of sample after esterification, mmol/g.

2.3.5. Hydration heat test

The hydration heat test was conducted in accordance with GB/T12959-2008 "Cement hydration heat determination method".

3. Experimental results and discussion

3.1. Effect of esterification catalysts on esterification rate

To increase double bond retention, the catalyst is preferred at a lower esterification temperature of 70°C. The amount of fixed catalyst was 1.0% of the sum of the mass of acrylic acid and (2-hydroxyphenyl) phosphoric acid. Other experimental conditions are the same. Different types of catalysts are used to study the influence of the type of catalyst on the esterification rate. The experimental results are shown in Table 1:

Table 1. Effects of catalyst types on properties of esterification products

Catalyst type	Esterification rate(%)
Blank	65
Sulfuric acid	86
p-Toluenesulfonic acid	84
Dodecyl benzene sulfonic acid	83
Periodic acid	92

From the experimental results in Table 1, it can be seen that at 70°C, periodic acid has a better catalytic effect on the esterification reaction than other currently used esterification catalysts, resulting in the highest esterification rate of the product. Therefore, periodic acid is selected as the esterification catalyst.

3.2. Effect of the amount of polymerization inhibitor on the retention of double bonds

Other experimental conditions keep unchanged. The amount of polymerization inhibitor used in the esterification reaction was adjusted to study the effect of the amount of polymerization inhibitor on the retention of the double bond. The amount of polymerization inhibitor is expressed as a percentage of the total mass of acrylic acid and (2-hydroxyphenyl) phosphoric acid. The experimental results are shown in Figure 1:

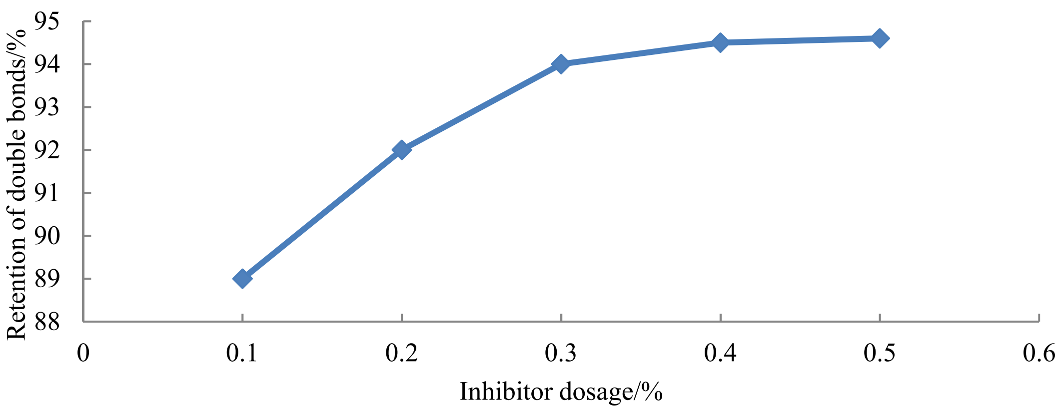

Figure1. Effect of the amount of polymerization inhibitor on the retention rate of double bonds.

As shown in Fig.1, with the increase of the amount of polymerization inhibitor, the double bond retention rate of the esterification product gradually increased and then stabilized. This is because the polymerization inhibitor can prevent the copolymerization of acrylic acid when heated which can consume its double bond, so the addition of the polymerization inhibitor is beneficial to improve the retention rate of the double bond. When the amount of polymerization inhibitor is 0.3%, its amount is enough to control the retention rate of the double bond in a relatively high range, continue to increase the amount, and the contribution of the retention rate of the double bond is not obvious, and the excessive addition thereof will also affect follow-up copolymerization, so choose the amount of polymerization inhibitor to be 0.3%.

IOP Conf. Series: Materials Science and Engineering **392** (2018) 052001 doi:10.1088/1757-899X/392/5/052001

3.3. The effect of esterification time on esterification rate and double bond retention.

The other experimental conditions were fixed and the esterification reaction time was adjusted. The effect of esterification reaction time on esterification rate and double bond retention rate was studied. The experimental results are shown in Figure 2:

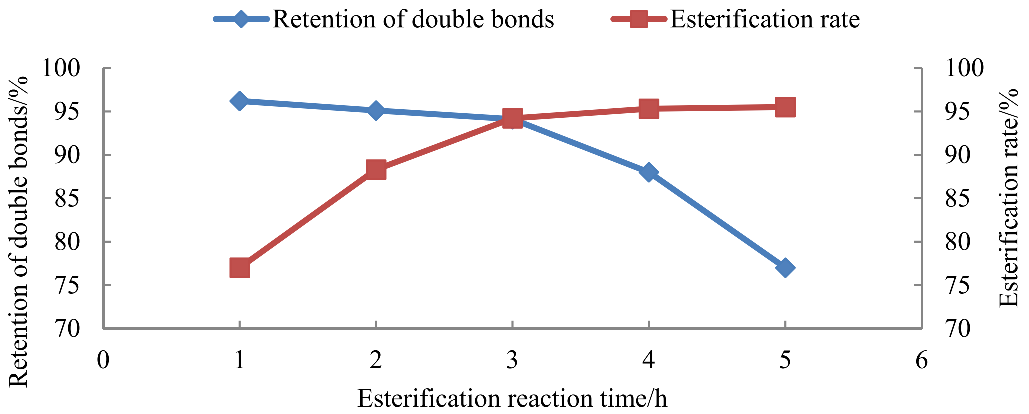

Fig.2. Effect of esterification time on esterification rate and double bond retention.

As shown in Fig.2, as the esterification reaction time is prolonged, the esterification rate gradually increases, and the double bond retention rate gradually decreases. This is mainly because the longer the reaction time is, the more water is carried out by nitrogen gas, which is more beneficial to increase the esterification rate. However, the longer the esterification time was, the higher the probability of the double bond of acrylic acid being reacted out, and the retention rate of the double bond gradually decreased. Therefore, considering the two factors of the esterification rate and the retention rate of the double bond, 3 h is selected as the esterification time.

3.4. Influence of molar ratio of acrylic acid and (2-hydroxyphenyl) phosphoric acid on esterification rate

The other experimental conditions were fixed and the molar ratio of acrylic acid and (2-hydroxyphenyl) phosphoric acid was adjusted to study the effect of the molar ratio of acrylic acid and (2-hydroxyphenyl) phosphate on the esterification rate. The experimental results are shown in Figure 3:

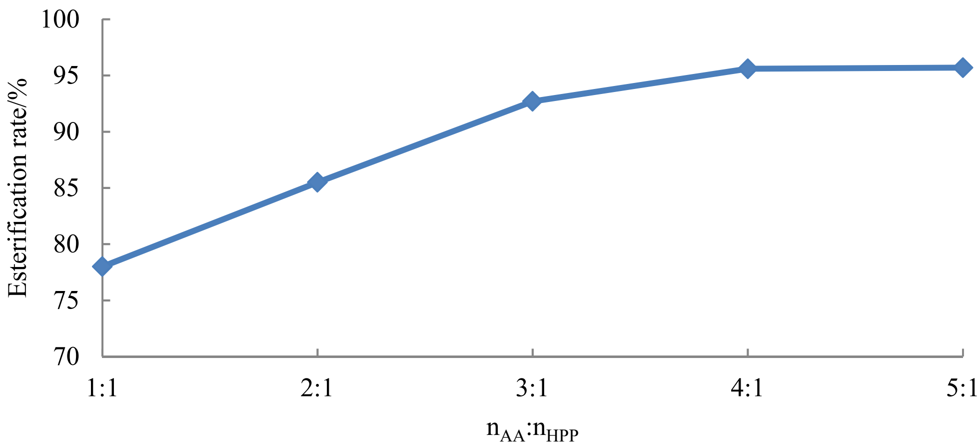

Figure3. Effect of molar ratio of acrylic acid and (2-hydroxyphenyl) phosphoric acid on esterification rate.

As shown in Figure3, as the molar ratio of acrylic acid to (2-hydroxyphenyl) phosphoric acid increases, the esterification rate also gradually increases and then stabilized. This is because the esterification reaction is a reversible reaction, and the excess of acrylic acid favors the shift to the esterification direction, thereby increasing the esterification rate. When nAA:nHPP exceeds 4:1, the continuous increase in nAA:nHPP does not greatly contribute to the improvement of the esterification rate, so 4:1 is selected as nAA:nHPP.

3.5. Preparation and performance test of low hydration thermal polycarboxylate superplasticizer P-DR

The esterification catalyst is periodic acid, and the amount used was 1.0% of the sum of the mass of acrylic acid and (2-hydroxyphenyl) phosphoric acid. The polymerization inhibitor was hydroquinone, and the amount used was 0.3% of the sum of the mass of acrylic acid and (2-hydroxyphenyl) phosphoric acid. Esterification reaction temperature is 70 ° C. Esterification reaction time is 3h. The molar ratio of acrylic acid to (2-hydroxyphenyl) phosphoric acid is 4:1 during esterification. The esterified monomer P1 was obtained by esterification reaction, and P1 and TPEG were copolymerized to prepare low hydration thermal polycarboxylate superplasticizer P-DR. Test the paste fluidity and 1d heat of hydration of P-DR and PCE. Test results are shown in Table 2:

Table 2. comparison of P-DR and PCE performance

Sample	Cement paste fluidity /mm	1d heat of hydration/J•g-1
PCE	263	236
P-DR	298	153

As shown in table 2, the cement paste fluidity and 1d hydration heat of P-DR are significantly better than that of PCE. It shows that P-DR has a higher water reduction rate and can significantly reduce the 1d heat of hydration of cement.

4. Conclusions

At 70°C, periodic acid has a better effect on the esterification reaction than other esterification catalysts, resulting in the highest esterification rate of the product.

With the increase of the amount of polymerization inhibitor, the double bond retention rate of the esterification product gradually increased and then stabilized. Taking into account that too much polymerization inhibitor will affect the subsequent copolymerization, so choose the amount of polymerization inhibitor to be 0.3%.

As the esterification reaction time is prolonged, the esterification rate gradually increases, and the double bond retention rate gradually decreases. Therefore, considering the two factors of the esterification rate and the retention rate of the double bond, 3 h is selected as the esterification time.

As the molar ratio of acrylic acid to (2-hydroxyphenyl) phosphoric acid increases, the esterification rate also gradually increases and then stabilized. When nAA:nHPP exceeds 4:1, the continuous increase in nAA:nHPP does not greatly contribute to the improvement of the esterification rate, so 4:1 is selected as nAA:nHPP.

A low hydration thermal polycarboxylate superplasticizer P-DR was synthesized from P1 and TPEG. P-DR has a higher water reduction rate and can significantly reduce the 1d heat of hydration of cement.

References

[1] Yuchao Wan. Research Progress of Mass Concrete [J]. China Concrete, 2016(6):70-72.
[2] Maximilienne Bishop，Simon G Bott，Andrew R Barron. A new mechanism for cement hydration inhibition ： solid-state chemistry of calcium nitrilotris (methylene) triphosphonate[J].Chem. Mater.，2003，15：3074-3088.
[3] Guo X Q. Synthesis, Properties and Engineering Applications of Green Energy-Saving Slump

IOP Conf. Series: Materials Science and Engineering **392** (2018) 052001 doi:10.1088/1757-899X/392/5/052001

Retaining Agent[J]. Advanced Materials Research, 2013, 671-674:1923-1927.