Synthesis and Properties of Multi-arm Polyether Polycarboxylic Superplasticizer

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Abstract

Pentaerythritol was esterified with acrylic acid (AA) to produce PETA, a multi-arm star esterified intermediate. APEG was used as the large monomer, PETA was copolymerized with AA and maleic anhydride (MAH) to obtain multi-arm polyether polycarboxylic superplasticizer. The optimum molar ratio of raw materials was AA: APEG: MAH: SMAS= 4:1:1.2:1.2 through orthogonal experiment and parallel experiment. The amount of initiator is 0.15% of the mass of monomers.At the same time, the effects of polymerization temperature on the performance of the superplasticizer were investigated. When the dosage of superplasticizer is 0.2% and the water-cement ratio is 0.29, the fluidity of cement paste reaches 290mm. Compared with the conventional using only APEG and AA, the mortar fluidity with the superplasticizer is significantly improved, and the fluidity retention time is longer. The new multi-arm polyether type superplasticizer has good dispersibility.

Keywords

Surperplasticizer; Polyether; Multi-arm; Maleic anhydride; Fluidity.

1. Introduction

Surperplasticizer is one of the important concrete additives, which can reduce the water cement ratio and the water consumption, improve the rheological properties of concrete mixture, strength and durability. In recent years, polycarboxylic acid series superplasticizer has been developed as the third generation, among which polyether type superplasticizer is an important product. Its comb structure is adsorbed on the cement particles and blocks the proximity of other cement particles, resulting in fluidization of cement slurry [1]. Under the comprehensive effect of electrostatic repulsion and steric effect, it has the advantages of high water reducing rate and good slump retention. In recent years, it has become a hot spot of research and development at home and abroad [2,3].

At present, the synthesis of polycarboxylic acid surperplasticizer is mainly based on APEG, TPEG and MPEG. Considering conversion rate, water reduction rate, production cost and other factors, APEG has a broader prospect because of its advantages[4]. At present, the main way to prepare surperplasticizer with macromonomer APEG is to copolymerize it with (methyl) acrylic acid [5], which can improve the slump retention property , but it will reduce the water reducing rate and the product performance is not stable[6].

Polymer with multi arm structure has been widely concerned because of its unique structure, performance and potential application, but there are few reports in the field of superplasticizer[7-9]. We used acrylic acid to react with pentaerythritol to produce pentaerythritol tetraacrylate (PETA).Then APEG2400， AA and MAH were added to synthesize the multi arm polyether polycarboxylic acid superplasticizer NPCE. Study and analyze the optimum monomer ratio and polymerization process , the properties of the multi arm structure superplasticizer.

2. Experimental

2.1 Experimental materials and instruments

2.1.1 Materials

Allyl polyoxyethylene ether (APEG2400), industrial grade. Acrylic acid (AA), analytical pure. Maleic anhydride (MAH), analytical pure.Pentaerythritol, analytical pure. Ammonium persulfate (PSAM), analytical pure.Sodium methacrylate sulfonate (SMAS), analytical pure. Sodium hydroxide, analytical pure. Deionized water.

Cement PO42.5. Sand, fineness modulus is 2.7.Gravel, particle size 2.5-31.5mm continuous grading.General polyether type superplasticizer SPCE, control group.

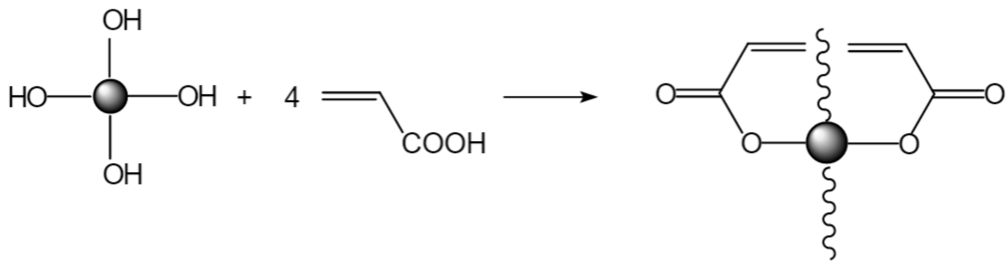
2.1.2 Instruments

JJ-1 electric mixer, constant temperature water tank, cement paste mixer, concrete mixer, VERTEXT 80V infrared spectrometer.

2.2 Synthesis of superplasticizer.

2.2.1 Water reducing agent synthesis process

Add PETA and AA solution to a four-neck round-bottom flask with a stirrer.Then add the catalyst, continue stirring and heating to generate a multi arm esterification product PETA. The synthesis schematic diagram is shown in Figure 1.



 Represents the chemical structure of pentaerythritol except hydroxyl.

Fig. 1 Synthesis of PETA intermediate.

After esterification, APEG2400 and maleic anhydride are added into the feed once. Heat to dissolve the raw material, stir continuously and raise the temperature to 65 ℃. Equip two constant pressure funnels to the device and add AA and PSAM solution.Add an hour under the premise of controlling the dropping speed, then raise the temperature to 80 ℃, and react for 6 hours at the constant temperature.The NaOH aqueous solution was used for adjusting the pH value to 6-7 followed by cooling to room temperature after reacting.Finally the surperplasticizer was obtained. The synthesis process is shown in Figure 2.

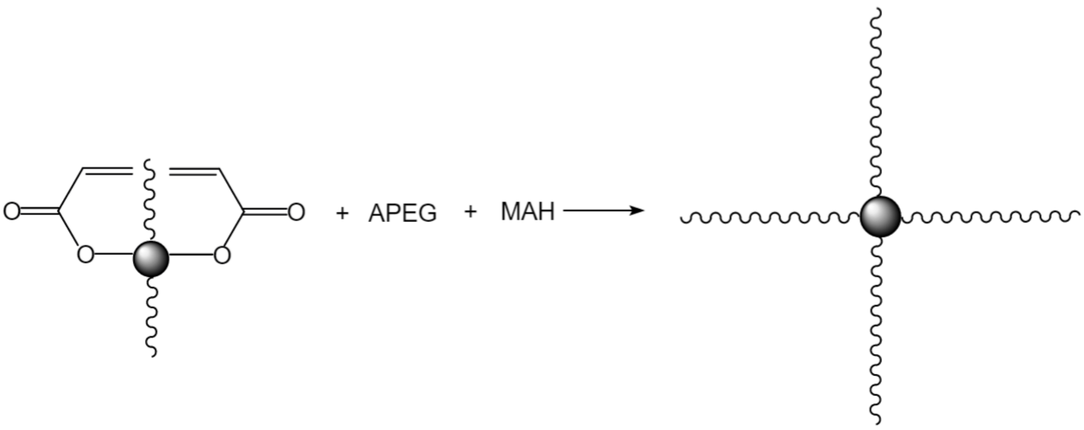


Fig. 2 Synthesis diagram of surperplasticizer

In Fig. 2, part (a) of the product is an arm like branched chain of a multi arm compound, which is condensed by acrylic acid AA, APEG and MAH, its schematic structure is shown in Fig. 3.

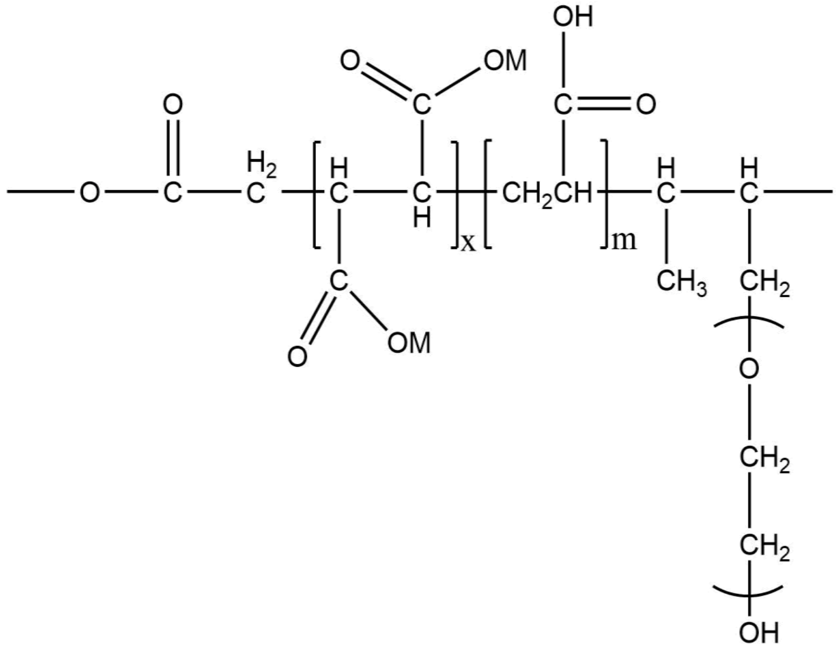


Fig. 3 Structural diagram of long arm of multi arm superplasticizer

2.2.2 Orthogonal experimental design of synthetic proportion of superplasticizer

All the solutions in the experiment are prepared into 20% aqueous solution. Study the effects of chain transfer agent SMAS, small monomer AA, large monomer APMG and small monomer MAH on the properties of polymer products. Selecte four factors and three levels in the orthogonal experiment design. The orthogonal experiment design of L_9 (3^4) was adopted. See Table 1 for details.

Table 1 L_9 (3^4) orthogonal experiment table

Facters	Level 1	Level 2	Level 3
Molar fraction of SMAS/mol	0.5	1	1.5
Molar fraction of AA/mol	3	5	7
Molar fraction of APEG/mol	1	1.25	1.5
Molar fraction of MAH/mol	1	1.5	2

Note: the molar fraction is the ratio of the mole number of the substance to the total mole number of the raw material.

2.2.3 Determination of solid content

Weigh the fully dried watch glass with a balance accuratly, weigh 5g of sample into the watch glass.Place it in a constant temperature drying oven, then dry it at 105 ° C for 8h to constant weight, and calculate its solid content as follows:

$$\text{Solid content} = \frac{\text{Sample quality}}{\text{Samplin}} \times 100\%$$

2.2.4 Product analysis and performance testing

The fluidity and water reducing rate of cement paste were tested according to GB8077-2000. The water-cement ratio was 0.29, and the amount of superplasticizer was 0.2%.

Carry out the concrete slump test according to GB8076-2008.

Test the mechanical properties of concrete according to GB / T50081-2002.

Apply the sample to the KBr tablet for infrared testing.

3. Results and discussion

3.1 Orthogonal test results and analysis

Record the initial fluidity of the cement paste and the fluidity at 60 minutes according to the ratio in the table. The experimental results and analysis details are shown in Table 2.

Table 2 Orthogonal test design and range table

Number	Molar fraction of SMAS/mol	Molar fraction of AA/mol	Molar fraction of APEG/mol	Molar fraction of MAH/mol	Initial fluidity / mm	60 minutes fluidity / mm	Quantified total value *
1	0.5	3.0	1.00	1.0	/	/	0
2	0.5	5.0	1.25	1.5	270	245	8
3	0.5	7.0	1.50	2.0	210	/	3
4	1.0	3.0	1.25	2.0	295	275	8
5	1.0	5.0	1.50	1.0	130	/	1
6	1.0	7.0	1.00	1.5	260	190	7
7	1.5	3.0	1.50	1.5	290	280	8
8	1.5	5.0	1.00	2.0	295	280	8
9	1.5	7.0	1.25	1.0	/	/	0
R	1.7	2.3	1.30	7.3	/	/	/

*Note: It is divided into corresponding scores of 1, 2, 3 and 4 according to the fluidity of cement paste 100-150, 150-200, 200-250 and 250-300; the quantized total value is the sum of the scores of initial fluidity and 60 minute fluidity.

The fluidity of the clean slurry reflects the dispersity. After the superplasticizer are added to the cement, they are directionally adsorbed on the surface of the cement. So that they have the same charge and generate electrostatic repulsion. The fluidity of the cement slurry increases because the cement particles change from agglomerated state to dispersed state, the flocculation structure is destroyed and the water wrapped in the flocculation center is released.

It can be seen from the analysis of range result that the amount of AA influences the dispersibility of superplasticizer. The larger the amount is, the lower the dispersibility is. Due to the increase of molecular weight of polymer, the increase of AA will increase the viscosity and the dispersion through the number of superplasticizer molecules per unit mass reducing. The difference between 60 minute and initial fluidity reflects the retention of superplasticizer fluidity, which is related to the gel action of superplasticizer. The increase of SMAS will not only increase the dispersity, but also affect the gelation [10]. The more the amount of superplasticizer is, the lower the adhesion and mobility will be. Because the chain transfer effect is too strong and the polymerization degree of the product becomes smaller due to the excessive amount of SMAS. Appropriate MAH can improve the retention of superplasticizer molecules on the dispersion of cement paste particles. Because anhydrides will gradually hydrolyze into dicarboxylic groups in a weak alkaline environment, giving the superplasticizer stronger polarity. So that it has a slow-release function. However, the molecular polarity will be too large along with large MAH content. It is not conducive to maintaining the repulsive force between the molecules of superplasticizer, so as to reduce the water reducing effect. Carboxyl group and sulfonic group can improve the steric resistance effect of superplasticizer. They can improve the fluidity of cement paste by forming a layer of solvated water film with lubrication effect on the surface of cement particles. Comparing the four factors, we can see that D is the main factor. A, B, C is the secondary factor, the best combination is A3, B2, C2, D2, so the best molar ratio of AA: APEG: MAH: SMAS is 4.0:1.0:1.2:1.2.

3.2 Effect of initiator dosage on the performance of superplasticizer

Under the conditions of n (AA): n (APEG): n (MAH): n (SMAS) = 4.0:1.0:1.2:1.2 and polymerization temperature of 80 ℃, investigate the effect of initiator dosage on the performance of superplasticizer. The results are shown in Figure 3.

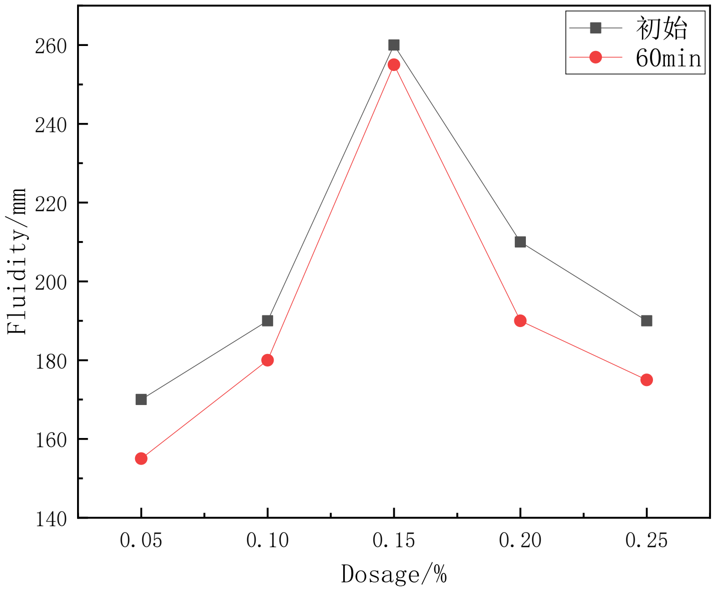


Fig. 3 Effect of initiator dosage on performance of surperplasticizer

It can be seen from Figure 3 that the fluidity increases first and then decreases with the increase of initiator dosage, because the proper amount of initiator can effectively improve the conversion rate of monomer. But when the initiator dosage is too large and the initiation efficiency is high, the explosive polymerization may occur, so as to reduce the molecular weight of the polymer. Finally have a negative impact on the performance.

3.3 Effect of polymerization temperature on properties of superplasticizer.

Under the condition of n (AA): n (APEG): n (MAH): n (SMAS) = 4.0:1.0:1.2:1.2, the initiator amount accounts for 0.15% of the mass of monomer, investigate the effect of polymerization temperature on the performance of surperplasticizer. The results are shown in Figure 4.

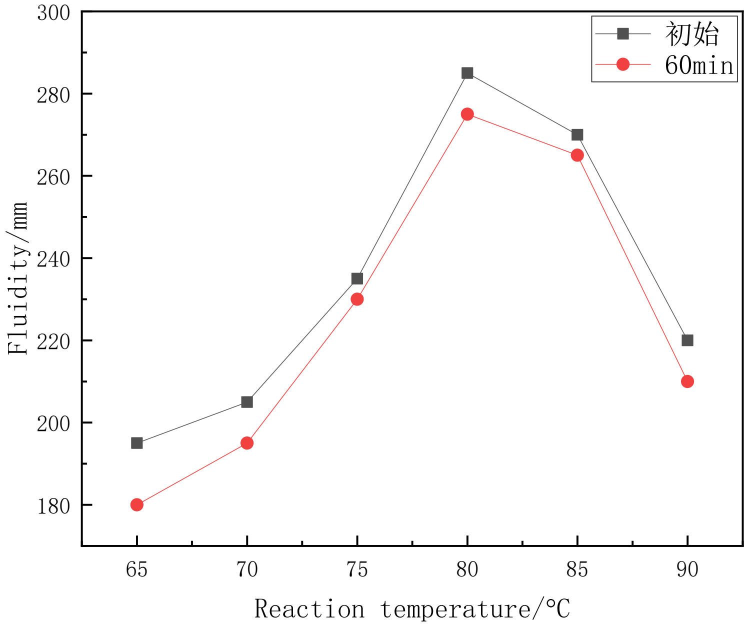


Fig. 4 Effect of polymerization temperature on properties of superplasticizer

The polymerization temperature affects the molecular weight of the product and produces side reactions. It can be seen from Fig. 4 that the fluidity of the surperplasticizer puree is the largest at 80 ℃, and the fluidity first increases and then decreases with the increase of temperature. Because the initiator efficiency is low when the temperature is low, the residual amount of the initiator is large, the concentration of free radicals is low, which leads to the low monomer conversion rate. And finally slow or even impossible polymerization. When the temperature is too high, the initiator decomposes quickly. It leads to the lack of sufficient initiator and the increase of side reactions. There may be polymerization of AA at high temperature, which makes it difficult to copolymerize with large monomers, and finally affects the dispersion of superplasticizer.

3.4 IR spectrum analysis of water reducing agent.

The polyether type surperplasticizer NPCE, which is prepared by adopting the optimal molar ratio reaction. Infrared test it. The results are shown in Fig. 5.

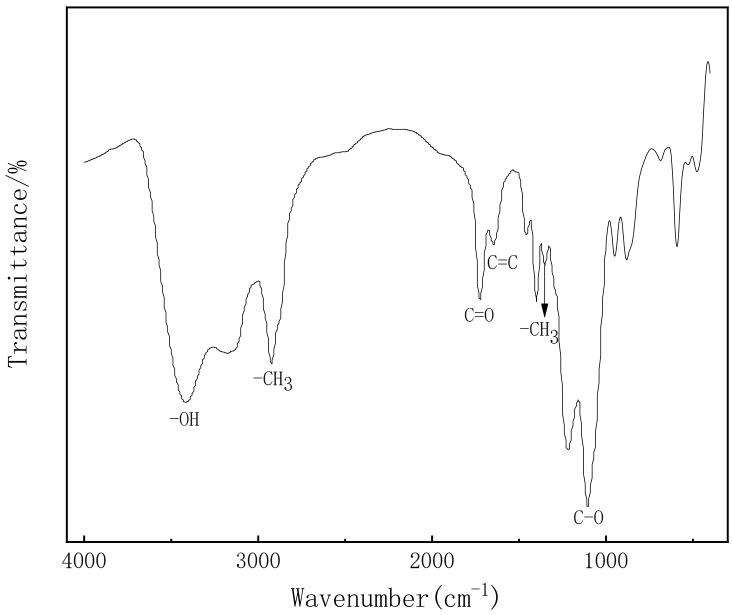


Fig. 5 IR spectrum of polyether surperplasticizer

The peak of 2923.49 cm^{-1} to the vibration corresponding to C-H may come from the end of the product side chain and the chain segment of polyoxyethylene $-CH_2CH(CH_3)O-$ and the carbon skeleton of the main chain $-CH_2CH_2-$. In addition, 1727.13 cm^{-1} corresponds to the stretching vibration of carbonyl C = O of unsaturated carboxylic acid ester [10], which proves that there is ester group in the synthesis. The peak of 1352.32 cm^{-1} is the bending vibration of methyl $-CH_3$. The peak of 1106.62 cm^{-1} is the stretching vibration peak of ether C-O. The peak of 3417.21 cm^{-1} corresponds to the stretching vibration O-H of associated carboxylic acid [11]. The peak of 1649.28 cm^{-1} is the stretching vibration double bond C = C. The analysis shows that the synthesized superplasticizer contains hydroxyl, carbonyl, ether and other functional groups. It is confirmed that the copolymerization between the monomers has taken place and the expected polyether type superplasticizer has been formed.

3.5 Performance of water reducing agent.

The surperplasticizer prepared by NPCE is a light yellow liquid with solid content of 19.4%. Test NPCE for cement paste according to the national standard. The initial fluidity of cement paste reflects the adsorption, fluidity and construction performance of water reducing agent in the early stage of cement hydration. When the number of water reducing agent molecules adsorbed on the surface of cement particles is more, the fluidity of cement paste is better. However, the bleeding volume of the cement paste should also be considered when the fluidity is improved. When NPCE content is 0.2% and water cement ratio is 0.29, the initial net slurry fluidity of cement can reach 290mm. After 60 minutes, the net slurry fluidity of cement can be reduced to 270mm, and the bleeding water volume is very low. It can be seen that the multi arm polyether type superplasticizer makes the net slurry of cement have excellent fluidity and strong fluidity retention, which meets the engineering requirements

To test the application performance of concrete , NPCE water reducing agent is selected to compare with a common polycarboxylic acid water reducing agent SPCE.The concrete mix ratio is cement: Sand: Stone: water = 380:770:1090:168 (kg / cm^3), and the water reducing agent content is 0.2%. The application performance of concrete is shown in Table 3.

Table 3 Performance data of concrete

Name of water reducing agent	Water cement ratio	Water reduction rate /%	Slump / expansion / mm		Compressive strength / MPa	
			0	1h	7d	28d
NPCE	0.442	30.9	227/615	223/612	55.6	64.3
SPCE	0.442	27.5	210/610	205/606	49.6	58.7

It can be seen from table 3 that the water reducing rate and slump data of NPCE are higher than those of SPCE, and the slump loss is small, and the 28d compressive strength is greatly improved, so the performance of NPCE water reducing agent is better than that of commercial water reducing agent.

4. Conclusion

(1) Using pentaerythritol and acrylic acid as raw materials to form the intermediate of multi arm through esterification, and then copolymerize it with AA, APEG and MAH to prepare multi arm polyether surperplasticizer. IR spectrum test showed that the expected structure was formed.

2) Orthogonal and parallel experiments determine the optimal reaction ratio n (AA): n (APEG): n (MAH): n (SMAS) = 4.0: 1.0: 1.2: 1.2, the amount of initiator is 0.15% of the monomer.

3) Mix the product with cement at a dosage of 0.2%. Under the condition of water-cement ratio of 0.29, the initial fluidity of cement paste reached 290mm, and the fluidity of the paste and the slump retention of the mixed concrete are strong. Performance is better than commercially ordinary polycarboxylic acid surperplasticizer.

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