Research on synergistic optimization of preparation of polycarboxylate superplasticizer

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Abstract: To optimize the preparation process of the PCEs, this paper studied the synergistic effect of the three parameters of initiator dosage, synthesis temperature and synthesis time on the viscosity and the performance of the PCEs. The results showed: (1) For the viscosity of the PCEs, when the synthesis temperature was high, the viscosity could be improved by reducing the initiator dosage or by extending the synthesis time; When the synthesis temperature was low, the viscosity could be improved by increasing the amount of initiator dosage or shortening the synthesis time appropriately. At the same time, these three parameters had a similar synergistic relationship with the performance of the PCEs. (2) Through kinetic factors, establish a process model of these three parameters and the viscosity of the PCEs: \[ \eta = 2.97 \times e^{5.85 \times t \times m^{-1}}. \] The model provided a theoretical basis for the optimization of the preparation process of the PCEs. (3) When the viscosity of the PCEs was in the range of 200-370 mPa*s, its effect on cement dispersibility was better.

1 Introduction

PCEs is widely used in modern concrete engineering because of its high water-reducing rate, high dispersion and green environmental protection¹⁻². Therefore, the preparation of the PCEs with excellent performance has always been a hot spot in the construction industry.

Zhao et al. [³] studied the effect of different initiator systems on the performance of the PCEs. The results showed that when ammonium persulfate was used as the initiator, maleic anhydride was more suitable as a small monomer. When ammonium persulfate and hydrogen peroxide were used as the initiator system at the same time, it was more appropriate to choose acrylic acid as the small monomer. Wang [⁴] studied the effect of synthesis time on the performance of the PCEs. The results showed that the fluidity of the cement paste was enhanced first and then decreased with the increase in synthesis time. Hideo Ogawa et al. [⁵] studied the effect of synthesis temperature on the performance of the PCEs. Studies showed that too high a temperature would cause the polymerization rate to be too fast, resulting in agglomeration; and too low a temperature would reduce the monomer conversion rate. However, the preparation process of the PCEs is complicated, and the process parameters that affect the performance of the PCEs will interact, thereby affecting the polymerization reaction process. Therefore, it is necessary to find the mutual influence relationship between them and carry out coordinated regulation.

During the preparation of the PCEs in the laboratory, it was found that the synthesis temperature, synthesis time and the initiator dosage had a significant effect on the performance of the PCEs, and there
was a certain synergy between the three. Therefore, by exploring the synergistic law of multiple factors, this paper transformed qualitative analysis into quantitative analysis, and conducted a synergistic optimization study on the preparation process of the PCEs. The relationship between the viscosity and performance of the PCEs was also found, and the process parameter model was established.

2 Experiment

2.1 Experimental raw materials
(1) Methylallyl polyoxyethylene ether: industrial grade, produced by Nanjing Yangtze-Auck Company
(2) Acrylic acid: industrial grade, produced by Shanghai Maclean Biochemical Technology Co., Ltd.
(3) Azobisisobutylamidine hydrochloride: industrial grade, produced by Shanghai Yihe Biological Co., Ltd.
(4) Cement: Nanjing Xiaoyetian PꞏII52.5 cement

2.2 Experimental mix ratio
Using PꞏII52.5 cement produced by Nanjing Xiaoyetian with a water-cement ratio of 0.29. The amount of the PCEs was based on the percentage of solid content in the amount of cement. In this experiment, the amount of 0.1% was used.

2.3 Experimental method

2.3.1 Test of viscosity of the PCEs. The viscosity of the PCEs was tested with NDJ-8S digital display viscometer. Place the liquid to be measured in a container with a diameter of not less than 70 mm, and select the appropriate rotor to screw into the rotor connector. Adjusting the height of the rotor in the liquid so that the mark on the rotor is flush with the liquid surface. Start the machine and the liquid viscosity could be read.

2.3.2 Test of cement paste fluidity. Refer to GB/T 8077-2000 "Test method for homogeneity of concrete admixture" to test the fluidity of cement paste.

3 Results and discussion

3.1 Research on synergistic optimization of the viscosity of PCEs

3.1.1 Synergistic Study on the binary parameters of synthesis temperature and initiator dosage to the viscosity of the PCEs. The synthesis temperature was selected as 50°C, 55°C, 60°C, 70°C, and the initiator dosage was 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%. Exploring the synergy between the synthesis temperature and the initiator dosage when the synthesis time was 3h.
Figure 1 Synergistic relationship between synthesis temperature and initiator dosage at 3h on the viscosity of the PCEs.

From Figure 1, at higher temperatures, the greater the dosage of initiator, the greater the viscosity of the PCEs. When the temperature was moderate, the viscosity of the PCEs increased with the increase of the initiator dosage, but the increase rate was relatively gentle. Because when the temperature was moderate, increasing the amount of initiator could increase the decomposition efficiency of free radicals when the polymerization was not too violent. Low temperature would reduce the decomposition rate of the initiator, so the molecular weight of the polymerization product was low. Therefore, when the temperature was higher, the lower initiator dosage was suitable; when the temperature was moderate, the initiator dosage should also be moderate; when the temperature was lower, the higher initiator dosage was suitable.

3.1.2 Synergistic Study on the binary parameters of synthesis time and initiator dosage to the viscosity of the PCEs. The synthesis time was selected as 1h, 2h, 3h, 4h℃, and the initiator dosage was 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%. Exploring the synergy between the synthesis time and the initiator dosage when the synthesis temperature was 60℃.

Figure 2 Synergistic relationship between synthesis time and initiator dosage at 60℃ on the viscosity on the PCEs.

From Figure 2, at the same initiator dosage, the viscosity of the PCEs increased with the increase of synthesis time; at the same synthesis time, the viscosity of the PCEs generally increased with the increase of the initiator dosage. So, when the synthesis time was shorter, the lower initiator dosage was more suitable; when the synthesis time was longer, the initiator dosage could be increased appropriately.

3.1.3 Synergistic Study on the binary parameters of synthesis time and synthesis temperature to the viscosity of the PCEs. The synthesis time was selected as 1h, 2h, 3h, 4h, and the synthesis temperature was 50℃, 55℃, 60℃, 70℃. Exploring the synergy between the synthesis time and the synthesis temperature when the initiator dosage was 0.2wt%.
Figure 3 Synergistic relationship between synthesis time and synthesis temperature at 0.2wt% initiator dosage on the viscosity of the PCEs

It can be seen from Figure 3 that when the synthesis temperature was higher, the viscosity of the PCEs decreased with the increase of the synthesis time. Because the synthesis temperature was higher, the molecular weight of the polymer increased rapidly. With the increase of the synthesis time, the polymerization reaction eased, so the viscosity decreased. When the synthesis temperature was moderate, the viscosity of the PCEs increased slowly as the synthesis time increased. When the synthesis temperature was too low, the initial viscosity of the polymer was high. With the increase of the synthesis time, the polymerization products were gradually ordered, and the viscosity decreased to a certain extent. Therefore, when the synthesis temperature was higher or lower, the synthesis time should be longer; when the synthesis temperature was moderate, the moderate synthesis time was more appropriate.

3.2 Research on synergistic optimization of the cement dispersibility

3.2.1 Synergistic study on the binary parameters of synthesis temperature and initiator dosage to the cement dispersibility. The synthesis temperature was selected as 50℃, 55℃, 60℃, 70℃, and the initiator dosage was 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%. Exploring the synergy between the synthesis temperature and the initiator dosage when the synthesis time was 3h.

Figure 4 Synergistic relationship between synthesis temperature and initiator dosage at 3h on the cement dispersibility
It can be found from Figure 4 that at the same temperature, the fluidity of cement paste increased firstly and then decreased with the increase of the initiator dosage. When the initiator dosage was 0.2wt%, the fluidity of cement paste at different temperatures was relatively large. When the initiator dosage was the same, the fluidity of cement paste was best around 60°C. If the temperature was too low or too high, the fluidity of the cement paste would decrease. Therefore, when the temperature was higher, the amount of initiator dosage should be less; when the temperature was lower, the initiator dosage should be increased appropriately.

3.2.2 Synergistic Study on the binary parameters of synthesis time and initiator dosage to the cement dispersibility. The synthesis time was selected as 1h, 2h, 3h, 4h°C, and the initiator dosage was 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%. Exploring the synergy between the synthesis time and the initiator dosage when the synthesis temperature was 60°C.

![Figure 5 Synergistic relationship between synthesis time and initiator dosage at 60°C on the cement dispersibility](image)

It can be found from Figure 5 that when the initiator dosage was the same, the fluidity of cement paste increased firstly and then decreased as the synthesis time extended. The reaction was inadequate owing to the short synthesis time, so the dispersion of PCEs to cement was not good; If the synthesis time was too long, the continued synthesis would cause part of the side chains to fall off, affecting the performance of the PCEs, thereby making its dispersion to cement worse. When the synthesis time was the same, the fluidity of cement paste would increase first and then decrease as the initiator dosage increased. Therefore, when the synthesis time was short, the smaller initiator dosage was more appropriate; when the synthesis time was longer, the initiator dosage amount could be increased appropriately.

3.2.3 Synergistic Study on the binary parameters of synthesis time and synthesis temperature to the cement dispersibility. The synthesis time was selected as 1h, 2h, 3h, 4h°C, and the synthesis temperature was 50°C, 55°C, 60°C, 70°C. Exploring the synergy between the synthesis time and the synthesis temperature when the initiator dosage was 0.2wt%. 
Figure 6 Synergistic relationship between synthesis time and synthesis temperature at 0.2wt% initiator dosage to the cement dispersibility

It can be found from Figure 6 that, under the same synthesis time, the fluidity of cement paste increased firstly and then decreased with the increase of synthesis temperature. Because when the temperature was too low, the initiation efficiency was also too low, and when the temperature was too high, the initiation rate was too fast, so the monomer conversion rate was not guaranteed. Therefore, if the temperature was too high or too low, the cement dispersibility was not good. When the synthesis temperature was the same, the fluidity of cement paste increased firstly and then decreased with the increase of synthesis time. So, when the synthesis temperature was moderate, it was better to control the synthesis time at about 2h. When the synthesis temperature was higher, the synthesis time could be extended appropriately.

3.3 The establishment of synergy
The above experiments analyzed the effects of the synthesis temperature, synthesis time and initiator dosage on the viscosity and performance of the PCEs, and found that there was a certain relationship between the viscosity and the performance of the PCEs. Therefore, the quantitative method was used to study the effects of the three parameters on the viscosity of the PCEs, and to explore the relationship between the viscosity of the PCEs and the dispersibility of cement.

3.3.1 Study on the logarithmic relationship between the initiator system and the viscosity of the PCEs.
In free radical polymerization, it could be found from the kinetic chain length formula that the viscosity of the PCEs was proportional to the concentration of the monomer and inversely proportional to the square root of the initiator dosage \[\text{[6]}\]. Therefore, the logarithmic processing of the measured viscosity and initiator dosage was selected at the same time to explore the relationship between initiator dosage and the viscosity of the PCEs.
From Figure 7, by changing the different synthesis temperature and synthesis time in the polymerization process, the logarithm of the viscosity and the logarithm of the initiator dosage had a good linear relationship. Therefore, the conjecture that the viscosity had a linear relationship with the square root of the initiator was also verified.

3.3.2 Study on the exponential relationship between synthesis temperature and the viscosity. Because the effect of temperature on the growth rate conforms to the Arrhenius equation \(^{[7]}\), the relationship between the logarithm of the viscosity of the PCEs and the reciprocal of the synthesis temperature was explored below. Therefore, take the abscissa as 100/RT and the ordinate as \(\ln(\eta)\), and then explore the relationship between the two.

It can be seen from Figure 8, by changing different synthesis time and initiator dosage, \(\ln(\eta)\) and 100/RT had a good linear relationship.

3.3.3 Study on the linear relationship between the initiator system and the viscosity. Fan et al. \(^{[8]}\) explored the synthesis process of the PCEs, including the effect of synthesis time on the molecular weight of the PCEs. The study found that with the extension of the synthesis time, the conversion rate of the monomer gradually increased, the molecular weight gradually increased, and showed a linear relationship.
From Figure 9, the viscosity had a good linear relationship with the synthesis time. As the synthesis time increased, the conformation of the macromolecule changed from spherical to random coil, at this time, the internal friction between the molecules decreased. And the monomer conversion rate gradually increased, so the molecular weight and viscosity increased.

3.4 Establishment of process parameter model
It can be known from the above test content that the viscosity of the PCEs had a certain functional relationship with the synthesis time, the initiator dosage and the synthesis temperature. Among them, the viscosity of the PCEs was inversely proportional to the square root of the initiator dosage, proportional to the synthesis time and exponentially related to the synthesis temperature. Several process parameters were now unified into a synergistic model of the PCEs synthesis process parameters. At 180gTPEG, the initial temperature was 50-70℃, the dropping time was 1-4h and the initiator dosage was in the range of 0.1wt%-0.4wt%, the following formula was obtained by fitting:

$$\eta = 2.97 \times e^{\frac{100}{Rt}} \times t \times m^{-1}$$

Among them: R-general gas constant, t-synthesis time, m-initiator dosage, T-synthesis temperature.

Through research, there was also a certain relationship between the performance and the viscosity of the PCEs \[^9-10^\]. The viscosity would affect the dispersion performance on the cement.

It can be seen from the scatter plot in Figure 10 that there was a correlation between the performance and the viscosity of the PCEs. From the two oblique black lines, we can see the appropriate range corresponding to the viscosity and the performance of the PCEs. When cement paste dispersibility was in the range of 140-300mm, the viscosity of the PCEs is 170-420mPa*s. The area enclosed by the two
vertical and two horizontal lines reflected the viscosity range of the PCEs corresponding to the better performance of the PCEs to the cement dispersibility. When the viscosity was in the range of 200-370 mPa*s, the synthesis process of the PCEs was better. There would be no phenomenon of explosion polymerization. At this time, the PCEs had suitable viscosity and good performance.

4 Conclusion
(1) There was a synergistic relationship between the effects of synthesis temperature, synthesis time and initiator dosage on the viscosity of the PCEs: when the synthesis temperature was high, the viscosity could be improved by reducing the initiator dosage or extending the synthesis time. When the synthesis temperature was low, the viscosity could be improved by increasing the initiator dosage or shortening the synthesis time appropriately. At the same time, these three parameters had similar synergistic relationship to the dispersion performance of the PCEs for cement.

(2) Through kinetic factor analysis, establish a process model of these three parameters and the viscosity of the PCEs: \( \eta = 2.97 \times e^{\frac{RT}{1000}} \times t \times m^{-1} \). The model provided a theoretical basis for the optimization of the preparation process of the PCEs.

(3) When the viscosity of the PCEs was in the range of 200-370 mPa*s, its effect on cement dispersibility was better.

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