Effect of different pre-curing conditions on the performance of low-temperature early strength polycarboxylate superplasticizers

Shaohong Zhu

KZJ New Materials Group Co., Ltd, FuJian, China

*Corresponding author’ s E-mail: hong521203402@163.com

Abstract. This study involved the optimization of the process for low-temperature early strength polycarboxylate superplasticizers (PCE), and determined the optimal DW07 process with excellent low-temperature early strength performance: n(AA)/n(EPEG)=9.45, n(TGA)/n(EPEG)=0.23, n(U1)/n(EPEG)=0.72, n(M1)/n(EPEG)=0.36. Additionally, the influence of different pre-curing conditions on the early strength performance of the PCE at low temperatures was investigated. Furthermore, concrete tests were conducted to further validate the strengthening effect of DW07 at low temperatures. The experiments demonstrated that selecting a pre-curing time of 3 h and a pre-curing temperature of 15°C as the optimal pre-curing conditions, the addition of DW07 low-temperature early strength PCE significantly enhanced the 1 d, 3 d, and 28 d strength performance of mortar.

Keywords: low-temperature early strength polycarboxylate superplasticizers; mortar; early strength performance; pre-curing time; pre-curing temperature

1 Introduction

The performances of concrete were influenced by various factors in actual construction projects. To ensure that the concrete achieved the expected strength and performance, not only reasonable proportions and mixing techniques were required, but also appropriate curing conditions were required[1-4]. Among them, the pre-curing temperature and pre-curing time played a crucial role in the hydration and hardening process of cementitious materials in concrete. Especially during winter construction, the ambient temperature was much lower than the normal curing temperature of concrete[5, 6].

In order to overcome these problems, researchers were continuously researching and developing polycarboxylate ether (PCE) based superplasticizers to meet the requirements of early strength and strength performance of concrete[7,8]. Low-temperature early strength PCEs can not only improve the flowability and early strength of concrete, but address the demands of construction in cold environments[9]. By adjusting the formulation and production processes of superplasticizers, low-temperature early strength PCEs suitable for different low-temperature conditions can be prepared[10-12].

D. Li et al. (eds.), *Proceedings of the 2023 9th International Conference on Architectural, Civil and Hydraulic Engineering (ICACHE 2023)*, Advances in Engineering Research 228,
https://doi.org/10.2991/978-94-6463-336-8_66

This article prepared a series of low-temperature early strength PCEs and compared them with commonly used early-strength PCEs in the market. Further analysis was conducted in the impact of low-temperature early strength PCE on the early strength of mortar under different pre-curing temperatures and pre-curing times.

2 Materials and Methods

2.1 Experimental raw materials

Synthesis materials.

Synthetic materials: Ethylene glycol monovinyl polyethylene glycol ether (EPEG, molecular weight 5000), acrylic acid (AA), thioglycolic acid (TGA), Brygmann chemical reagent TP1351, Hydrogen peroxide (H_2O_2), 3-methacryloyloxypropyltrimethoxysilane (U1), sodium hydroxide solution (NaOH), ferrous sulfate ($FeSO_4$), self-made functional monomer (M1).

Test materials.

Cement (C): Chunchi P.O 42.5 R cement (C, as shown in the Table 1); Sand (S): the Chinese ISO standard (S); Water(W); Polycarboxylate superplasticizer: DW (solid content of 40%, self-made) and SK-1 (40%).

Table 1. Cement Performance Indicators

Strength level	Stability	Setting time /min		Compressive strength /MPa		Flexural strength /MPa	
		Initial setting	Final setting	3 d	28 d	3 d	28 d
42.5 R	qualified	171	252	30.8	49.5	6.1	9.5

2.2 Performance testing and characterization

Fluidity of cement paste.

The fluidity of cement paste was tested according to GB/T 8077-2012 "Test Method for Homogeneity of Concrete Admixtures". Among them, the admixtures content was 0.2% (reduced solid).

Strength of cement mortar.

The standard procedure was carried out following the GB/T 17671-1999 "Method for Testing the Strength of Cement Mortar (ISO Method)". The dosages of admixture were adjusted until the flowability of the cement mortar reaches (180±5) mm. Mortar specimens measuring 40 mm × 40 mm × 160 mm were formed, with a fixed water-cement ratio of 0.35 and a cement-sand mass ratio of 1:3.

2.3 Preparation Method

This text describes the synthesis method for producing low-temperature early strength polycarboxylate superplasticizer through a free radical copolymerization approach. Firstly, EPEG-5000, H_2O_2, a portion of NaOH, U1 and 1% $FeSO_4$ were dissolved in separate round-bottom flasks according to the specified quantities. The reaction temperature was maintained at 15°C, and high-speed stirring was applied to achieve uniform mixing. Then mixture solution of AA and M1, as well as TGA and TP1351 were slowly added dropwise. After completing the addition, the mixture was kept at a constant temperature for a certain period. Finally, the low-temperature early strength polycarboxylate superplasticizer (Figure 1) was obtained by neutralization with NaOH.

Fig. 1. The low-temperature early strength polycarboxylate superplasticizer

3 Results & Discussion

3.1 Optimization of synthesis process for different low-temperature early strength PCE

AA, TGA, U1, and M1 were chosen as variable factors for orthogonal composite process adjustment. This was done in conjunction with changes in cement paste performance, mortar flowability, and 1 d compressive strength of mortar to investigate the impact of different factor conditions on the performance of low-temperature early strength PCE, as illustrated in Table 2, Table 3, and Figure 2.

Table 2. Orthogonal Experiment Adjustment and Performance Changes

Samples	n(AA) /n(EPEG)	n(TGA) /n(EPEG)	n(U1) /n(EPEG)	n(M1) /n(EPEG)	cement paste fluidity (mm)	mortar fluidity (mm)	1 d compressive strength of mortar (MPa)
DW01	8.29	0.23	0.48	0.29	203	180	5.5
DW02	8.29	0.26	0.60	0.36	200	190	6.1
DW03	8.29	0.29	0.72	0.43	205	195	6.5
DW04	8.87	0.23	0.60	0.43	221	200	5.9
DW05	8.87	0.26	0.72	0.29	206	195	6.8
DW06	8.87	0.29	0.48	0.36	215	205	6.4
DW07	9.45	0.23	0.72	0.36	210	210	7.2
DW08	9.45	0.26	0.48	0.43	225	205	5.9
DW09	9.45	0.29	0.60	0.29	220	205	6.3

It can be observed that with the change of n(AA)/n(EPEG), the cement paste fluidity of low-temperature early strength PCEs showed a highly positive correlation n(AA)/n(EPEG) and n(M1)/n(EPEG). Among them, the highest fluidity of cement slurry was DW08 (225 mm), followed by DW04 (221 mm) and DW09 (220 mm).

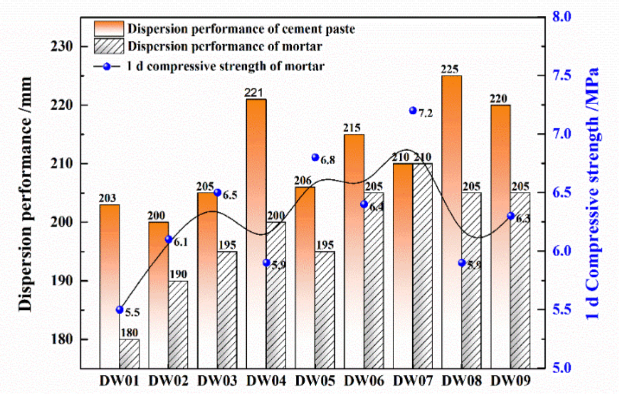

Fig. 2. Orthogonal performance testing of different low-temperature early strength PCEs

Regarding the dispersibility of the mortar by the low-temperature early strength PCEs, its trend of change was generally similar to the trend in cement paste fluidity. Similarly, it showed a positive correlation with the changing trends of n(AA)/n(EPEG) and n(M1)/n(EPEG). In the performance tests of DW05, DW08, and DW09, there were a certain degree of decrease in mortar flowability.

Based on the 1 d compressive strength results, it can be seen that the early strength performance of the low-temperature early strength PCEs was less correlated with the variation in n(AA)/n(EPEG). Instead, it showed a similar trend to the change in n(U1)/n(EPEG). Among them, the mortar compressive strength of DW07 sample exhibited the highest at 7.2 MPa, followed by DW05 sample (6.8 MPa), which was 14.3% and 7.9% higher than the average early strength performance at 1 d, respectively.

Table 3. Range analysis and calculation results of orthogonal performance test

Testing	Impact factors	n(AA) /n(EPEG)	n(TGA) /n(EPEG)	n(U1) /n(EPEG)	n(M1) /n(EPEG)
cement paste fluidity (mm)	K_{1j}	202.67	211.33	214.33	209.67
	K_{2j}	214.00	210.33	213.67	208.33
	K_{3j}	218.33	213.33	207.00	217.00
	R	15.67	3.00	7.33	8.67
mortar fluidity (mm)	K_{1j}	188.33	196.67	196.67	193.33
	K_{2j}	200.00	196.67	198.33	201.67
	K_{3j}	206.67	201.67	200.00	200.00
	R	18.33	5.00	3.33	8.33
1 d compressive strength of mortar (MPa)	K_{1j}	6.03	6.20	5.93	6.20
	K_{2j}	6.37	6.27	6.10	6.57
	K_{3j}	6.47	6.40	6.83	6.10
	R	0.43	0.20	0.90	0.47

By conducting a range analysis of the cement paste fluidity and mortar flowability test results for the low-temperature early strength PCEs (Table 3), it can be concluded that the factors affecting their dispersion performance from large to small were AA > M1 > U1 > TGA. Among them, DW08 exhibited the best cement paste dispersibility.

Furthermore, the influencing factors on the 1 d compressive strength performance of mortar were U1>M1>AA>TGA, with DW07 exhibited the highest strength.

There was mainly because increasing n(AA)/n(EPEG) and adding U1 and M1 monomers can enhance the density of side-chains, and gradually promote its steric hindrance effect and electrostatic repulsion effect. It can also effectively improve the dispersion of cement particles, increase the contact surface between cement and water, accelerate the hydration reaction. Thus, the hydration products such as Aft crystal, acicular C-S-H gel and CH particles can be promoted to interpenetrate and overlap with each other, further improving their compactness and early strength performance.

Based on the results of cement paste performance, mortar flowability, and 1 d compressive strength performance of the low-temperature early strength PCE, as well as its range analysis, it can be concluded that DW07 exhibits the most significant performance improvement. Therefore, the optimal synthesis process adjustment for low-temperature early strength PCE were: n(AA)/n(EPEG)=9.45, n(TGA)/n(EPEG)=0.23, n(U1)/n(EPEG)=0.72, n(M1)/n(EPEG)=0.36.

3.2 Effect of different pre-curing times on the performance of mortal

This article, in accordance with standardized testing methods and the practical application of concrete in low-temperature environments, selected DW07 and SK-1 for testing cement mortar performance. The dosage of additives was adjusted separately until the cement mortar fluidity reached (180±5) mm before forming.

After the mortal blocks were formed, they were placed in a curing room (20°C, RH>90%) for pre-curing times of 1 h, 2 h, 3 h, 4 h, and 5 h, respectively. Subsequently, they were transferred to a refrigerator under conditions of 5°C and further cured for 23 h, 22 h, 21 h, 20 h, and 19 h, to complete a total curing time of 24 hours. After this period, the specimens were demolded, and their compressive strength performance at 1 d, 3 d, and 28 d were be tested, as shown in Figure 3.

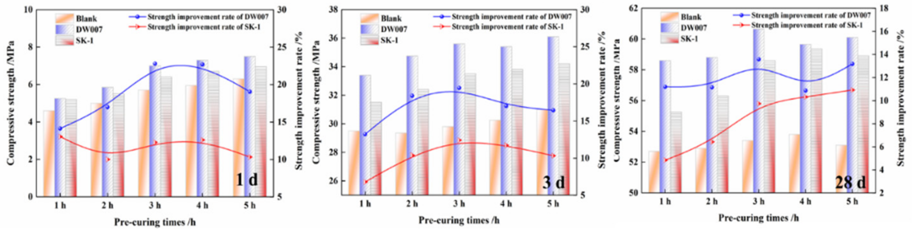

Fig. 3. Effect of different pre-curing times on the strength performance of mortal

From Figure 3, it can be observed that the compressive strength of the mortar containing DW07 and SK-1 at 1 d, 3 d, and 28 d showed an increasing trend with the extension of the pre-curing time at 20°C (1 h ~ 5 h). The trend of strength for the mortar at different pre-curing times can be summarized as follows: DW07 > SK-1 > Blank. Comparing the 1 d compressive strength pre-cured for 5 h and 1 h, the strength of the Blank group (without admixtures) increased from 4.6 MPa to 6.3 MPa. In contrast, the low-temperature early strength PCE (DW07) increased by 42.9%, while SK-1 only 33.7%.

Meanwhile, with the extension of pre-curing time, the 1 d compressive strength of DW07 and SK-1 samples increased significantly, reaching a peak when the pre-curing time reached 3 h. Continuing to extend the pre-curing time, its strength improvement rate remained relatively constant and even started to decline. Specifically, the 1 d compressive strength of the mortal added with DW07 increased by 14.1% (1 h), 17.0% (2 h), 22.8% (3 h), 22.7% (4 h), and 19.0% (5 h) compared to the blank group, respectively.

However, when comparing the 3 d compressive strength test results, it can be found that the strength of the blank group only increased by 5.1% compared to pre-curing 1 h after pre-curing for 5 h. In contrast, DW07 showed an increase of 8.1%, and SK-1 was 8.6%. After 28 days, its strength of the blank group pre-cured for 5 h only increased by 0.8% compared to 1 h, DW07 was 2.6%, and SK-1 was 6.6%. This indicates that low-temperature conditions have a significant impact on the 1 d strength. Low temperatures will inhibit the rate of chemical reactions within the cement, leading to a slower formation of hydration products, requiring more time to reach the design strength.

When the pre-curing time was 3 h, the 3 d strength improvement rate with DW07 reached the maximum (19.5%) compared to the blank group, and SK-1 only 12.4%. The 28 d strength growth rates were 13.6% (DW07) and 9.7% (SK-1), respectively. This indicates that a pre-curing time of 3 h was the optimal time for achieving the highest improvement strength at 1 d, 3 d, and 28 d.

3.3 Effect of different pre-curing temperatures on the performance of mortal

Based on the optimal pre-curing time of 3 h, The mortar specimens were prepared and placed in a curing chamber (RH>90%) with different pre-curing temperatures of 25°C, 20°C, 15°C, 10°C, and 5°C respectively. After pre-curing and demolding, its strength performance was shown in Figure 4.

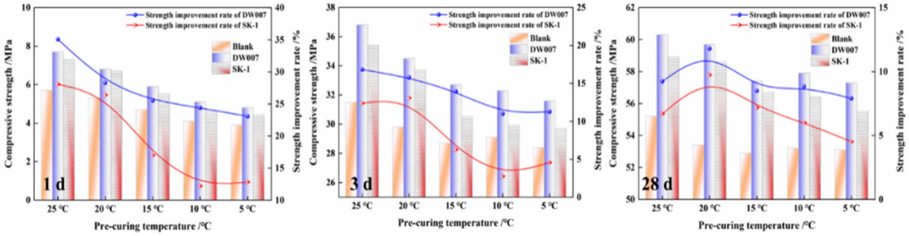

Fig. 4. Effect of different pre-curing temperatures on the strength performance of mortal

From Figure 4, it can be observed that the trends in compressive strength for the mortar specimens under various pre-curing temperatures were as follows: DW07 > SK-1 > Blank. As the pre-curing temperature decreases, the 1 d compressive strength of the mortar also reduced. When the pre-curing temperature decreased from 25°C to 15°C, there were a significant drop in strength. However, the trends of strength decrease slowed down between 15°C and 5°C. Comparing the 1 d mortar strength pre-cured at 25°C and 5°C, the 1 d compressive strength of the blank group decreased from 5.7 MPa to 3.9 MPa, representing a 31.6% reduction. DW07 decreased from 7.7 MPa to 4.8 MPa, a decrease of 37.7%, while SK-1 showed a reduction of 39.7%.

In comparison to the blank group, when pre-cured at a temperature of 25°C, the 1 d compressive strength of mortal (added DW07) increased the most significantly, with a strength growth rate of 35.1%. Moreover, the strength growth rate also shows a decreasing trend with the decrease of pre-curing temperature. At a pre-curing temperature of 15°C, the strength improvement rate was 25.5%. When the pre-curing temperature was further reduced, the strength growth rate remained relatively stable, at 24.4% (10°C) and 23.1% (5°C), respectively. However, at a pre-curing temperature of 10 °C, the strength improvement rate of SK-1 tended to flatten out at 12.2% (compared to the Blank).

The change in 3 d compressive strength was negatively correlated with the pre-curing temperature, similar to the trend observed at 1 d. However, the overall change in 3 d strength was relatively small. Comparing the 3 d compressive strength after pre-curing at 25°C and 5°C, the reduction in strength for the blank group was only 9.8%. The decrease in DW07 was 14.1%, while the decrease in SK-1 was 16.1%. The pre curing temperature at 25 °C is 16.8% (DW07) and 12.4% (SK-1), respectively. When the pre curing temperature is 15 °C, it is 13.9% and 6.3% respectively. In addition, the strength growth rate for the mortar with the addition of DW07 and SK-1 was lower when compared to the blank group. At a pre-curing temperature of 25°C, the strength improvement rates were 16.8% (DW07) and 12.4% (SK-1), respectively. At 15°C, the growth rates were 13.9% and 6.3%. Continuing to lower the pre-curing temperature, the strength growth rate will not change much.

In contrast to the changes of 1 d and 3 d strength, the 28 d compressive strength of the mortar showed a gradual trend of increasing and then decreasing with the change of pre-curing temperature. The 28 d compressive strength reached its peak at a pre-curing temperature of 20°C. However, because the hydration reaction of cement was mostly complete by 28 d, the reduction in strength for the blank group was only 3.8% from pre-curing 25°C to 5°C. The decrease in DW07 was 5.0%, while the decrease in SK-1 was 5.8%. Similarly, comparing the 28 d mortal strength of DW07 and SK-1 with the blank group, their strength growth rates also reached their maximum values of 11.8% and 9.7%, respectively.

Analyzing the 1 d、3 d and 28 d compressive strength under different pre-curing temperatures, it can be observed that at lower temperatures, the movement rate of free water in the mortar was slower. There were resulted in a decrease in the reaction rates of C_2S and C_3S, thereby delaying the overall cement hydration process. As the pre-curing temperature increased, the mobility of free water in the mortar accelerated, resulting in a significant increase in 1 d strength with rising temperature.

However, the total amount of free water was fixed, and when it reached saturation conditions, the cement hydration reaction also reached a certain degree of saturation. Therefore, when the pre-curing temperature was 15°C, the reinforcement effect on the 1 d、3 d and 28 d strength performance of the mortal mixed with DW07 and SK-1were the best.

4 Conclusions

By testing and analyzing the early strength performance of low-temperature early strength PCE under different pre curing conditions, the following conclusions were obtained:

(1) In terms of process optimization, the best process for low-temperature early strength PCE product (DW07) was determined by adjusting the variable factors of AA, TGA, U1, and M1. The optimal process parameters were as follows: n(AA)/n (EPEG)=9.45, n(TGA)/n(EPEG)=0.23, n(U1)/n(EPEG)=0.72, n(M1)/n(EPEG)=0.36.

(2) Regarding pre-curing conditions, extending the pre-curing time can significantly enhance the 1 d early compressive strength of mortar, especially 3 h. As the temperature increased, the early strength of the mortar gradually improved. When the pre-curing temperature was 15°C, the best enhancement effect will be achieved on the1 d, 3 d, and 28 d strength performance of the mortar.

References

1. Erezengin S, Kaya K. The properties of cement systems superplasticized with methacrylic ester-based polycarboxylates[J]. Construction and Building Materials, 2018, 166: 96-109.
2. Xiang, B. F., Zhang, L. J., Du, J., et al. Experimental study on the effect of curing temperature on the early compressive strength of concrete [J]. Cement, 2022 (07): 26-28.
3. Liu, L., Zhou, G. F., Zhang, L. Study on the effect of reservation temperature impact on concrete compressive strength [J] Forestry Science and Technology Intelligence, 2005 (02): 29-30.
4. Wang, H. F. Discussion on Winter Concrete Construction Methods in Building Engineering [J]. Heilongjiang Science and Technology Information, 2007 (06): 221.
5. Guan, B. Study on thermal properties of the low-heat cement concrete at early-age under variable curing temperature [D] Three Gorges University, 2022.
6. Sakai E, Kawakami A, Daimon M. Dispersion mechanisms of comb type superplasticizers containing grafted poly (ethylene oxide) chains[J]. Macromol Symp,2001,175(3):367-376.
7. Song, Z. B. Preparation and Application of Multi-functional Polycarboxylate Superplasticizer Based on Molecular Structure Design [D]. China Building Materials Research Academy, 2016.
8. Chen, M. Synthesis and Properties of Multifunctional Polycarboxylate Superplasticizer [D]. Shaanxi University of Science and Technology, 2015.
9. Yang, M. F., Ni, X. Q., Zong, X., et al. Impact of complex-admixture on anti-permeability of low-temperature high-performance concrete [J]. Western Exploration Engineering, 2005 (12): 232-233.
10. Zhang, F., Bai, Y., Cai, Y. B., et al. Properties and early strength mechanism of compound early strength accelerator at 5°C [J]. Journal of Tongji University: Natural Science Edition, 2019, 47 (11): 9.
11. Li, J., Cao, Y. Y., Zhang, H., et al. Impact of compounded low-temperature early strength agent on concrete properties [J]. New Building Materials, 2022,49 (03): 140-143.
12. Zhao, L., Xu, R. P., Lu, Y., et al. Study on the properties of a novel early strength polycarboxylic acid water-reducing agent for low temperature operation [J]. New Building Materials, 2019, 46 (07): 128-130.