Preparation and Properties of Anti-mud and Viscosity-Reducing polycarboxylate superplasticizer

Kelu Du*, Huanhuan Hou, Zunyu Liu, Xianghe Li, Qingru Wen,
Henan KZJ New Materials Co. Ltd., Xinxiang, Henan 453731, China
*Corresponding author, E-mail: dkl8801@163.com

Abstract: In this paper, the electropositive amide and phosphoric acid functional groups are introduced on the basis of the synthesis of common polycarboxylate superplasticizer, so as to reduce the sensitivity of the polycarboxylate superplasticizer to clay. In this paper, a small amount of 2-Capped1-Phoshate Easter containing olefin functional group was introduced into the polycarboxylate superplasticizer molecule by free radical reaction, which improved the negative electricity of the polycarboxylate superplasticizer and reduced sensitivity to clay. The performance test results show that the product can effectively reduce the sensitivity to clay during the process of mixing concrete with sandstone material with high mudstone content, and improve the fluidity of concrete and effectively reduce the viscosity of concrete.

1. Introduction
Polycarboxylate superplasticizer is the most rapid development of new water reducing agent in recent years. It has the characteristics of high water reduction rate, better environmental protection and excellent comprehensive performance. It is recognized as the development direction of concrete admixture in the future, but its development in China is still in initial stage. The research on polycarboxylate superplasticizer in China began in 1990s, and its industrial production and application in the early 21st century. And now, it was widely used in railway passenger dedicated lines, port terminals, hydropower dams, municipal projects, etc [1].

In recent years, with the rapid increase in infrastructure projects, the annual consumption of sand and gravel is large, resulting in fewer and fewer high-quality sandstone resources, and the grain shape and gradation of sandstones are not reasonable enough. Moreover, the high mud content in the sandstone not only reduces the strength and durability of the concrete and increases the shrinkage of the concrete, but also has a very significant influence on the workability of the water-reducing agent-mixed concrete, especially the polycarboxylate superplasticizer [2-5]. At present, the amount of sand and gravel in commercial concrete is high. Many enterprises have not cleaned the sandstone in order to save costs. As a result, many concretes with polycarboxylate superplasticizers have poor workability or excessive slump loss, poor concrete performance and poor durability [6-7]. Now, whether the problem of adaptability of polycarboxylate superplasticizer to clay minerals can be solved is an important prerequisite for the widespread use of polycarboxylate water reducers.

2. Experimental

2.1. Materials
Acrylic acid (AA), industrial grade; TPEG ,Mn=2400; HPEG, Mn=2400; thioglycolic acid, industrial grade; sodium formaldehyde sulfoxylate, industrial grade; ascorbate, food grade; hydrogen peroxide,
industrial grade, 27.5%; 2-Capped1-PhoshateEaster, industrial grade; dibasic ester, industrial grade; sodium hydroxide (NaOH), 30% aqueous solution, industrial grade; PCE (Similar polycarboxylate superplasticizer on the market); sand: river sand with a fineness modulus of 2.7, containing 0%, 4%, 8%, 12% mud; stone: continuous graded gravel with a nominal diameter of 5–20 mm; cement: Meng Dian P.0 42.5 Cement.

2.2. synthesis technology
TPEG and water were placed in a four-necked flask, stirred until homogeneously dissolved, and an aqueous solution of sodium formaldehyde sulfoxylate, a mixed aqueous solution of AA, 2-Capped1-PhoshateEaster, dibasic ester, and an aqueous solution of thioglycolic acid were started to be dropped at 45 °C, respectively. The reaction is carried out at a temperature of 45 °C, and the dropwise addition time is 3 h to obtain a copolymerization product, and then the pH value is 5.0 to 7.0 by using a NaOH solution to obtain a desired anti-mud viscosity-reducing polycarboxylate superplasticizer KZJ-KN.

2.3. Performance test methods
Cement paste fluidity test according to GB/T8077-2012 "concrete admixture uniformity test method" implementation, water/cement is 0.29, admixture mixing amount is 0.20%, cement use Meng Dian P.O42.5 ordinary Portland cement.
Concrete performance in accordance with GB/8076-2008 "concrete admixture" related standards, test using Meng Dian P.O42.5 ordinary Portland cement; River sand with a fineness modulus of 2.7 is cleaned and dried. Gravel, 5–20 mm continuous grading, cleaned and dried; the silt content of fine aggregate was adjusted by using different bentonite in place of river sand of corresponding quality.

3. Experimental results and discussion
3.1. Cement paste fluidity test
The most characteristic of the anti-mud polycarboxylate superplasticizer KZJ-KN is that it is particularly suitable for sandstone materials with high mud content. The experiment compares the effect of KZJ-KN and common polycarboxylate superplasticizer on the cement paste fluidity of Meng Dian cement under different clay contents. The amount of water reducing agent is 0.2% (folding). The experimental results are shown in Table 1.

| mudstone content | PCE       | KZJ-KN    |
|------------------|-----------|-----------|
|                  | Initial fluidity | 40min fluidity | Initial fluidity | 40min fluidity |
| 0                | 232       | 203       | 241       | 224       |
| 4%               | 226       | 190       | 235       | 214       |
| 8%               | 196       | 155       | 209       | 196       |
| 12%              | 162       | 132       | 189       | 162       |

It can be seen from the above table that KZJ-KN has better performance than PCE, both in terms of initial fluidity and fluidity retention performance, and this advantage is more obvious as the mud content increases; especially when the mudstone content reaches 8%, the slurry with PCE has no fluidity after 40 minutes, and the liquidity of KZJ-KN is more than 190 mm after 40 minutes. This shows that KZJ-KN has good material adaptability and is more suitable for sandstone materials with higher mud content.

3.2. Concrete slump test
In the concrete test process, the concrete is brought to the same initial fluidity by adjusting the amount of the admixture. Concrete composition is shown in Table 2.
Table 2 Concrete composition

| Material    | Cement | Artificial sand | Sand | Gravel | Fly Ash | Mineral powder | Water |
|-------------|--------|----------------|------|--------|---------|----------------|-------|
| Amount (g)  | 230    | 680            | 220  | 950    | 80      | 70             | 170   |

Table 3 shows the results of the concrete experiment.

Table 3 Concrete test results

| Serial number | Sample type | Mudstone content (%) | Dosage (g) | Concrete slump /mm |
|---------------|-------------|----------------------|------------|--------------------|
|               |             |                      |            | Initial slumps/ divergence | 40min slumps/ divergence |
| 1             | PCE         | 0                    | 13         | 220/590            | 210/480             |
| 2             | KZJ-KN      | 0                    | 13         | 220/595            | 210/500             |
| 3             | PCE         | 4%                   | 15         | 220/580            | 205/500             |
| 4             | KZJ-KN      | 8%                   | 15         | 220/590            | 210/560             |
| 5             | PCE         | 12%                  | 17         | 220/600            | 205/500             |
| 6             | KZJ-KN      | 12%                  | 19         | 220/570            | 205/500             |
| 7             | PCE         | 8%                   | 19         | 220/570            | 210/530             |
| 8             | KZJ-KN      | 12%                  | 19         | 220/570            | 210/530             |

As can be seen from the above table, the performance of KZJ-KN in concrete corresponds to the results in cement paste fluidity, that is, as the clay content increases, the initial slump of the concrete mixed with the anti-mud polycarboxylate superplasticizer KZJ-KN is greater than that of the comparative sample, especially the 40 min retention performance is better; especially when the mud content reaches 8%, its performance advantage is more obvious.

3.3. Concrete viscosity test

The initial expansion of concrete was controlled at (600 ± 20) mm, and the V-funnel and L-box were tested on KZJ-KN and PCE. Concrete composition is shown in Table 4.

Table 4 Concrete composition

| Material    | Cement | Artificial sand | Sand | Gravel (10-20) | Gravel (0-5) | Fly Ash | Mineral Powder | Water |
|-------------|--------|----------------|------|----------------|--------------|---------|----------------|-------|
| Amount (g)  | 430    | 583            | 100  | 702            | 290          | 50      | 100            | 155   |

The concrete viscosity test results are shown in Table 5.

Table 5 Concrete viscosity

| Sample type | V-funnel flow time / s | L-box flow time / s | Compressive strength |
|-------------|------------------------|---------------------|----------------------|
|             | Initial | 40min | Initial | 40min | 7d | 28d      |
| PCE         | 29      | 76    | 11      | 32    | 63.4 | 76.3    |
| KZJ-KN      | 18      | 56    | 8       | 22    | 62.6 | 75.2    |

As can be seen from the above table, the initial V-funnel flow time and L-box flow time of KZJ-KN are shorter than the PCE, the initial viscosity reduction effect of KZJ-KN is obviously better than PCE; after 40min gradual loss, the viscosity reduction effect of KZJ-KN is obviously better than PCE. This may be due to the introduction of ester functional groups in KZJ-KN, which can slowly hydrolyze and release carboxyl functional groups in the alkaline environment of concrete, thereby delaying the loss of fluidity and increasing the flow rate of concrete after gradual loss.

3.4. Mechanism analysis

Polycarboxylate superplasticizer is used in sand and stone materials with high mud content. Due to the strong adsorption capacity of mud, polycarboxylate superplasticizer molecules are adsorbed by mud in the process of concrete, which leads to the enhance of polycarboxylate superplasticizer molecules to effectively adsorb with mud particles, resulting in the fast of gradual loss of concrete. In this study, by
introducing the calcium ion adsorption ability of 2-Capped 1-Phosphate Ester with phosphoric acid functional groups, causes the polycarboxylate superplasticizer to adsorb to cement particle surface, strengthen its directional adsorption on cement surface, the equivalent of reduced mud adsorption of polycarboxylate superplasticizer molecules, and phosphate functional group is advantageous to the mud dispersion and stability in concrete, which improves the performance of polycarboxylate superplasticizer of slump loss resistant property.

By introducing other dibasic ester monomer with hydrophobic functional groups, special hydrophobic groups will be formed on the cement particle surface, the other end is a hydrophilic layer consisting of a side chain of polyoxyethylene ether.

A certain mechanical strength of the water film layer have made by the joint action of the both layer in the cement particle surface, it can release the free water between the cement particles, it is beneficial to destroy the flocculation structure of cement particles, improve the lubrication effect between cement particles and aggregates; in addition, small amount of unsaturated ester used in the experiment make the polymer micro-crosslinked, to achieve good dispersion, good slump loss resistant property, and excellent viscosity reduction, can greatly reduce the viscosity of high performance or ultra-high performance concrete.

3.5. FT-IR test

![Figure 1 FT-IR of KZJ-KN and PCE](image)

Among them, the asymmetric stretching vibration absorption peak of -OH of PCE is $3110 \text{cm}^{-1} - 3660 \text{cm}^{-1}$. The stretching vibration absorption peak of ester group -C=O- is $1715 \text{cm}^{-1}$. The characteristic absorption peaks of -CH- and -CH2- are $2868 \text{cm}^{-1}$, $1455 \text{cm}^{-1}$, $1349 \text{cm}^{-1}$, and the characteristic absorption peak of polyether long chain -C-O-C- is $1106 \text{cm}^{-1}$. It can be seen from the FT-IR of the above figure that the functional groups of ordinary PCE and KZJ-KN are basically the same, only a small displacement of the absorption peak occurs. However, KZJ-KN has an additional functional group absorption peak at $1644 \text{cm}^{-1}$, indicating that a phosphoric acid functional group was successfully introduced into the polycarboxylate superplasticizer structure during the synthesis.

4. Conclusions

Based on the molecular design principle and the free radical copolymerization method, this paper synthesized a high performance water-reducing agent of anti-mud and viscosity break polycarboxylate superplasticizer. Through the study, the main conclusions are as follows:

1) By using the 2-Capped 1-Phosphate Ester as the raw material, functional groups of amide and phosphoric acid with positive electricity are introduced into the polycarboxylate superplasticizer molecules. On the premise of high water reduction rate, good anti-mud adsorption performance is achieved.

2) By introducing dibasic ester monomers with hydrophobic functional groups, the purpose of reducing the viscosity of concrete is achieved, especially in high performance or ultra-high performance concrete, which can obviously reduce the viscosity of concrete.
References:
[1] Wang Z M. Polycarboxylate Superplasticizer—Preparation, performance and application [M]. China Building Industry Press, 2009.
[2] Chen G X, Zhu Y R, Shen Y P, et al. Study on the synthesis and performance of clay compatibility polycarboxylate superplasticizer [J]. Concrete, 2014(4): 87-89.
[3] Wang W L, Yang X X, Fang Y T, et al. Preparation and performance of form-stable polyethylene glycol silicon dioxide composites as solid-liquid phase change materials [J]. Applied Energy, 2009, 86(2):170-174.
[4] Shi W, Hou J P. Composite method on temperature control concrete with PCM [J]. Concrete, 2011(10): 41-42,45.
[5] AHMET S, ALI K. Preparation, thermal properties and thermal reliability of palmitic acid expanded graphite composite as form-stable PCM for thermal energy storage [J]. Solar Energy Materials and Solar Cells, 2009, 93: 571-576.
[6] Zhan H, Wang Y K, Zhao F, et al. Preparation and properties of anti-clay type polycarboxylate Superplasticizer [J]. Concrete, 2015(3): 102-103.
[7] Kong F M, Sun X M, Yang L G, et al. Effect of sand on technical-economic index of concrete with polycarboxylic high performance water reducer [J]. Concrete, 2011(2): 95-97.