Synthesis and performances of polycarboxylate superplasticizer with clay-inerting and high slump retention capability

Shanshan Qian, Haidong Jiang, Bei Ding, Yi Wang, Chunyang Zheng and Zhaolai Guo
Jiangsu China railway ARIT new materials Co.Ltd., Jiangsu Nanjing 211505 China
E-mail: aritqss@163.com

Abstract. Macromolecules with pendant chlorine groups on their main chains were synthesized via free-radical copolymerization of 2-hydroxyethyl acrylate(HEA), TPEG and vinylbenzyl chloride(VBC) in the presence of initiator and chain transfer agent according to molecular structure design principle. The subsequent Arbuzov reaction between trimethoxyphosphine(TMP) and chlorine groups of macromolecules(PHVT) gave rise to new type of polycarboxylate superplasticizer with clay-inerting and high slump retention capability. The molecular structure of superplasticizer was determined by Fourier Transform Infrared Spectroscopy (FT-IR) and Gel Permeation Chromatography (GPC), respectively. The adaptability of clays, Zeta potential, adsorption behavior and application performance in concrete were measured. The results shows that the polycarboxylate superplasticizer we prepared has good clay compatibility, excellent clay-inerting and high slump retention capability.

Keywords: clay-inerting, slump retention, Arbuzov reaction, trimethoxyphosphine, polycarboxylate superplasticizer

1. Introduction
Polycarboxylate superplasticizer, with its outstanding performance of low adding amount, high water reduction rate, well restraint of slump loss, high adjustability of molecular structure and environmental protection etc., has been used more and more widely in major projects like water conservancy, hydroelectricity, bridges, high-speed railways and motorways, and general civil construction [1]. However, with polycarboxylate superplasticizer, the expanding rang of using and largely applied in the practical engineering, a great amount of project cases and researches indicate that, comparing with traditional naphthalene, melamine and aminosulfonic acid water reducing agent, polycarboxylate superplasticizer, is more sensitive to clay content of aggregates, which absorbs the water reducing agent and with the increase of clay, the water reducing and dispersing ability and the effects of slump keeping decrease sharply, which results in the working performance of fresh mixed concrete decreases largely, all these problems disturbs cement manufacturer, concrete construction company and additive manufacturer [2-4].

As the fast development of construction industry, sandstone resources of high quality have gradually been depleted, and degraded in various places, especially in large and medium-sizes cities, which the sandstones used containing more clays [5,6]. To solve these problems, it is usually to add a
lot of slump agent, retarding agent and other agents which can improve the performance, while the methods can solve the problem of heavy loss of slump, but it also brings problems like high cost, delaying the setting time and compressive strength [7-9]. Therefore based on the molecular structure of polycarboxylate superplasticizer, introduce some functional groups which are able to decrease adsorption of clay, develop a polycarboxylate superplasticizer which resists clays and keeps slump to solve the construction problems in the sites, improve the application of PCE nationwide, which will be of vital importance to the development of construction industry.

In this paper, hydroxyethyl acrylate (HEA), 4-vinylbenzyl chloride (VBC) and terminal alkenyl polyoxyethylene ether(TPEG) are used as the main raw materials, which is first synthesized a halogen-containing copolymer (PHVT), and then polycarboxylate superplasticizer containing phosphate functional groups is synthesized by Arbuzov reaction with trimethyl phosphate (TMP). The polycarboxylate superplasticizer grafts the free phosphate ester into the polymer by chemical bonding. On the one hand, the phosphate group is chemically bonded to the polymer backbone. Compared with the free phosphate, it has strong steric hindrance and can solve the problem of large slump loss. On the other hand, adsorption ability of the phosphonic acid groups formed by hydrolysis of phosphate groups is stronger than carboxylic acid groups, preferentially adsorbs to the clay surface in the aggregate, which occupies the adsorption activity point of clay surface, and reduces the adsorption of carboxylic acid groups on the clay, so that reduces the sensitivity of the polycarboxylate superplasticizer to the mud-containing aggregate. This significantly improves the dispersion of superplasticizer and the ability to maintain slump, especially for the mud-containing gravel material has a significant slump retention effect.

2. Experiment

2.1. Materials

Macromonomer (TPEG) with molecular weight of 2400, commercial grade, Oxiranchem Yangzhou Company Ltd.. Vinylbenzyl chloride(VBC), trimethoxyphosphine(TMP), AR, available from Shandong Xiya Chemical Reagent Co., Ltd.. 2-hydroxyethyl acrylate(HEA), 3-Mercaptopropionic acid (MPC), hydrogen peroxide, AR, available from Sinopharm Chemical Reagent Co., Ltd. vitamin C, commercially available.

The chemical and mineral compositions of reference cement (P•O 42.5) are shown in table 1.

| Clay   | SiO₂ | A₂O₃ | F₂O₃ | CaO | MgO | SO₃ | N₂Oeq | f-CaO | C₃S | C₂S | C₃A | C₄AF |
|--------|------|------|------|-----|-----|-----|-------|-------|-----|-----|-----|------|
| Ca-MTT | 22.91| 4.29 | 2.89 | 66.23| 1.93| 0.34| 0.71  | 0.63  | 58.68| 21.48| 6.49 | 8.79 |
| illite | 77.07| 10.78| 2.80 | 0.96 | 4.29| 0.29| 1.53  | 0     | 0   | 0   | 15.69|
| Kaolin | 74.17| 14.25| 1.81 | 0.72 | 2.32| 3.61| 2.26  | 0.08  | 0   | 0   | 7.65 |

Ca-MTT, illite and Kaolin were commercial grade provided by Hangzhou Chong Ke Chemical Co., Ltd., the chemical and mineral compositions of clay are shown in table 2.

| Clay   | SiO₂ | Al₂O₃ | MgO | Fe₂O₃ | CaO | Na₂O | K₂O | TiO₂ | SO₃ | Loss |
|--------|------|-------|-----|-------|-----|------|-----|------|-----|------|
| Ca-MTT | 58.05| 25.70 | 0.68| 0.68  | 1.16| 1.41 | 1.58| 1.00 | 0.37| 12.76|

The macadam is 5~20 mm continuous grading macadam. the density is 2630kg/m³ and the bulk density is 1540 kg/m³.

The medium sand has a fineness modulus M=2.7, density of 2551kg/m³ and bulk density of 1461kg/m³.

The macadam and medium sand is washed and dried, Tap water is used.
2.2. Synthesis of polycarboxylate superplasticizer

2.2.1. Synthesis of polycarboxylate superplasticizer with clay-inerting and high slump retention capability: 1) Preparation of chlorine-containing copolymer (PHVT): Hydroxyethyl acrylate (HEA), terminal alkenyl polyoxyethylene ether (TPEG) and 4-vinylbenzyl chloride (VBC) by the action of hydrogen peroxide, Vc, 3-Mercaptopropionic acid (MPC), through the oxidation-reduction radical-polymerization reaction at room temperature obtains a chlorine-containing copolymerization product.

2) Preparation of polycarboxylate superplasticizer with clay-inerting and slump retention(PCE): The chlorine-containing copolymerization product is reacted with a certain proportion of trimethyl phosphate (TMP) for Arbuzov reaction, and then dialysis purification is carried out for a certain period of time to obtain a containing phosphoric acid ester group polycarboxylate superplasticizer with clay-inerting and slump retention(20 wt%).

2.2.2. Synthesis of polycarboxylate superplasticizer with high slump retention capability. Preparation of polycarboxylate superplasticizer (PCE-0) with general slump retention: Hydroxyethyl acrylate (HEA) and terminal alkenyl polyoxyethylene ether (TPEG) by the action of hydrogen peroxide, Vc, 3-Mercaptopropionic acid(MPC),through the oxidation-reduction radical-polymerization reaction at room temperature obtains a copolymerization product, and then dialysis purification to obtain a polycarboxylate superplasticizer with general slump retention(20 wt%).

2.3. Structural characterization and property measurement
Dry the sample to a constant weight and mix the sample with KBr powder to make tablets. Place the sample under VERTEX70-type Fourier infrared spectrometer of German Bruker to make a record of infrared spectrum. Waters 1515 gel permeation chromatograph is used to test the molecular weight and its distribution of the synthesized samples. The mobile phase is 0.1 mol.L-1 NaNO₃ solution, the flow rate is 1.0 mL/min, and the stationary phase is gelatinous porous filler. The fluidity and maintaining performance of cement paste are conducted according to GB 8077-2012 Methods for Testing Uniformity of Concrete Admixture. The water-cement ratio is 0.29 and the mixing amount of superplasticizer is 0.13%. TOC-II total organic carbon analyzer is used to measure concentration of original polycarboxylate superplasticizer solution and solution after absorption balance concentration difference of which is based to calculate adsorbing capacity of cement particle. Zetasizer Nano series of nanoparticle size analyzer produced by Malvern Instruments Ltd. could be used to measure Zeta potential on the surface of cement particle mixed with polycarboxylate superplasticizer. The fluidity and maintaining performance of cement paste are conducted according to GB 8077-2012 Methods for Testing Uniformity of Concrete Admixture. The water-cement ratio is 0.29 and the mixing amount of superplasticizer is 0.5%. Test the slump flow of concrete mixes and the variation of slump flow according to GB / T50080-2002 "ordinary concrete mixture performance test method standard". Test concrete 7d, 28d compressive strength, the content of water reducer is 0.2% of cement quality (converted into solid) according to GB / T50081-2002 "ordinary concrete mechanical properties test method standard".

3. Results and discussion
With HEA, 4-vinylbenzyl chloride (VBC) and terminal alkenyl polyoxyethylene ether (TPEG) as reactants, preparation of side-chain chlorine-containing copolymer products (PHVT) and then with trimethyl phosphate (TMP) for Arbuzov reaction, and forms a new containing phosphoric acid ester group of PCE. The reaction equation is shown in figure 1.

3.1. The molecular weight and distribution of PCE and fluidity of cement paste
The molecular structure of polycarboxylate superplasticizer is capable of being designed. Design the molecular structure by oxidation-reduction radical polymerization and Arbuzov reaction to obtain polycarboxylate superplasticizer with the expected molecular structure. This is mainly to analyze the
dispersion and dispersion retention of the synthesized containing phosphate ester functional group polycarboxylate superplasticizer with clay-inerting and slump retention in the reference cement by analyzing the ratio of monomers, the molecular weight and its distribution. The results are shown in table 3.

Figure 1. Reaction equation of PCE.

| Sample | PCE     | Feed ratio (n(HEA):n(VBC):n(TPEG)) | Dosage% | Fluidity/mm  | GPC results |
|--------|---------|----------------------------------|---------|---------------|-------------|
|        |         |                                  |         | 0.5h   | 1h   | 2h   | M_n g.mol⁻¹ | M_w g.mol⁻¹ | PDI   |
| A      | PCE-0   | n(HEA):n(TPEG) = 6:1             |         | 105    | 225  | 205  | 25500       | 34200       | 1.34  |
| B      | PCE-1   | 4.0:5:1                          |         | 110    | 210  | 190  | 28000       | 39500       | 1.39  |
| C      | PCE-2   | 4:1:1                            |         | 120    | 230  | 210  | 31000       | 43800       | 1.41  |
| D      | PCE-3   | 4:2:1                            |         | 100    | 200  | 180  | 35200       | 50100       | 1.42  |
| E      | PCE-4   | 5:0:5:1                          |         | 105    | 210  | 195  | 31300       | 45100       | 1.43  |
| F      | PCE-5   | 5:1:1                            |         | 125    | 235  | 215  | 35100       | 49500       | 1.40  |
| G      | PCE-6   | 5:2:1                            |         | -      | 190  | 160  | 36200       | 53300       | 1.47  |
| H      | PCE-7   | 6:0:5:1                          |         | 110    | 225  | 200  | 35400       | 52400       | 1.48  |
| I      | PCE-8   | 6:1:1                            |         | 130    | 245  | 225  | 35700       | 53700       | 1.50  |
| J      | PCE-9   | 6:2:1                            |         | 105    | 205  | 185  | 36100       | 56100       | 1.55  |
| K      | PCE-10  | 7:0:5:1                          |         | 120    | 225  | 185  | 35900       | 56000       | 1.56  |
| L      | PCE-11  | 7:1:1                            |         | 110    | 220  | 200  | 36400       | 56100       | 1.54  |
| M      | PCE-12  | 7:2:1                            |         | 100    | 200  | 170  | 39200       | 60100       | 1.52  |
From table 3, the initial fluidity and fluidity retention composite property of the polycarboxylate superplasticizer with clay-inerting and slump retention are: PCE-8 > PCE-5 > PCE-2 > PCE-0 > PCE-11 > PCE-7 > PCE-4 > PCE-10 > PCE-1 > PCE-12 > PCE-9 > PCE-6 > PCE-3. This is due to the molecular structure of polycarboxylate superplasticizer with clay-inerting and slump retention contains hydrophobic groups, so that the surface tension becomes low, the lower the surface tension, the easier to reduce the gas-liquid interface surface energy. Superplasticizer would adsorb to the gas-liquid interface, and form a relatively solid liquid film, plus the ester-based in the molecular structure hydrolysis into a negative group adsorption, so that liquid film with negative electricity to form a stable, dense bubbles [10, 11]. Air bubbles with negative and the gap between the air bubbles and cement particle are dispersed due to electrostatic repulsion, showing a significant excellent fluidity retention performance [12]. But with increasing the content of 4-vinylbenzyl chloride (VBC), when the hydrophobic group phenyl group increases beyond a certain range, the association in such a comb-like structure is enhanced. Aggregation occurs in an aqueous solution in a manner that the hydrophobic structure shrinks together, the hydrophilic structure is distributed inside the aggregates, resulting in water-soluble decline, and making the water-reducing agent macromolecule failed to anchor cement particle surface. The repulsion of the side chain is sufficiently realized, so the fluidity of the slurry is deteriorated [12].

3.2. Infrared spectroscopy analysis of PCE-8

Infrared spectrogram of the synthesized PCE-8 is shown as figure 2.

![IR spectrum of PCE-8](image)

Figure 2. IR spectrum of PCE-8.

From literature [13~16] and IR spectrum in figure 2. In the IR spectrum of the synthesized PCE-8, 3024 cm⁻¹, 3060 cm⁻¹, 3082 cm⁻¹ is the stretching vibration peak of C-H on benzene ring, 2092 cm⁻¹, 2849 cm⁻¹ is the stretching vibration peak of saturated CH and CH₂, 1600 cm⁻¹ is the framework vibration peak of benzene ring, 1494 cm⁻¹ is the in-plane bending vibration peak of C-H on the benzene ring, 676 cm⁻¹ is the stretching vibration peak of C-Cl, 1428 cm⁻¹ is the in-plane bending vibration peak of C-Cl, 1252 cm⁻¹ is the stretching vibration peak of P=O, 1093 cm⁻¹ is the absorption peak of C-O-C ether linkage on long-chain of polyoxyethylene of polyether side chain, its stretching vibration peak is at 2866 cm⁻¹, 1380 cm⁻¹ is the vibration peak of C-H on the methyl and the main chain of methyl of the side chain phosphate in the structure. It can be seen through the analysis of infrared spectroscopy, the functional groups such as phosphate ester, carbonate ester, phenyl group, methyl group and ether group are included in the polycarboxylate superplasticizer with clay-inerting and slump retention, showing that the synthesized product has the expected molecular structure.

3.3. Adaptability test results of PCEs to different clays
Selection of polycarboxylate superplasticizer with clay-inerting and slump retention PCE-2, PCE-5, PCE-8, PCE-11 and polycarboxylate superplasticizer with general slump retention PCE-0, the fluidity of the slurry is tested by using calcium-montmorillonite, illite, kaolin (internal doping, instead of 3 g cement with the same quality) respectively, and under the same superplasticizer proportion and test conditions, the adaptability of polycarboxylate superplasticizer with clay-inerting and slump retention to different clays is investigated. The test results are shown in table 4.

**Table 4.** Adaptability test results of PCEs to different clays.

| Sample | PCE     | Clay | Dosage % | Fluidity (mm) |
|--------|---------|------|----------|---------------|
| A      | PCE-0   |      |          | 0.5h 1h 2h    |
| B      | PCE-2   |      | 100      | 208 198 175   |
| E      | PCE-5   | Ca-MTT | 0.5       | 213 206 185   |
| H      | PCE-8   | illite |          | 228 213 190   |
| K      | PCE-11  |       |          | 175 160 130   |
| A      | PCE-0   |      | 100      | 208 185       |
| B      | PCE-2   |      | 114      | 223 202       |
| E      | PCE-5   | illite | 105      | 236 223 205   |
| H      | PCE-8   | kaolin | 118      | 246 230 210   |
| K      | PCE-11  |       | 110      | 204 190 170   |

From the influencing rule of the three kinds of clay cement mixed with PCE to the fluidity of cement paste can be seen, the negative effect of calcium-montmorillonite on cement paste is the largest, which is not conducive to superplasticizer to play its role in water dispersion, especially the negative effect of the polycarboxylate superplasticizer with general slump retention PCE-0 in water reduction and dispersion is particularly serious. Illite to the fluidity of the cement slurry shows an overall downward trend, and the decreasing trend of the cement slurry fluidity of polycarboxylate superplasticizer with general slump retention is more obvious than that of polycarboxylate superplasticizer with clay-inerting and slump retention. The presence of kaolin has no negative effect on the cement slurry fluidity of the polycarboxylate superplasticizer with and slump retention, and does not affect the polycarboxylate superplasticizer to play its role in water dispersion.

As the clay crystal structure adsorbs a lot of metal cations, if the clay mineral crystal structure is unstable, clay-adsorbing cations such as Mg$^{2+}$, Ca$^{2+}$ and other polyvalent metal cations react with a
large number of anions such as -COO’ on the branch chain of the polycarboxylate superplasticizer to produce complexes that is insoluble in water, polycarboxylate superplasticizer is consumed, resulting in the polycarboxylate superplasticizer molecules used to disperse water decreased, which resulted in slurry fluidity losses [13]. From the date of table 4 can be obtained: The prohibition effect of polycarboxylate superplasticizer with clay-inerting and slump retention on the negative effect of clay is significant, especially the prohibition effect on calcium-montmorillonite is especially obvious. Polycarboxylate superplasticizer with clay-inerting and slump retention is a kind of polymer with strong adsorption property, its molecular structure contains a great deal of functional groups such as carbonic ester, hydroxyl group, phosphoric ester, initially it hydrolyzes a small amount of -COO’, and only adsorbs Mg$^{2+}$, Ca$^{2+}$ and other polyvalent metal cations, and not reacts with the metal cations to produce a complex that is insoluble in water and is consumed. With the cement hydration, the carbonic ester and phosphoric ester in the polycarboxylate superplasticizer with clay-inerting and slump retention are respectively turned into carboxylic acid and phosphonic acid by hydrolysis, the adsorption capacity of phosphonic acid group is stronger than-COO’ ,and preferential adsorbs to the soil surface, thereby further reduces the consumption of -COO’. Hydrophilic groups dissolve in the solution to form an adsorption film, the hydrophobic groups reduce the surface tension and is more conducive to adsorbing the cement particle, so that they are closely connected together and like charges with the same electrical charge. According to the electrostatic force, the same kind of electric charges repel each other. Flocculent structure formed by cement-water is forcibly destroyed, and the free water inside the package is released, the free water content of the slurry increases, so greatly improves the flow of cement paste.

3.4. Electrical properties of cement particle in cement-PCE solution

In this study, using a water-cement ratio of 800: 1 system, 0.5g of reference cement mixes with 400ml various concentration of PCE, stirs for 20 min, and the mixture is well mixed. After standing for 10 min, take the upper suspension solution into the U-type electrophoresis tank, begin measuring zeta potential. Select the appropriate cement particle for testing, and apply a positive and negative voltage each time, and take ten as a group, to determine the zeta potentials of cement particle with different concentrations of PCE.

![Figure 3](image)

**Figure 3.** Influence of different concentration of PCE on Zeta potential.

Figure 3. shows that the surface of pure cement particle is positively charged, while the surface of cement colloid particle with PCE is negatively charged. The absolute value of the zeta potential of cement particle at saturation content is: PCE-8 (-21.941mV) > PCE-5 (-18.507mV) > PCE-2 (-
16.463mV) > PCE-0 (-12.257mV) > PCE-11 (-8.997 mV). The larger the absolute value of zeta potential, the greater the anionic charge intensity on the cement particle surface, and the anion charge originates from the hydrolysis of the carbonic ester and phosphate ester in the molecular structure of the polycarboxylate superplasticizer. The hydrophobic group content in the molecular structure of PCE-11 exceeds a certain range, so that the association between molecules increases, the hydrophobic structure shrinks together, and the hydrophilic structure is distributed inside the aggregates, shields the part of the charge itself, so the zeta potential absolute is minimum. The molecular structure of PCE contains phosphate ester, which hydrolysis to produce phosphonate group with two negative charges, with a strong adsorption, and easy to adsorb in the cement particle surface, so the absolute value of zeta potential is greater than polycarboxylate superplasticizer with general slump retention PCE-0. The phenyl content in the branch-chain structure of PCE-2 and PCE-5 superplasticizer is large, that makes the stiffness of superplasticizer molecular increasing, and the steric hindrance effect is much greater than the PCE-8, so the adsorption probability of the adsorbed polar point of the polycarboxylate macromolecule and the surface of the cement particle is reduced.

3.5. Absorptive capacity of PCE in clay and cement paste

In order to find out whether there are differences in absorptive capacity of polycarboxylate superplasticizer with general slump retention and polycarboxylate superplasticizer with clay-inerting and slump retention for different types of clay minerals, and to determine absorptive capacity of polycarboxylate superplasticizer with clay-inerting and slump retention for cement particle and a variety of clay minerals, so as to reveal the root cause of different effects on concrete performance. In this paper, the TOC total organic carbon analyzer would be used to determine the absorptive capacity of five polycarboxylate superplasticizer with slump retention (PCE-0, PCE-2, PCE-5, PCE-8, PCE-11) for cement and cement respectively mixed with three kinds of monogenic clay mineral (calcium-montmorillonite, illite and kaolin) under the same conditions. The preparation process of TOC test sample is as follows, weighs 1 g powder (with the presence of a monogenic clay mineral, the doped quality is 1% of powder ), adds to 50 ml concentration of 4 g / L of polycarboxylate superplasticizer solution prepared by pure water ,stirs 20 min. After standing for 10 min, the solution is filtered using a sand core active filtration device and a microfiltration membrane, and takes 5 ml filtrate liquid to dilute 10 times as a TOC test sample; And then using the TOC total organic carbon analyzer to measure the organic carbon content of the sample, from the total amount of mixed with polycarboxylate superplasticizer with slump retention minus the total organic carbon content in filtrate is the solid particle adsorbed by superplasticizer. The experimental results are shown in figure 4.

![Figure 4. Adsorption of PCE on cement and clay.](image-url)
As can be seen from figure 4, in the pure cement system, different polycarboxylate superplasticizers with slump retention have different adsorption capacities to cement, which is due to the polycarboxylate superplasticizer with clay-inerting and slump retention grafts the free phosphate ester structure to different positions of molecular structure of superplasticizers by chemically bonded by Arbuzov reaction, and the introduction of a 4-vinylbenzyl chloride and trimethyl phosphite (TMP) performs Arbuzov reaction will be produced two phosphate ester. The molar ratio of phosphate ester in PCE-2 is 33.2%, the phosphate ester content of PCE-5 is 28.6%, the phosphate ester content of PCE-8 is 25%, the phosphate content ester of PCE-11 is 22.2%, the hydrolysis of the part of carbonic ester into -COO- and of part of phosphate ester into phosphonic acid group in molecular structure adsorbs on the surface of cement or hydration products, and phosphonic acid group with two negative charges, its adsorption capacity is stronger than -COO-, so the adsorbing capacity is PCE-8 > PCE-5 > PCE-2 > PCE-0 > PCE-11. In the cement system with three kinds of 1% clay, the influence of different clay on the adsorption capacity of polycarboxylate superplasticizer is different, and the adsorbing capacity is PCE-11 > PCE-0 > PCE-2 > PCE-5 > PCE-8. On the one hand relative to the free phosphate material, the different molecular structure of polycarboxylate superplasticizer with clay-inerting and slump retention contains phosphate ester at different locations, hydrolysis and decomposition into phosphate group anions and adsorption with clay, and the polar end of the benzene ring group forms an organic layer on the clay surface, by preventing the contact between the clay and the water molecules to suppress the expansion of the clay so that the interlayer spacing is increased or refined into particle having a larger specific surface area, and to reduce the adsorption of clay to polycarboxylate superplasticizer and mixing water; On the other hand, the adsorption capacity of the phosphate group is stronger than that of the carboxylic acid group, which is preferentially adsorbed on the clay surface in the aggregate. The benzene ring has large steric hindrance and occupies the adsorption activity point on the clay, thus reduces the adsorption of the clay to the polycarboxylate superplasticizer.

3.6. Concrete application performance test
The properties of concrete with different polycarboxylate superplasticizer with clay-inerting and slump retention admixture are compared test. Concrete mix proportion and test requirements are implemented in accordance with GB / T8076-2008, concrete reference mix proportion is shown in table 5.

| Table 5. Mix proportion of concrete (kg/m³). |
|--------------------------------------------|
| Cement | Sand  | Coarse aggregate | PCE | Water |
|--------|-------|------------------|-----|-------|
| 390    | 785   | 1040             | 3.9 | 165   |

According to concrete reference mix proportion, clay content (1% of the amount of cement) is instead of sand doped with the same quality, the effect of polycarboxylate superplasticizer on workability and strength of concrete with different clay content is studied. The results are shown in table 6.
As can be seen from table 6, the effect of PCE on the negative effect of clay on the workability of concrete mixed with polycarboxylate superplasticizer is remarkable. PCE introduces hydrophobic groups into its molecular structure, such as the introduction of part of the phenyl group to reduce its surface tension, it can be rapid dispersion and adsorption in the concrete; The introduction of part of the phosphate ester, phosphate ester hydrolysis into phosphonic acid with two negative charges, preferentially adsorbs and occupies the adsorption activity points of the clay surface, through the polar end of the benzene ring group to form a organic layer in the clay surface to prevent the clay and water molecules in contact, to inhibit the expansion of clay, and makes the interlayer spacing increased or refined into particle with larger specific surface area, and reduces the adsorption of clay to polycarboxylate superplasticizer and mixed water; Such as the introduction of part of the carbonate
ester hydrolysis into carboxy, continue to play a role in the dispersion, and enhance the slump retention ability of superplasticizer. The introduction of the phosphate ester, carbonic ester and phenyl group in the molecular structure of polycarboxylate superplasticizer with clay-inerting and slump retention, so that it has remarkable soil adaptability.

Table 6. Polycarboxylate superplasticizer influent on properties of concrete mixed different clay.

| Sample | PCE   | Clay         | Slump/Flow/mm/mm | Compressive strength/MPa |
|--------|-------|--------------|------------------|--------------------------|
|        |       |              | 0.5h 1h 2h 7d 28d|                           |
| A      | PCE-0 | -/-          | 110/- 210/500 210/480 | 33.7 42.6                |
| B      | PCE-2 | -/-          | 150/- 215/510 210/490 | 34.2 43.5                |
| E      | PCE-5 | -/-          | 165/- 215/520 210/505 | 35.3 45.3                |
| H      | PCE-8 | -/-          | 180/- 220/540 215/520 | 36.4 46.3                |
| K      | PCE-11| -/-          | 200/- 210/480 205/465 | 33.4 42.9                |

| A      | PCE-0 | -/-          | 90/- 210/480 210/460 | 32.8 41.9                |
| B      | PCE-2 | -/-          | 130/- 215/495 210/480 | 33.2 44.6                |
| E      | PCE-5 | -/-          | 145/- 215/505 210/495 | 35.7 45.7                |
| H      | PCE-8 | -/-          | 170/- 220/530 215/510 | 36.6 45.6                |
| K      | PCE-11| -/-          | 70/- 210/455 205/440  | 33.1 43.4                |

4. Conclusion
According to the molecular design principles, using oxidation - reduction free radical polymerization and Arbuzov reaction method, a kind of polycarboxylate high performance water reducing agent is synthesized, a kind of PCE is synthesized, the main conclusions are as follows:

(1) With hydroxyethyl acrylate (HEA), 4-vinylbenzyl chloride (VBC) and terminal alkenyl polyoxyethylene ether (TPEG) as reactants, based on different weight ratio, a series of polycarboxylate superplasticizer (PCE) with clay-inerting and slump retention by introduced phenyl group, phosphate ester and carbonic ester functional groups are synthesized by Arbuzov reaction.
(2) IR spectra prove the existence of the characteristic functional groups, and the synthesized products have the expected molecular structure. The results of GPC show that the molecular weight distribution of the synthesized product is narrow and the conversion rate of the reactants is high, and the resulting product has an ideal molecular structure.

(3) The experimental results of the surface tension, the zeta potential of slurry system and the adsorption capacity of the polycarboxylate superplasticizer to the powder show that, polycarboxylate superplasticizer with clay-inerting and slump retention can reduce the adsorption capacity of clay to polycarboxylate superplasticizer and inhibit the expansion of soil so as to reduce the adsorption of polycarboxylate superplasticizer and mixed water.

(4) The adsorption capacity of the polycarboxylate superplasticizer with slump retention in the presence of clay and cement is larger than that of the pure cement with the same quality. It is shown that the clay adsorbs some polycarboxylate superplasticizer. PCE is conducive to the dispersion and stability of cement particle to improve the flow effect, and to inhibit the expansion of clay to reduce the adsorption of polycarboxylate superplasticizer and mixed water, and has a very good adaptation with clay.

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