Synthesis and rheological properties of retarding polycarboxylate superplasticizers

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Abstract. In this paper, different types of retarding polycarboxylate superplasticizers (PT-1, PT-2 and PT-3) were synthesized. The structure information and functional groups of the water reducing agent were characterized by gel chromatography and infrared spectroscopy. The rheological properties of the retarding polycarboxylate superplasticizers for cement paste were studied. The results show that PT-1 containing sulfonic group and hydroxyethyl ester has good initial dispersion, while PT-2 containing hydroxyethyl ester and hydroxypropyl ester has long-term slump-retaining effect. The shear stress of PT-1, PT-2 and PT-3 on cement paste increases with the increase of shear rate, while the apparent viscosity decreases rapidly at first and then tends to be stable gradually with the increase of shear rate. The research results are of great guiding significance for the design of different types of retarding polycarboxylate superplasticizers.

1. Introduction
Polycarboxylic acid water reducer is a green and environmentally friendly chemical admixture for concrete, because its excellent water reducing performance is gradually widely used in the industry. The traditional polycarboxylic water reducer can usually achieve good dispersion effect or water reducing performance [1-3]. But many problems follow, one of the most common problems is how to control the rapid loss of concrete slump. Starting from the molecular structure design of polycarboxylic water reducer, the slump-retaining performance of concrete can be improved by introducing functional groups. Wang Hao et al[4] prepared different types of polycarboxylate superplasticizer by introducing styrene (SM), sodium p-styrene sulfonate (SSS) and p-styrene phosphate (VPPA), and studied their effects on the fluidity, zeta potential and adsorption capacity of cement paste. Wang Xiumei et al[5] prepared polycarboxylic water reducer by introducing hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), acrylamide (AM), 2-acrylamide-2-methacrylamide (AMPS), and studied their influence on zeta potential, dispersion and adsorption of cement paste. The effects of polycarboxylic water reducer with functional monomers on rheological properties were not considered in the above studies.

In this paper, three kinds of functional monomers, hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and sodium methacrylate sulfonate (SMAS) were introduced to prepare different types of retarding polycarboxylate superplasticizers, and their effects on dispersion, zeta potential and rheological properties of cement pastes were studied. In order to find out the effect of functional groups on the rheological properties of retarding polycarboxylate superplasticizers that providing a basis for the preparation of polycarboxylic water reducer.
2. Experimental

2.1. Materials
The main performance test raw materials for experiment: The reference cement is produced by Shandong Lucheng Cement Co., Ltd. and it is P.I 42.5 grade. The characteristics and compositions of the sample are given in Table 1.

| Sample | Fe₂O₃/% | Al₂O₃/% | SiO₂/% | CaO/% | MgO/% | SO₃/% | K₂O/% | Na₂O/% | fCaO/% |
|--------|---------|---------|--------|-------|-------|-------|-------|-------|-------|
| Cement | 5.83    | 6.20    | 17.85  | 61.77 | 0.50  | 2.94  | 0.37  | 0.09  | 1.11  |

The main synthetic experimental raw materials: The monomers used were hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), acrylic acid (AA), sodium methacrylate sulfonate (SMAS), all of which were of analytical grade. Pre-pentenol polyoxyethylene ether (TPEG) with a molecular weight of 2,400, was produced by Liaoning Aoke Chemical Co., Ltd. The initiator of hydrogen peroxide (H₂O₂), the chain transfer agent of thioglycolic acid, and the reducing agent of ascorbic acid Vc were all chemically pure.

2.2. Preparation of retarding polycarboxylate superplasticizers
Using prenol polyoxyethylene ether (TPEG) as a macromonomer, under the initiator system, the mixture of acrylic acid (AA) and functional monomer was dripped at the prescribed dosage in accordance with the prescription, and then dripped in a certain period of time. After a period of constant temperature, 30% sodium hydroxide solution was added to adjust the pH value to 6.0-7.0, and then the retarding polycarboxylate superplasticizers of PT-1, PT-2 and PT-3 were obtained.

2.3. Performance test method

2.3.1. Infrared spectroscopy measurement
The synthesized liquid sample was precipitated with ethanol, filtered and dried, mixed with potassium bromide and compressed, and the infrared spectrum was measured by an infrared spectrometer.

2.3.2. Gel chromatography measurement
The US Waters 1515 Isocratic HPLP Pump/Waters 2414 Differential Detector and Breeze Software Acquisition and Analysis System were used. The column was connected in series by Ultrahydrage™ 250 and Ultrahydrage™ 500, and the mobile phase was 0.1 mol/L sodium nitrate solution at a flow rate of 0.80 ml/min.

2.3.3. Fluidity of cement paste measurements
According to the standard method in GB/T 8077-2012 "Test method for homogeneity of concrete admixture".

2.3.4. Zeta potential measurements
The zeta potential of the cement surface was measured by a JS94K2 microelectrophoresis apparatus from Shanghai Zhongchen Company.

2.3.5. Rheological properties measurements
The zeta potential of the cement surface was measured by a JS94K2 microelectrophoresis apparatus from Shanghai Zhongchen Company at a constant temperature of 20°C.
3. Experimental results and discussion

3.1. Characterization of retarding polycarboxylate superplasticizers

3.1.1 Gel chromatography

The molecular structure information of the retarding polycarboxylate superplasticizers are shown in Table 2.

| Sample | Functional monomer | Mw1  | Mp1  | Mw1/Mn1 | Mp2  | Conversion rate/% |
|--------|--------------------|------|------|---------|------|------------------|
| PT-1   | HEA, SMAS          | 132909 | 68108 | 3.21118 | 2941 | 85.28           |
| PT-2   | HEA, HPA           | 92608  | 55024 | 2.357889 | 2548 | 79.68           |
| PT-3   | HEA                | 70047  | 46544 | 2.176077 | 4680 | 82.06           |

As shown in Table 2, the highest conversion rate of PT-1 is 85.28, the lowest conversion rate of PT-2 is 79.68. From the molecular weight distribution, the molecular weight distribution of PT-3 is narrower, the degree of polymerization is 2.17, the molecular weight distribution of PT-1 is widest, the degree of polymerization is 3.21, and its macromolecular polymer is more.

3.1.2 Infrared Spectrum

Figure 1 of (a), (b) and (c) are infrared spectra of PT-1, PT-2 and PT-3 respectively. It can be seen that the characteristic absorption peaks of PT-1, PT-2 and PT-3 are 3310 cm\(^{-1}\), 3290 cm\(^{-1}\) and 3342 cm\(^{-1}\), respectively. The characteristic absorption peaks of carbonyl (C=O) are 1732 cm\(^{-1}\), 1732 cm\(^{-1}\) and 1736 cm\(^{-1}\), and the stretching vibration peaks of aliphatic ethers are 1108 cm\(^{-1}\), 1116 cm\(^{-1}\) and 1108 cm\(^{-1}\), respectively. In addition, the stretching vibration absorption peak of S-O at 1350 cm\(^{-1}\) in Figure 1(a) indicates that sulfonic acid group is introduced into PT-1.

![Figure 1. Infrared Spectrum of PT-1, PT-2 and PT-3](image)

3.2. Effect of retarding polycarboxylate superplasticizers on dispersion of cement paste

Figure 2 shows the variation of slurry fluidity of PT-1, PT-2 and PT-3 with slump retention time at 0.35% concentration. From Figure 2, it can be seen that the slurry fluidity of the three kinds polycarboxylate superplasticizers increase at first and then decrease with the prolongation of slump retention time at the same dosage. The best initial dispersion is PT-1, which is due to the introduction of sulfonic acid group into PT-1, which increases the adsorptive activity of polycarboxylate superplasticizer molecule to cement particles, resulting in the increase of initial fluidity of cement paste. And PT-2 has the best slump retention in the later stage, because hydroxypropyl acrylate is introduced into PT-2 that its hydrolysis speed is slower than hydroxyethyl acrylate, which can further promote the increase of fluidity. Therefore, the decreased of the slurry fluidity of PT-2 in the later stage is less than that of PT-3.
3.3. Effect of retarding polycarboxylate superplasticizers on the zeta potential of cement pastes
Figure 3 shows the change trend of zeta potential of PT-1, PT-2 and PT-3 with slump retention time at 0.35% concentration.

Figure 3 shows that the zeta potential of cement particles with three kinds of polycarboxylate superplasticizers varies with the prolongation of slump retention time. When the slump retention time of PT-3 is 1 h, the absolute zeta potential reach the maximum, then decrease, while the absolute zeta potential of PT-1 and PT-2 reach the maximum at the slump retention time of 2 h, and both of them are larger than PT-1. This is because PT-1 contained sulfonate besides ester group and PT-2 contained hydroxyethyl ester and hydroxypropyl ester. It is speculated that the increase of zeta potential absolute value with the increase of slump retention time is due to the increase of short side chains caused by hydrolysis of long side chains. More water reducer molecules are adsorbed on the surface of cement particles, thus increasing the zeta potential absolute value. While, the zeta potential absolute value of PT-1 and PT-3 decrease with the prolongation of slump retention time, which is due to the completed hydrolysis of hydroxyethyl ester and the decrease of water reducer molecules adsorbed on the surface of cement particles, resulting in flocculation between cement particles [6-7].

3.4. Effect of retarding polycarboxylate superplasticizers on the rheological behavior of cement pastes
Figures 4-6 show the rheological behavior curves of PT-1, PT-2 and PT-3 at 1 h, 2 h and 3 h at 0.35% concentration. All diagrams (a) represent the rheological curves of shear rate and shear stress, and all diagrams (b) represent the rheological curves of shear rate and viscosity.

From Figure 4, it can be seen that when the slump retention time is 1 h, the shear stress and viscosity are PT-2 > PT-3 > PT-1 at the same shear rate, indicating that PT-2 cement paste is thicker at this time, forming a large number of flocculating structures, and the friction resistance between cement particles is larger, while PT-3 and PT-1 have better dispersion performance, and the hydrolysis rate of ester groups is fast, destroying the flocculation structure of the slurry, so that the shear stress and viscosity are relatively small.
It can be seen from Figure 5 that when the retention time is 2h, the shear stress and viscosity are PT-3>PT-2>PT-1 at the same shear rate, indicating that with the prolongation of slump retention, hydroxypropyl ester begins to hydrolyze and the dispersion of PT-2 becomes better, while PT-3 is completely hydrolyzed by hydroxyethyl ester, resulting in less water reducing agent adsorbed on the surface of cement particles, and there is strong interaction force between cement particles, and the flocculation structure is formed, resulting in deterioration of dispersion retention performance.

![Figure 5](image)

**Figure 5. Rheological behavior curve of slump retention time of 2 h**

From Figure 6, it can be seen that the shear stress of cement paste increases with the increase of shear rate when the slump retention time is 3 h, and the effect of retarding polycarboxylate superplasticizers containing different functional monomers on shear stress and viscosity of cement paste is also different. The shear stress and viscosity at the same shear rate are PT-3 > PT-1 > PT-2, which indicates that PT-2 has a long-term effect on slurry slurry.

![Figure 6](image)

**Figure 6. Rheological behavior curve of slump retention time of 3 h**

From figures 4-6 can be seen that the shear stress of cement paste with PT-1, PT-2 and PT-3 containing different functional monomers increases with the increase of shear rate, while the apparent viscosity decreases rapidly at first and then tends to be stable. It can also be seen that at the same shear rate, the shear stress and viscosity of PT-2 decrease gradually with the prolongation of slump retention time, and show shear thinning behavior. When slump retention time is 3 h, the viscosity of cement paste increases with the increase of shear rate, and shear thickening behavior occurs, which may be water in the paste. The hydrodynamic pressure of mud particles is greater than the interaction force between the particles. The cement particles are fully dispersed and become disordered, which greatly increases the flow resistance of cement paste.

4. Conclusions
   (1) At the same dosage, with the prolongation of slump retention time, the slurry fluidity of the three water reducers increase at first and then decrease in varying degrees. PT-1 containing sulfonate and hydroxyethyl ester has good initial dispersion, while PT-2 containing hydroxyethyl ester and hydroxypropyl ester has long-term slump retention.
(2) The variation range of zeta potential on the surface of cement particles with three kinds of water reducers varies with the prolongation of slump retention time. It is speculated that the increase of zeta potential absolute value with the increase of slump retention time is due to the increase of short side chains caused by hydrolysis of long side chains and the decrease of zeta potential absolute value of more water reducers adsorbed on the surface of cement particles, while the decrease of Zeta potential absolute value is due to the decrease of water reducing agent molecules adsorbed on the surface of cement particles, resulting in flocculation between cement particles.

(3) The shear stress of PT-1, PT-2 and PT-3 on cement paste increased with the increase of shear rate, while the viscosity decreases rapidly at first and then tends to be stable gradually with the increase of shear rate.

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