Synthesis and Properties of a Debonded Polycarboxylic Acid Superplasticizer

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Abstract. High-strength concrete has always had the problem of high viscosity which is not easy to construct, but reducing viscosity will inevitably affect the strength of concrete. In this paper, a kind of polycarboxylic acid series viscosity reducing agent JN-1 was synthesized by adjusting the synthetic raw material, which can reduce the viscosity and ensure the strength of high strength concrete for 28 days to reach or exceed 100%, Synthesis Key points are the use of acrylamide and the control side chain length.

1. Introduction
In order to achieve high strength of high-grade concrete, a large number of cementitious materials and low cement ratio are used, which leads to poor workability of concrete and viscosity can greatly affect the construction, especially for pumping high-grade concrete; a large number of cementitious materials also make high-grade concrete hydration heat, which is easy to produce internal cracks and has a great influence on the strength[1-3].

At present, the treatment of high grade concrete problem is generally to increase the admixture content and adjust the admixture content, the increase of admixture content will not only prolong the setting time, but also have the problem of bleeding water grasping the bottom after over-doping, and the increase of the cost is also not conducive to the construction[4-6]. Domestic research on viscosity reducing polycarboxylate superplasticizer was lacking. The best products on the market were BASF RHEOPUS series products, but the unit price is very high. Therefore, it is urgent to develop a good viscosity reducing superplasticizer.

In this study, the molecular design was carried out by using the crosslinking monomer ethylene glycol dimethacrylate as the active macromonomer, and the amide group was added while polymerizing with the carboxylic acid group small monomer to strengthen the hydrophobicity of the molecular structure, and finally in the aqueous solution Viscosity-reducing polycarboxylic acid water reducing agent is obtained through polymerization. The results show that the synthetic JN-1 viscosity-reducing polycarboxylic acid superplasticizer can effectively solve the problem of excessive viscosity of high strength concrete and keep the strength for 28 days within the limits of eligibility.
2. Test section

2.1. Experimental raw materials and main experimental instruments

2.1.1. Synthetic raw material
Crosslinking monomer ethylene glycol methacrylate, Nanjing Shining Industry and Trade Co., Ltd. Isopentenol polyoxyethylene ether (TPEG), Liaoning Oak Co., Ltd. Acrylic acid (AA) Kaitai Chemical Industry; Acrylamide, Dongguan Dingsheng Environmental Technology Co., Ltd. Hydrogen peroxide Weisheng Chemical Industry, Xiamen; mercaptopropionic acid Jinan Xinshun Chemical Industry New reducing agent liquid alkali Hebei Huikai Chemical Products Sales Co. Ltd.

2.1.2. Instruments and equipment
DF101S Magnetic Heating Mixer; BT100-01 Creep Pump, Electronic Balance; Constant Temperature Water Bath Pot; HJW600 Single Axis Mixer; Infrared Spectrometer IR; Vacuum Dryer.

2.2. Debonded polycarboxylic acid superplasticizer Synthesis process
The measured tpeg-1000 and water were added into a 250 mL four flask after mixing evenly, the acrylic acid and hydrogen peroxide were added. the mixed aqueous solution of crosslinked monomer dimethyl glycol methacrylate and acrylamide and the mixture of acrylic acid and mercaptopropionic acid and new reducing agent were added at room temperature. after adding 3 h, the constant temperature was 1 h, and then the liquid alkali was added to adjust the pH to obtain JN-1. where n(AA): n(TPEG)=3: 1, where the new reducing agent, acrylamide, dimethylethylene glycol ester and mercaptopropionic acid were 0.16%, 1%, 2.5% and 0.8% of the total monomer mass, respectively, and n (new reducing agent): n (hydrogen peroxide)=1: 4.

2.3. Performance testing methods

2.3.1. Infrared spectrum
Infrared spectral analysis of JN-1, such as shown in Figure 1.

![Infrared Spectrogram](image)

Figure 1. Debonded polycarboxylic acid superplasticizer JN-1 Infrared Spectrogram
As you can see from figure 1, at 3301.1 cm⁻¹ The characteristic absorption peak of -OH appeared at 2967.2 cm⁻¹, 1469.7 cm⁻¹ for -CH₃, -CH₂, C-H ground motion at 1682.0 cm⁻¹. The absorption peak of amides appeared at 1153.9 cm⁻¹ where the stretching vibration peak of the fat ether and the ether bond of the large monomer TPEG-1000. So the structure of JN-1 is the same as the molecular structure of the design.

2.3.2. Emptying test and compressive strength test raw materials.
Four polycarboxylic acid superplasticizer samples were collected for comparison experiments with JN-1, and the parameters were shown in Table 1.
Table 1. Sample parameters

| Model  | Sd%  | pH  | Appearance | Characteristics                  |
|--------|------|-----|------------|----------------------------------|
| JN-1   | 49.3 | 5.21| Colorless  | KZJ Debonding Type               |
| JN-2   | 50.4 | 5.33| Light yellow| Market type of viscosity reduction|
| JN-3   | 49.8 | 5.65| Brown      | Market type of viscosity reduction|
| JN-4   | 49.6 | 5.31| Colorless  | Market type of viscosity reduction|
| PT-5   | 49.6 | 6.01| Colorless  | KZJ General Type                 |

2.4. Performance of experimental raw materials and mix ratio of experiments

2.4.1. Cement: hailuo cement, P.O52.5 ordinary Portland cement and hongshi cement, P.O52.5, its performance index is shown in Table 2.

Table 2. Cement performance indicators

| Cement variety | Specific surface area (m²/kg) | Stability | Setting time (min) | flexural strength (MPa) | Compressive strength (MPa) |
|----------------|-------------------------------|-----------|--------------------|------------------------|---------------------------|
|                |                               |           | Initial setting    | Final setting          | 3d  | 28d  | 3d  | 28d  |
| Hailuo P.O52.5 | 382                           | Qualified | 134                | 184                    | 6.2 | 9.1  | 33.1| 60.9 |
| Hongshi P.O52.5| 390                           | Qualified | 130                | 180                    | 5.9 | 8.8  | 33.5| 60.7 |

2.4.2. Mineral powder: Xinze mineral powder, S95 grade slag powder, specific surface area 420 m²/kg, the 28 d activity index was 97%.

2.4.3. Silica ash: The density of silica fume is 2.25 g/cm³ at a silica fume production base in Jiangxi with a fineness of 2.7% and a specific surface area of 29 m²/g.

2.4.4. Sand and stone: On the market, sand is medium sand, fineness modulus 2.4, stone is continuous gradation, diameter 5-20 mm basalt gravel, the rest of the indexes are in accordance with the second grade sand and stone standard.

2.4.5. Admixtures: viscosity-reducing polycarboxylic acid water reducing agent developed by KZJ of Guangdong Province and viscosity-reducing polycarboxylic acid water reducing agent sold on the market. The experimental mix ratio adopts the mix ratio of C100, the design requirement is P15, D300, see Table 3 in detail.

Table 3. Experimental mix ratio

| Cement  | Silica Ash | Mineral powder | Sand  | Stone | Water | Admixture |
|---------|------------|----------------|-------|-------|-------|-----------|
| 480     | 100        | 70             | 670   | 1100  | 112   | 13        |

2.5. Experimental steps

2.5.1. Tirring: Pour the weighed cement, silica fume, mineral powder and sand into the mixer for 3 min first. Pour the water reducer and water into a blender for another 3 min.
2.5.2. Emptying test: according to GB/T 50080 standard for performance test method of common concrete mixture. Firstly, the slump tube is put upside down and sealed tightly, then the concrete mixture is added into the slump tube in two layers, the seal cover is opened, and the time of total emptying of concrete mixture is measured by stopwatch to 0.01 s.

2.5.3. Extensibility: in the emptying experiment, the expansion of the concrete is measured after all the concrete mixture is emptied, and the maximum diameter of the expansion surface and the diameter of the vertical maximum diameter are measured in two directions. The measurement results are accurate to 1 mm, and the result is revised to about 5 mm.

2.5.4. Molding: The concrete mixture is poured into 100mm×100mm×100mm triple mold and vibrated on the shaking Table for 20 s.

2.5.5. Curing: After the mixture is formed, put it in the curing room for 3 days, 7 days and 28 days, and then carry out the compressive strength test.

3. Results Discussion

3.1. Emptying test

Hailu cement experimental data data are shown in the Table 4, 5, 6.

Table 4. Emptying time/S

| Model  | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|--------|------|------|------|------|------|
| Experimental values | 8.31 | 8.99 | 10.00 | 8.36 | 11.2 |
| Experimental values | 8.22 | 9.21 | 9.77 | 8.64 | 12.1 |
| Mean value | 8.3 | 9.1 | 9.9 | 8.5 | 11.7 |

Emptying time from small to large: JN-1, JN-4, JN-2, JN-3, PT-5.

Table 5. Extension/mm

| Model  | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|--------|------|------|------|------|------|
| Measurements | 580 | 570 | 562 | 572 | 550 |
| Measurements | 577 | 564 | 566 | 576 | 549 |
| Mean value | 580 | 570 | 565 | 575 | 550 |

Extensibility from large to small are: JN-1, JN-4, JN-2, JN-3, PT-5. Among them, the emptying time of JN-1 and JN-4 is significantly shorter than that of PT-5, and the fluidity is improved well. It is proved that JN-1 and JN-4 can effectively reduce the yield stress in concrete system. Essentially, the increase of free water makes the viscosity reduction effect obvious.

Figure 2. Emptying time and flow trends
Table 6. Compressive strength/MPa

| Model | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|-------|------|------|------|------|------|
| 3d    | 71.2 | 68.2 | 66.7 | 70.2 | 78.1 |
| 7d    | 99.8 | 96.1 | 100.4| 98.9 | 102.3|  
| 28d   | 115.1| 110.2| 113.6| 111.7| 118.7|  

28 d compressive strength from large to small: PT-5, JN-1, JN-3, JN-4, JN-2

![Strength data](image)

Figure 3. Strength data

Hongshi cement data are shown in the Table 7, 8, 9.

Table 7. Emptying time/S

| Model         | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|---------------|------|------|------|------|------|
| Experimental values | 8.44 | 9.01 | 11.5 | 8.21 | 11.9 |
| Experimental values | 8.67 | 9.33 | 11.1 | 8.96 | 12.8 |
| Mean value    | 8.6  | 9.2  | 11.3 | 8.6  | 12.4 |

Emptying time from small to large: JN-1, JN-4, JN-2, JN-3, PT-5.

Table 8. Extension/mm

| Model         | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|---------------|------|------|------|------|------|
| Measurements  | 578  | 560  | 570  | 567  | 548  |
| Measurements  | 570  | 558  | 566  | 560  | 548  |
| Mean value    | 575  | 560  | 565  | 565  | 550  |

Extensibility from large to small are: JN-1, JN-4, JN-3, JN-2, PT-5. After replacing the hongshi cement, the overall viscosity increases, it should be that the specific surface area of the hongshi cement is larger, the standard consistency water consumption is higher, so the water demand is higher, in which the emptying time and fluidity of JN-3 change greatly, which indicates that its sensitivity to the material is more general, and the viscosity reduction effect is greatly affected by the cement performance.
Figure 4. Emptying time and flow trends

Table 9. Compressive strength/MPa

| Model | JN-1 | JN-2 | JN-3 | JN-4 | PT-5 |
|-------|------|------|------|------|------|
| 3d    | 70.5 | 69.3 | 68.7 | 69.9 | 76.5 |
| 7d    | 96.7 | 97.3 | 99.7 | 96.4 | 103.2|
| 28d   | 112.3| 112.7| 117.0| 111.4| 115.5|

28 d compressive strength from large to small: PT-5, JN-3, JN-2, JN-1, JN-4.

Figure 5. Strength data

4. Conclusions

(1) The synthetic JN-1 has shorter emptying time than that of the inverted slump cylinder of the commercial viscosity reducing agent under the same conditions, 3.5 s shorter than that of the general water reducing agent PT-5, and the fluidity is also obviously improved under the same amount, and the strength of 28 days were greater than 100% of the design strength of the mix ratio at the same time of achieving the viscosity reduction effect.

(2) The change of experimental law after replacing cement is more consistent, only JN-3 has poor raw material sensitivity, the data fluctuate greatly after replacing with hongshi cement, JN-1 and JN-4 have the same viscosity reduction effect, the emptying time is 30% lower than that of ordinary water reducing agent, and the 28 d strength of JN-1 and JN-3 is higher, reaching 102.1% of the design strength.

(3) The polyoxyethylene side chain of the synthesized JN-1 is short, the association of chain structure and water molecules can effectively reduce the viscosity of concrete, and the addition of acrylamide makes the amide group and water molecules form more hydrogen bonds, and it can also effectively reduce the viscosity of concrete.

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