The Structure and Composition Analysis, Synthetic Design and Performance Research of Unknown Polycarboxylate Superplasticizer

Yunhui Fang¹,²,*, Yuliang Ke¹,², Xiaofang Zhang¹,², Yanmei Lin¹,², Geli Li¹,², Yuanqiang Guo¹, Miao Miao Gui², Xiu Xing Ma¹,²

¹ KZJ New Materials Group CO.,LTD., Xiamen, China
² Xiamen Academy of Building Research Group CO.,LTD., Xiamen, China
* Corresponding author (Tel: 86-13959294150; E-mail: fangyunhui@126.com)

Abstract. In this paper, the unknown polycarboxylate superplasticizer was separated and purified by ultrafiltration technology. Some instrumental analysis method were used in order to research the structure and composition such as IR, NMR, LC, GC, GPC. According to the analysis results, the synthetic polycarboxylate superplasticizer was obtained by free radical polymerization through orthogonal experiment. Comparing by the structure and performance of the unknown and the synthetic sample, it could confirm that using the monitoring and tracking analysis technology on the latest research and development of new product can provide accurate information of science and technology and market information.

1. Introduction

The polycarboxylate superplasticizer can be prepared by molecular design and molecular tailoring technology to obtain appropriate molecular structure products. As the booming development of China’s social and economic, many enterprises and research institutions do much effort on the study of product development due to the higher request of practical application [1, 2].

In the research system of product design and development, it is much more effective with keeping a close eye on the lasted product structure and composition information by using the monitoring and tracking analysis technology. Comparing consulting literature, we can determine our research direction after understanding the peer research trends and the latest technical achievements [3].

The commercial polycarboxylate superplasticizers are a complex system containing multicomponents. The superplasticizers are fabricated by synthetic process and compounding process. The raw materials of the synthetic process are as follows: macromonomers, unsaturated acid or ester monomers, initiators, chain transfer agent, etc [4]. The raw materials of compounding process are as follows too: retarders, air-entraining agents, defoaming agents, thickening agent, etc.

Because of the complexity of the sample’s composition, the difficulties of the analysis process are also different. The general process is including two important parts. One is separation the various components of the complex system, the other is analyzing the structure and composition of the separated components.

2. Experiments

2.1 Materials
Unknown polycarboxylate superplasticizer (U-PCE); Methyl allyl polyoxyethylene ether (generally called HPEG in China); Acrylic acid (AA); Ascorbic acid (Vc); Hydrogen peroxide (H$_2$O$_2$); Thioglycolic acid (TA); 30% sodium hydroxide solution (NaOH).

CHUNCHI cement (C), P.O. 42.5; Fly ash (FA), II level; River sand (S), fineness modulus of 2.3-2.6; coarse aggregate (G), the particle size of 5-20 mm.

2.2 Instruments
Perkin Elmer Sperctrum 100 Fourier Transform Infrared Spectrometer; Millipore 8400 Ultrafiltration Cup, PES ultrafiltration membrane (intercept molecular weight 30000, 10000, 3000, respectively); Waters 1515 Gel Permeation Chromatography Spectrometer (mobile phase is 0.1 mol/L sodium nitrate aqueous solution, flow rate of 0.8 mL/min); Bruker AVANCE III 400MHz Nuclear Magnetic Resonance spectrometer (CDCl$_3$ as solvent, TMS as internal standard); Agilent 1100 Liquid Chromatography Spectrometer (C18 chromatographic column, mobile phase is 0.05 mol/L methanol/phosphate buffer); Agilent 6820 Gas Chromatograph Spectrometer (FID, injection port temperature 310℃, detector temperature 320℃)

2.3 Test Methods
Testing method is according to China National Standards (GB/T 8077-2012, GB/T 50080-2016 and GB/T 50081-2016).

3. Results and discussion

3.1 IR of U-PCE
The Infrared spectrometry is the most widely used method to analyze the molecular structure. Many information can be known, such as functional group and structure types. The IR of U-PCE is shown in Figure 1.

In Figure 1, the signals at 1350.43 cm$^{-1}$ are attributed to -CH$_3$-. The signals at 1457.53 cm$^{-1}$ are assigned to -CH$_2$-. The peaks at around 1720.53 cm$^{-1}$ are assigned to C=O. The ether group (-O-) appears at peaks about 1108.78 cm$^{-1}$. The analysis shows that U-PCE belongs to ether series polycarboxylate superplasticizer.

3.2 Composition analysis of Macromonomer in U-PCE
As the main ingredient in polycarboxylate superplasticizer, the types and properties of macromonomer determine the performance. So we should investigate the macromonomer firstly.

![Figure 1. IR of U-PCE](image-url)

The macromonomer is mainly synthesized by ethoxylation reaction in the presence of catalyst, epoxy ethane and nucleophilic reagent, which containing active hydrogen ring-opening condensation
addition reaction. The information of macromonomers and their starting agents is shown in the Table 1.

| Macromonomers | Structure Formula | Starting Agents | Molecular Formula |
|---------------|-------------------|-----------------|------------------|
| APEG          | CH₂=CH-CH₂-O-(CH₂CH₂0)ₙ-H | 2-propylene-1-ol | C₃H₆O            |
| HPEG          | CH₂=C(CH₃)-CH₂-O-(CH₂CH₂0)ₙ-H | Methyl-2-propene-1-ol | C₄H₈O           |
| TPEG          | CH₂=C(CH₃)(CH₂)₂-O-(CH₂CH₂0)ₙ-H | 3-methyl-3-butene-1-ol | C₅H₁₀O          |
| VPEG          | CH₂=CH-O-(CH₂)₄-O-(CH₂CH₂O)ₙ-H | 4-hydroxyl vinyl butyl ether | C₆H₁₂O₂        |

3.2.1 Ultrafiltration Pretreatment of U-PCE

Ultrafiltration is a membrane separation technology, is driven on fluid tangential flow and pressure filtration process, and according to the size of molecular weight to separate particles.

As a mixture of a series of different molecular weight polymer, the U-PCE should be separated and purified first before qualitative analysis. The separated and purified operating procedures of U-PCE are as follows: ultrafiltrating under the nitrogen pressure by through the PES membrane which molecular weight is 30000, 10000, 3000, respectively. The ultrafiltrates called 30000 ultrafiltrate, 10000 ultrafiltrate, 3000 ultrafiltrate, respectively.

3.2.2 GPC Analysis

The separation principle of GPC is that different molecular weight size polymers are separated when polymer solution flows through the chromatographic column.

After ultrafiltration pretreatment of U-PCE, the GPC analysis can be implemented. The GPC test data of U-PCE, ultrafiltrate and HPEG is shown in the Table 2.

| Sample        | Mn  | Mw  | MP  | Mn/Mw |
|---------------|-----|-----|-----|-------|
| U-PCE         | 23500 | 41305 | 37951 | 1.76   |
| Ultrafiltrate 30000 | 15845 | 18106 | 16764 | 1.14   |
| Ultrafiltrate 10000 | 1506 | 3385 | 2048 | 2.25   |
| Ultrafiltrate 3000 | 1024 | 1851 | 1895 | 1.81   |
| HPEG          | 1094 | 1720 | 1820 | 1.57   |

In Table 2, the molecular weight of ultrafiltrate is less than U-PCE which means the separation procedure is satisfactory. Which the GPC data is similar between 3000 ultrafiltrate and HPEG, it can be speculated that we can obtain relatively pure macromonomer by ultrafiltration pretreatment.

3.2.3 1H NMR Analysis

In order to know the kind of residual macromonomer in the U-PCE, the ¹H NMR is put into use. In organic structure analysis, the NMR technology gives accuracy structure information which is the one of the best spectroscopy method. It provides two kinds of main elements in organic molecules which is hydrogen and carbon. It also affords functional group, structure units and connection information of each other. The ¹H NMR of Ultrafiltrate 3000 is shown in Figure 2.
In Figure 2, the signals at 1.7ppm are attributed to the -CH₃- in the unsaturated end molecular chain. The signals at 4.9ppm are attributed to the -CH= in the unsaturated end molecular chain. The signals at around δ = 3.6ppm and 3.8ppm are attributed to -(CH₂CH₂O)n- in the repetition units in the molecular chain. The analysis shows that the residual macromonomer of U-PCE is HPEG which structure formula is CH₂=C(CH₃)-CH₂-O-(CH₂CH₂O)n-H.

3.3 Composition analysis of monomer in U-PCE

The unsaturated monomer also plays important roles in the free radical copolymerization process and performance of U-PCE. The chromatography such LC and GC can be use in unsaturated monomer composition analysis. As a set of peak retention time is similar, which suggesting the composition is relatively similar.

Chromatographic retention time of nine kinds of commonly used unsaturated monomer is shown in Table 3. LC of U-PCE is shown in Figure 3. GC of U-PCE is shown in Figure 4.

| NO. | Monomer                          | Retention time/min |
|-----|----------------------------------|--------------------|
| 1   | Maleic anhydride                 | 5.40               |
| 2   | Acrylamide                       | 5.48               |
| 3   | Fumaric acid                     | 5.67               |
| 4   | Sodium methallyl sulfonate       | 8.33               |
| 5   | Acrylic acid                     | 10.84              |
| 6   | Itaconic acid                    | 13.60              |
| 7   | 2-acrylamide-2-methyl propyl     | 13.68              |
| 8   | Sulfonic acid sodium hydroxyl ethyl acrylate | 17.57 |
| 9   | Methyl acrylic acid              | 36.21              |

Figure 2. ¹H NMR of Ultrafiltrate 3000
From Figure 3 and Figure 4, it can show that U-PCE contains residual monomer acrylic acid. Familiar and using in a variety of analytical instruments and methods, such as element analysis, structural analysis, component analysis, inorganic analysis and organic analysis, can provide more accurate structure and composition information.

3.4 Synthetic design

Although we obtain the most possible structure through various test methods, there may be some conclusions incomplete and inaccurate which due to the reasons such as the purity of the polycarboxylate superplasticizer sample, the limitation of the test instrument and method, the incomplete ability of analyst.

We choose synthesis as the way to confirm the analysis conclusion. Specific synthetic process is as follows: a certain amount of macromonomer (HPEG), hydrogen peroxide (H₂O₂) and water are charged in a glass bottom-rounded reactor equipped with mechanical stirrer, thermometer and reflux condenser. The system is purged with nitrogen and heated at a temperature. After the addition of ascorbic acid aqueous solution, ascorbic acid and thioglycolic acid mix aqueous solution in 3 hours, the system is further kept at a temperature for one hour and then neutralized with 30% NaOH. A light-colored polymer solution is obtained. The orthogonal experiment design is shown in Table 4.

| Sample | Factor A (H₂O₂) | Factor B (AA) | Factor C (TA) | Factor D (Vc) | Paste Fluidity/mm |
|--------|-----------------|---------------|---------------|--------------|------------------|
| 1#     | 0.55            | 17.3          | 0.64          | 0.11         | 196              |
| 2#     | 0.55            | 21.6          | 0.8           | 0.14         | 176              |
| 3#     | 0.55            | 25.9          | 0.96          | 0.17         | 182              |
| 4#     | 0.69            | 17.3          | 0.8           | 0.17         | 187              |
| 5#     | 0.69            | 21.6          | 0.96          | 0.11         | 211              |
| 6#     | 0.69            | 25.9          | 0.64          | 0.14         | 200              |
| 7#     | 0.83            | 17.3          | 0.96          | 0.14         | 190              |
| 8#     | 0.83            | 21.6          | 0.64          | 0.17         | 202              |
| 9#     | 0.83            | 25.9          | 0.8           | 0.11         | 220              |
| K₁₁    | 58.33           | 93.3          | 75.0          | 100.0        |                  |
| K₂₂    | 63.33           | 73.3          | 66.7          | 63.3         |                  |
| K₃₃    | 100.00          | 55.0          | 80.0          | 58.3         |                  |
| R      | 41.67           | 38.3          | 13.3          | 41.7         |                  |
In table 4, the optimized synthetic factor is A3B2C3D1 which called Optimized-PCE (O-PCE).

3.5 Performance test
The O-PCE is verified by IR, GPC and concrete test.

3.5.1 IR of O-PCE
The IR of O-PCE is shown in Figure 5.

![Figure 5. IR of O-PCE](image)

In Figure 5, the signals at 1350.58 cm\(^{-1}\) are attributed to -CH\(_3\). The signals at 1456.20 cm\(^{-1}\) are assigned to -CH\(_2\). The peaks at around 1722.09 cm\(^{-1}\) are assigned to C=O. The ether group (-O-) appears at peaks about 1108.19 cm\(^{-1}\). The analysis shows that O-PCE is similar to U-PCE after comparing the Figure 1 and Figure 5, which improve the credibility of analysis and synthesis process.

3.5.2 GPC elution curve of U-PCE and O-PCE
The GPC elution curve of U-PCE is shown in Fig.6. The GPC elution curve of O-PCE is shown in Figure 7.

![Figure 6. The GPC elution curve of U-PCE](image)
Figure 7. The GPC elution curve of O-PCE

Comparing with Figure 6 and Figure 7, the molecular weight is similar between the U-PCE and O-PCE which improve the credibility of analysis and synthesis process.

3.5.3 GPC of U-PCE and O-PCE

The concrete mix proportions are shown in Table 5. The concrete performance of U-PCE and O-PCE is shown in Table 6.

Table 5. Concrete mix proportions

| W (kg/m³) | C (kg/m³) | FA (kg/m³) | S (kg/m³) | G (kg/m³) |
|----------|-----------|------------|-----------|-----------|
| 175      | 320       | 80         | 740       | 1050      |

Table 6. Concrete performance of U-PCE and O-PCE

| Sample | (Slump/Extention) /mm | Compressive Strength/MPa |
|--------|------------------------|---------------------------|
| oh     | 1h                     | 3d                        | 28d                      |
| U-PCE  | 210/430                | 200/390                   | 18.9                     | 39.1       |
| O-PCE  | 210/400                | 190/380                   | 19.2                     | 38.7       |

In Table 6, the slump and extension of fresh mixed concrete, the 3d and 28d concrete compressive strength is similar between the U-PCE and O-PCE which improve the credibility of analysis and synthesis process.

4. Conclusion

Comparing the above, we can get the following conclusions:

(1) The similar structure and performance of U-PCE and O-PCE explain the process of analysis and synthesis has certain credibility.

(2) It will be provided us richer and more accurate information if we are proficient in using a variety of analytical instruments and methods, such as element analysis, structure analysis, composition analysis, inorganic analysis and organic analysis.

References

[1] Fang Yunhui, Ma Xiuxing, Gui Miaomiao. The molecular structure influence of polycarboxylate superplasticizer in concrete test [J]. Concrete, 2010, (12): 73-75.
[2] Jiang Zhuojun, Fang Yunhui, Guo Xinqi. The preparation of high concentration polycarboxylate superplasticizer[J]. Construction and Building Materials, 2013, (3): 29-31.
[3] Wang Jingzun, Qu Huisheng. Comprehensive analysis of complex samples - introduction to analysis technology[M]. Chemical Industry Press.
[4] Pan Zhure. Polymer chemistry[M]. Chemical Industry Press.