Effect of reaction time on properties of TPEG type polycarboxylate superplasticizer

Zhuojun Jiang \textsuperscript{1a*}, Renliang You \textsuperscript{1b}, Yunhui Fang \textsuperscript{1c}, Yuanqiang Guo \textsuperscript{1d}, Tianxing Lin \textsuperscript{1e}

KZJ New Materials Group Co., Ltd. Xiamen 361101, Fujian, China
\textsuperscript{a*jzj0407@126.com}

Abstract. The effects of dropping time and holding time on the properties of TPEG type polycarboxylate superplasticizer paste and concrete were studied with 20000l stainless steel reactor as production equipment, ammonium persulfate as initiator, sodium hypophosphite as chain transfer agent and reaction temperature of 60 °C. The experimental results show that within the experimental range, the dropping time has little effect on the initial dispersion effect of TPEG type polycarboxylate superplasticizer and has a great impact on the slump retention performance. The holding time has a great impact on the initial dispersion effect and slump retention effect of TPEG type polycarboxylate superplasticizer. The dropping time and holding time have little effect on the 3d, 7d and 28d concrete compressive strength of TPEG type polycarboxylate superplasticizer.

1. Introduction
Polycarboxylate superplasticizer has become the mainstream concrete superplasticizer product due to its good design, high water reduction rate and environmental protection [1-2]. TPEG (isoprenyl oxy polyoxyethylene ether) type polycarboxylate superplasticizer is the mainstream polycarboxylate superplasticizer in the market because of its outstanding water reducing performance [3].

The development of TPEG type polycarboxylate superplasticizer process generally passes the laboratory small-scale experiment first. Generally, 1L four port glass flask is used as the reaction vessel and equipped with laboratory mixer, while the production generally adopts enamel reactor or stainless steel reactor, with a volume ranging from 5000L to 50000L [4-7]. From small-scale test to production, the reaction amount varies greatly, and there are great differences in mass and heat transfer between the two. Therefore, the direct use of production equipment to study the impact of reaction time on the final product performance in the production of TPEG type polycarboxylate superplasticizer is of great significance to the industrial application of the product [8]. The reaction time in the production process of polycarboxylate superplasticizer includes dropping time and holding time. Therefore, this paper mainly studies the effects of dropping time and holding time on the properties of TPEG type polycarboxylate superplasticizer.
2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials
TPEG (industrial grade), Acrylic acid (industrial grade), Ammonium persulfate (industrial grade), Sodium hypophosphite (industrial grade), Sodium hydroxide (30% aqueous solution, industrial grade).

2.1.2. Main performance test raw materials for experiment
(1) Cement (C): the "Minfu" brand 42.5R ordinary portland cement of Fujian Minfu building materials, and its performance indexes are shown in Table 1.

| Particle size/mm | Apparent density / (kg/m³) | Bulk density / (kg/m³) | Void ratio /% | sediment percentage /% | needle and flake content /% |
|------------------|---------------------------|------------------------|---------------|-------------------------|---------------------------|
| 5~20             | 2660                      | 1560                   | 41            | 0.7                     | 2                         |
| 16~31.5          | 2640                      | 1580                   | 40            | 0.6                     | 1                         |

(2) Gravel: Granite gravel produced by a stone factory in Zhangzhou, with particle sizes of 5 ~ 20mm (G1) and 16 ~ 31.5mm (G2). See Table 2 for specific performance indexes of gravel.

2.2. Copolymerization
Add the measured water, TPEG and sodium hypophosphite into the 20000l stainless steel reactor, control the reaction temperature to 60 ℃, start dropping acrylic acid aqueous solution and ammonium persulfate aqueous solution, control it to drop at the time of experimental design, keep it warm for a period of time according to the time value of experimental design, add sodium hydroxide to adjust the pH value to 6.0 ~ 7.0, and then TPEG type polycarboxylate superplasticizer is obtained.

2.3. Performance test method

2.3.1. Net slurry fluidity test
The test shall be carried out according to the standard method in GB / T 8077-2012 test method for homogeneity of concrete admixtures.
2.3.2. Concrete test

(1) Concrete tests shall be carried out in accordance with GB/T50080-2016 Standard of Test Methods for Performance of Ordinary Concrete Mixtures.

(2) The formed concrete test block shall be subject to standard curing, and the 3d, 7d and 28d compressive strength of concrete shall be tested according to GB / T 50081-2002 standard for test methods of mechanical properties of ordinary concrete.

3. Experimental results and discussion

3.1. Effect of different dropping time on product performance

Adjust the dropping time of materials and keep the holding time after the reaction for 60 minutes. Investigate the effects of different dropping time on the net slurry fluidity and concrete performance of the product. The experimental results are shown in Fig. 1 and Fig. 2.

Fig. 1. Effect of different dropping time on fluidity of cement paste of the product

Fig. 2. Effect of different dropping time on properties of concrete of the product
As shown in Fig. 1 and Fig. 2, when the holding time during production is 60 minutes, with the extension of dropping time, the 0h net slurry fluidity and initial concrete fluidity (TK0h) of the production product change little, but the 0.5h net slurry fluidity and concrete 1h fluidity (TK1h) gradually increase, indicating that the slump retention performance of the product is gradually improved. In terms of concrete compressive strength, the products produced at different dropping times have little effect on the 3d, 7d and 28d compressive strength of concrete. Considering the production efficiency and product performance, the dropping time of 210 minutes is the best.

3.2. Effect of different holding time on product performance
When the dropping time is set to 210 minutes, the effects of heat preservation for 20 minutes, 40 minutes, 60 minutes and 80 minutes on the properties of product net slurry fluidity and concrete performance are investigated. The experimental results are shown in Fig. 3 and Fig. 4.

![Fig. 3. Effect of different holding time on fluidity of cement paste of the product](image)

![Fig. 4. Effect of different holding time on properties of concrete of the product](image)

As shown in Fig. 3 and Fig. 4, when the dropping time is 210 minutes, with the extension of the holding time, the 0h net slurry fluidity and the initial concrete fluidity (TK0h) of the production products gradually increase and then tend to be stable, and the 0.5h net slurry fluidity and the 1h
concrete fluidity (TK1h) also gradually increase and then tend to be stable, indicating that the slump retention performance of the products is gradually improved. In terms of concrete compressive strength, the products produced at different dropping times have little effect on the 3d, 7d and 28d compressive strength of concrete. Considering the production efficiency and product performance, the effect of holding time of 60 minutes is the best.

4. Conclusions
   (1) Within the experimental range, the dropping time has little effect on the initial net slurry fluidity and initial concrete fluidity of the product, but has a great impact on the slump retention performance of the product. Considering the production efficiency and product performance, the dropping time of 210 minutes is the best.
   (2) Within the experimental range, with the extension of holding time, the net slurry fluidity and concrete fluidity of the product gradually become better and tend to be stable. Considering the production efficiency and product performance, the effect of holding time of 60 minutes is the best.
   (3) Within the experimental range, the changes of dropping time and holding time have little effect on the compressive strength of 3d, 7d and 28d concrete.
   (4) From small-scale test to production, the dosage of reaction materials of TPEG type polycarboxylate superplasticizer varies greatly, there are great differences in mass and heat transfer between them, and there are also differences in reaction heat release under different initiation systems. Therefore, it is of great significance to directly use production equipment to study the impact of reaction time on final product performance during the production of TPEG type polycarboxylate superplasticizer to improve process effect and efficiency.

Acknowledgments
Thanks to Lin Tianxing and others for their guidance and help in the experiment. Thanks to them, my experiment can be successfully completed. Thanks to You Renliang, Fang Yunhui, Guo Yuanqiang for their guidance and help in the preparation of my thesis, which has greatly improved my study, scientific research and thinking. I would like to express my heartfelt thanks and deep respect to them.

References:
[1] Mo, X. Y., Jing, Y. J., Deng, M., et al. (2009) New research progress and summarization of polycarboxylate-type high performance superplasticizer. Concrete, (03):60-63.
[2] Lei L., Plank J. (2014) Synthesis and Properties of a Vinyl Ether-Based Polycarboxylate Superplasticizer for Concrete Possessing Clay Tolerance. Industrial & Engineering Chemistry Research, 53(3):1048-1055.
[3] Li, Y., Yang, C., Zhang, Y., et al. (2014). Study on dispersion, adsorption and flow retaining behaviors of cement mortars with tpeg-type polyether kind polycarboxylate superplasticizers. Construction and Building Materials, 64, 324-332.
[4] Liu, X., Wang, Z. M., Liang, X., et al. (2013). Preparation and characterization of polycarboxylate superplasticizer synthesized at non-aqueous condition. Applied Mechanics and Materials, 357-360, 1358-1361.
[5] Baoguo, M. A., Dai, Z., Xiao, J., Fang, C., et al. (2015). Design and implementation of functional regulation in production of polycarboxylate. New Building Materials, 42(2), 6-9.
[6] Tao, X. Design and application of intelligent controller for polycarboxylate superplasticizer automatic production line [D]. Beijing: Beijing University of technology, 2016.
[7] Fuying, Z. Research and design of polycarboxylic acid water reducer production process [D]. Beijing: Beijing University of technology, 2011.
[8] Su, Y., Yu, P., Huang, Z.J. (2003).Application of stirring technology in polymerization reactor [J]. Chemical propellant and polymer materials. 19(04), 19-23.