Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5502-5504

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18144

Experimental Study of Novel Polycarboxylate-Based Superplasticizer for Concrete†

FANKUI ZENG

Civil & Architectural Engineering School, Xi'an Technological University, Xi'an 710032, P.R. China

Corresponding author: Tel: +86 13359228981; E-mail: fankuizeng@126.com

AJC-15731

As a result of the rapid development of construction industry, plasticizers have been widely required in various cases. However, disadvantages such as high cost and complicated synthesis process have limited the large-scale application of current superplasticizers. In this article, we report an experimental study of polycarboxylate-based high performance superplasticizer. By using distinctive process, feedstock and ratio, carboxylic group was added to the molecules of amino sulfonic-based superplasticizer and a novel polycarboxylate-based superplasticizer was synthesized. The results revealed that both low cost and high performance (water reduction rate = 45 %) were achieved, indicating that this novel plasticizer can be applied in high performance concrete. Moreover, ready-mixed concrete by this plasticizer showed a slump loss less than 15 % in 2 h, which enables long distance transportation and pumping.

Keywords: Polycarboxylate-based superplasticizer, High performance concrete, Esterification, Poly-condensation.

INTRODUCTION

As a key factor in the synthesis of high performance concrete (HPC), plasticizer has been considered as one of the key admixtures to improve the rheology of concrete mixture. Indeed, the development of polycarboxylate-based superplasticizer with superior properties is one of the most popular topic in the field of additives for environmental friendly, multifunctional high and performance concrete[1]. Compared to other superplasticizers, polycarboxylate-based ones show good compatibility with cement and slag, superior water reduction rate and minimized slump loss[2]. In addition, polycarboxylic acid-based superplasticizers are environmental friendly and show negligible toxicity[3]. In virtue of these advantages, polycarboxylate-based superplasticizers have shown great potential in mass concrete and maritime projects. Thus, study of polycarboxylate-based superplasticizer is essential.

After the intensive study and wide range applications in the past years, polycarboxylate-based superplasticizers have attracted considerable attention and their market share is increasing rapidly, in virtue of their excellent compatibility with the concrete, superior water reduction rate, minimized slump loss and no air entrainment. In virtue of the wide range applications of aminosulfonic-based superplasticizers, various investigations on these superplasticizers have been done globally[4]. For instance, researchers in Japan, on their research on polycarboxylate-based superplasticizers, are focusing on the polycarboxylate-based superplasticizer, instead of naphthalene-based ones. In virtue of their fruitful work, the usage of polycarboxylate-based superplasticizers has exceeded that of naphthalene-based ones since 1995. Moreover, increasing studies of polycarboxylate-based superplasticizers with superior performance have been reported by researchers in North America/Europe recently. It is believed that their research focus has shifted from sulfonic-based superplasticizers to polycarboxylate-based ones. For example, the amount of articles on polycarboxylate-based superplasticizers published in the 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in 2000 was significantly higher than that of similar articles published in the 3rd conference in 1989. Indeed, most of the relevant reports focussed on the development of polycarboxylate-based superplasticizers, performance of fresh concrete and application of hardened concrete[5-7]. Likewise, considerable efforts have been made on polycarboxylate-based superplasticizers by researchers in China. For instance, researchers from Chemical Engineering Laboratory, South China University of Technology reported an investigation of aminosulfonic-based superplasticizer. With optimized relevant process parameters, high performance aminosulfonic-based superplasticizer (ASP) was achieved by polycondensation of sulfanilic acid, phenol and formaldehyde in aqueous solution. It was claimed that

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

this superplasticizer showed a water reduction rate higher than 25 % and negligible loss of relative fluidity after 2 h. In addition, the concrete involving this superplasticizer showed a significantly enhanced compressive strength. Nevertheless, this superplasticizer was limited by high cost, sensitivity to the content and segregation/weeping.

Thus, the large-scale application of polycarboxylate-based superplasticizers is limited by two factors. The first factor is the high cost, which is a result of the expensive phenol and sodium sulfanilate used. The other factor is its sensitivity to the content[8-10]. With low content of the plasticizers, dispersion of cement particles is ineffective and the slump loss is severe. With high content of the plasticizers, dispersion of cement particles will be over effective, which resulted in severe segregation and weeping, or even separation of slurry and water.

In this report, we proposed a solution to the existing issues by presenting a novel polycarboxylate-based superplasticizers and its investigation. This novel superplasticizer is considered as an excellent alternative to current superplasticizers as it offers industry scalable synthesis route, negligible toxicity and low cost.

EXPERIMENTAL

The esterification was done in the set-up shown in Fig. 1. This equipment consists of heater and four-inlet flask with mechanical stirrer, thermometer, water separator and N_2 inlet.

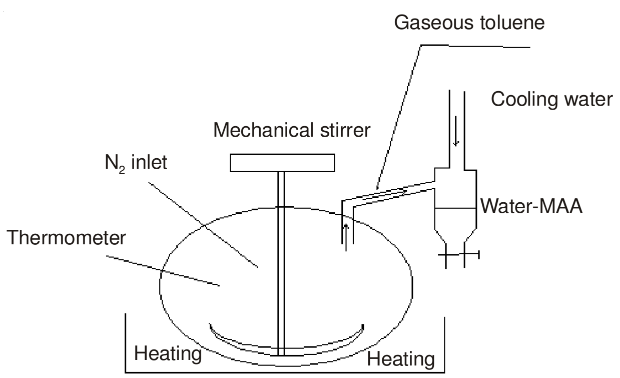

Fig. 1. Schematic diagram of esterification set-up

The co-polymerization was done in a set-up similar to that of esterification, as shown in Fig. 2. This equipment consists of heater and four-inlet flask with mechanical stirrer, thermometer and dropper.

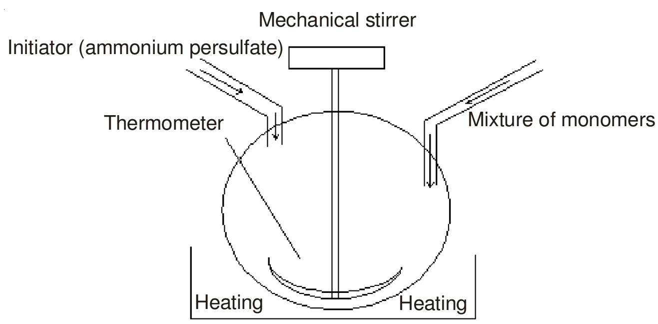

Fig. 2. Schematic diagram of co-polymerization set-up

Procedure: This experiment can be divided into two parts. The first part was esterification, which provided reactants (esterification monomer) for the following step. The second one was co-polymerization, where the esterification monomer was mixed with other reactants and the final product, polycarboxylate-based, was achieved. A summary of the esterification and co-polymerization reactions is shown in Table-1 below.

Test conditions 1: 35 g benzoic acid, 65 g phenol and 115 g concentrated sulphuric acid were added into the reactor and heated up to 85 ºC. Then, the container was kept at this temperature for 2 h so that sulfonation can be completed. After that, the pH value was adjusted to 7-8 by adding 30 % sodium hydroxide and sulfonated products were obtained. Then, 65 g sulfonated product, 50 g sodium sulfanilate, 30 g phenol and 240 g water were added into another reactor, which was heated to 80 ºC and the pH value was altered to 8-9 with sodium hydroxide solution. Afterwards, the solution was stirred for 15 min and 75 g formaldehyde was added in dropwise within 2 h. Finally, the solution was kept at 80 ºC for 6 h so that polycondensation can be completed and the novel amino-carboxylic-based superplasticizer was obtained.

Test conditions 2: 41 g benzoic acid, 60 g phenol and 105 g concentrated sulphuric acid were added into a reactor, which was heated to 85 ºC and kept for sulfonation reaction

TABLE-1
A SUMMARY OF ESTERIFICATION AND CO-POLYMERIZATION RATIO

	Esterification	Co-polymerization
Reactants	Methoxy polyethylene glycols (MPEG); methacrylic acid (MAA)	Sodium sulfanilate; co-polymerization monomer; formaldehyde
Feedstock	Benzoic acid; phenol; concentrated sulphuric acid; sodium hydroxide (solid content = 30 %)	Sulfonated product (solid content = 60 %); sodium sulfanilate; phenol; formaldehyde product (solid content = 60 %)
Mass ratio of feedstock	30-40: 75-65: 105-115: 185-195	65-75: 40-55: 30-35: 70-80
Optimized mass ratio of feedstock	30: 65: 115: 90	65: 45: 30: 70
Process	MPEG, MAA and acrylic acid (in ratio stated above) were added into the reactor and heated. At T = 70-80 ºC, inhibitor was added in; at T = 80-85 ºC, catalyst was added in and the container was protected by N2. Once the water content in distillate was lined up with the theoretical value, the reaction was stopped and the container was cooled down to 45 ºC. Then, the distillate was extracted and stirred to obtain the co-polymerization monomer.	Firstly, water was added in as the base. Together with water, phenol, sodium sulfanilate, sulfonated product was added into the container and heated to 75-85 ºC. Then, co-polymerization monomer and formaldehyde were added in simultaneously in 1.5-2.5 h, followed by further heating to 80-90 ºC. Afterwards, co-polymerization reaction was conducted by keeping the temperature at 80-90 ºC for 4-6 h. Finally, sodium hydroxide (l) was added in after cooling.

for 2 h. The pH value was then altered to 7-8 with 30 % sodium hydroxide solution and sulfonated products were obtained. After that, 72 g sulfonated product, 40 g sodium *p*-aminobenzenesulfonate, 31 g phenol and 240 g water were added into another reactor, which was heated to 85 ºC and the pH value was altered to 8-9 with sodium hydroxide solution. Then, the solution was stirred for 15 min and 72 g formaldehyde was added in dropwise within 2 h. In last, the solution was kept at 85 ºC for polycondensation for 6 h and the novel aminocarboxylic-based superplasticizer was obtained.

RESULTS AND DISCUSSION

With 0.35-0.60 % (solid content) of the sample, concrete showed various superior properties. Firstly, the water reduction rate can be 25-35 %. Secondly, its compression strength was 130-155, 135-171 and 125-145 % for 3 days, 7 and 28 days, respectively. Then, the slump loss was low (negligible loss after 2h), indicating that long distance transportation and pumping of this concrete are possible. Also, it showed excellent workability and low pumping resistance and no weeping or air entrainment was observed after 2 h. The strength of concrete was improved by 3 MPa with this superplasticizer. Other advantages include good compatibility[11] with various cements such as coal ash contained cement.

Conclusion

In summary, the advantages of this novel polycarboxylate-based superplasticizer include: low cost. The dosage of feedstock was kept constant while the cost was lower, as compared to traditional aminosulfonic-based superplasticizers. High water reduction rate. A water reduction rate of 45 % can be obtained and compatibility with cement is good. Minimized slump loss. For instance, ready-mixed concrete by this plasticizer showed a slump loss less than 15 % in 2 h. Significantly enhanced cement strength. The polycarboxylate-based high performance superplasticizer presented in this report has overcome issues in the traditional aminosulfonic-based superplasticizers and has shown great potential for industrial application in the future.

REFERENCES

1. J. Mao and J. Wang, *Sci. Technol. Overseas Build. Mater.*, **26**, 4 (2005).
2. H. Liang, G. Liu, *Guangdong Build. Mater.*, **1**, 23 (2005).
3. S. Hanehara and K. Yamada, *Cement Concr. Res.*, **29**, 1159 (1999).
4. X. Cheng, Effect of Raw Material on Application Performances of Super Plasticizer, University of Technology, Beijing (2010).
5. T. Izumi, T. Muzanama, M. Izuka and M. Fukuda, Slump Control with Reactive Polymeric Dispersant, Third CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Ottawa, pp. 243-262 (1989).
6. K. Yamada, T. Takahashi, S. Hanehara and M. Matsuhisa, *Cement Concr. Res.*, **30**, 197 (2000).
7. H. Uchikawa, S. Hanehara and D. Sawaki, *Cement Concr. Res.*, **27**, 37 (1997).
8. M. Gong, L. Chen and Y. Jiang, *Coal Ash China*, pp. 11-13 (2009).
9. H. Xiao, G. Liu and J. Xiao, *China Build. Mater. Sci. Technol.*, pp. 26-30 (2008).
10. Y. Zuo, Effects of Polycarboxylate Superplasticizers on the Performance of Fresh Concrete and Its Mechanism, China Building Materials Academy (2004).
11. R.I. Malek, Z.H. Khalil, S.S. Imbaby and D.M. Roy, *Cement Concr. Res.*, **35**, 1152 (2005).