Pergamon

Cement and Concrete Research 30 (2000) 1841–1845

CEMENT AND CONCRETE RESEARCH

Synthesis of sodium sulfanilate-phenol-formaldehyde condensate and its application as a superplasticizer in concrete

Meishan Pei, Dujin Wang*, Xianbo Hu, Duanfu Xu

State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 31 May 2000; accepted 4 June 2000

Abstract

Water-soluble sodium sulfanilate-phenol-formaldehyde condensate (SSPF) is synthesized with a simple synthetic process. The surface activity of SSPF and its performance in concrete was investigated. It was found that the synthesized SSPF has an advantage over conventional superplasticizers, such as sulfonated naphthalene formaldehyde condensate (SNF) and sulfonated melamine formaldehyde condensate (SMF), and is more suitable to prepare pumping concrete and self-compacting concrete.

Keywords: SSPF; Superplasticizer; High-performance concrete; Adsorption; Aggregate

1. Introduction

High-performance concrete (HPC) is a novel construction material that exhibits higher workability, greater mechanical properties, and better durability than the conventional concrete. Currently, this new material has been applied in the construction such as tall buildings, bridges, and offshore structures [1]. One key for successful preparation of HPC is the addition of proper superplasticizers, such as polycarboxylic acid (PC), sulfonated melamine formaldehyde condensate (SMF), and sulfonated naphthalene formaldehyde condensate (SNF) superplasticizers [2]. It has been reported that these admixtures exhibit very good dispersing effects on concrete, and can reduce water demand of concrete by up to 25% while still maintaining the flow characteristics of concrete. This has led to the development of very low water/cement (W/C) ratio HPC that exhibits very high compressive strength [3,4].

Due to the high-cost of PC and SMF, the relatively low-cost SNF is the main kind of superplasticizer being used in China, though its application is limited in preparing pumping concrete and HPC due to its higher content of sodium sulfanilate, which induces alkali–aggregate reaction, large slump-loss with time elapsed, and complicated synthetic process [5].

Because superplasticizers are one of the most important ingredients used in concrete, the research and development of superplasticizer have attracted great attention recently [6–12]. In order to develop a new superplasticizer, water-soluble sodium sulfanilate-phenol-formaldehyde condensate (SSPF) has been synthesized in our laboratory, and the surface activity, performance effects on concrete of SSPF were systematically investigated.

2. Experimental

2.1. Synthesis of SSPF

A reaction vessel equipped with a stirrer was charged with desired concentration of sodium sulfanilate and phenol in water, and a 40% aqueous sodium hydroxide solution was added to adjust the pH value. Then, the solution was heated to a given temperature, and a desired amount of formaldehyde was added while stirring, and the reaction mixture was stirred under a given temperature for some time. Thereafter, the reaction mixture was cooled, and the pH value was adjusted with a 40% aqueous sodium hydroxide solution. The mixture was stirred for a given time. The final solid

* Corresponding author. Tel.: +86-10-6256-3072; fax: +86-10-6255-9373.

E-mail address: djwang@pplas.icas.ac.cn (D. Wang).

PII: S0008-8846(00)00389-6

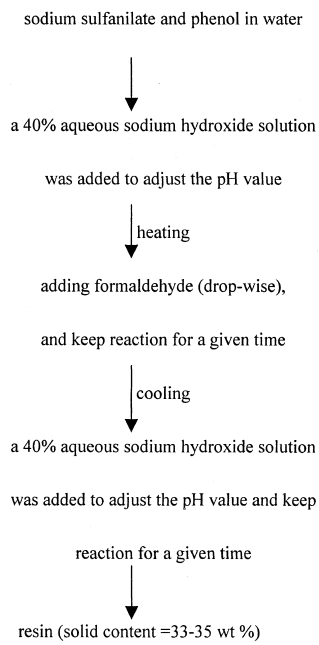

Fig. 1. Synthetic process of SSPF.

content of the reaction mixture was in the range from 33 to 35 wt.%. The synthetic process is shown in Fig. 1.

2.2. Adsorption property

Adsorption amount was measured by determining the adsorption ratio of dispersant with the amount of dispersant added ($C \times 0.5-1.5$ wt.%) [5]. In this test, the adsorption rate and amount of dispersant were measured using ultraviolet spectrophotometry and determined by Eq. (1):

$$\text{Adsorption } concentration\ (C_A) = \text{Initial concentration } (C_I) - \text{Residual concentration } (C_R) \quad (1)$$

2.3. Materials

The cement used is normal 525# Portland cement, fine aggregate siliceous sand with a fineness modulus of 2.70 and specified grading, and coarse aggregate crushed stone (MS = 20 mm) with specified grading. In addition, two commercial superplasticizers, i.e., SNF and SMF, were also used for comparison. The properties of these admixtures and the chemical structure of SSPF are shown in Table 1 and Fig. 2, respectively.

Table 1
Properties of chemical admixtures

Property	Chemical admixture		
	SSPF	SNF	SMF
Appearance	Dark brown liquid	Dark brown liquid	Transparent liquid
Solid content (%)	35	42	34
Specific gravity (g/cm^3)	1.15	1.16	1.18

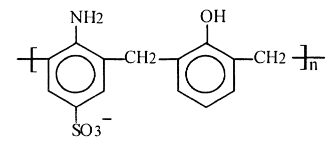

Fig. 2. The chemical structure of SSPF.

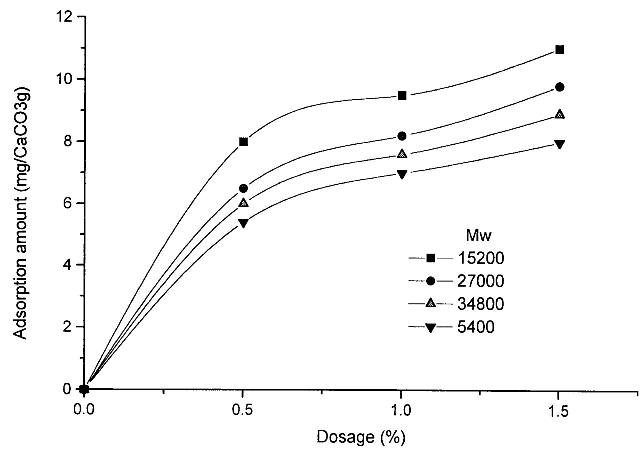

Fig. 3. Adsorption amount changes of various weight-average molecular weight dispersants with the increase of dispersant in $CaCO_3$ suspension solution ($W/CaCO_3 = 2.0$; contact time = 30 min).

2.4. Mix proportion of concrete

Mix proportion of concrete is given as follows: cement/sand/stone = 1:2.36:3.85, cement = 300 kg/cm^3, slump = 8 ± 1 cm, air content < 4.5%.

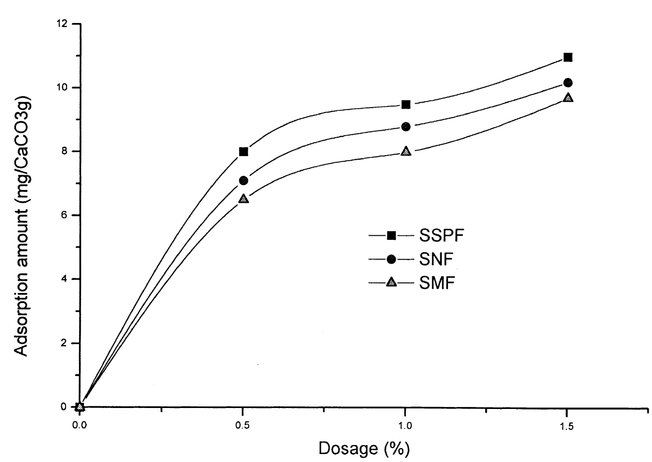

Fig. 4. Adsorption amount changes of various dispersants with the increase of dispersant in $CaCO_3$ suspension solution ($W/CaCO_3 = 2.0$; contact time = 30 min).

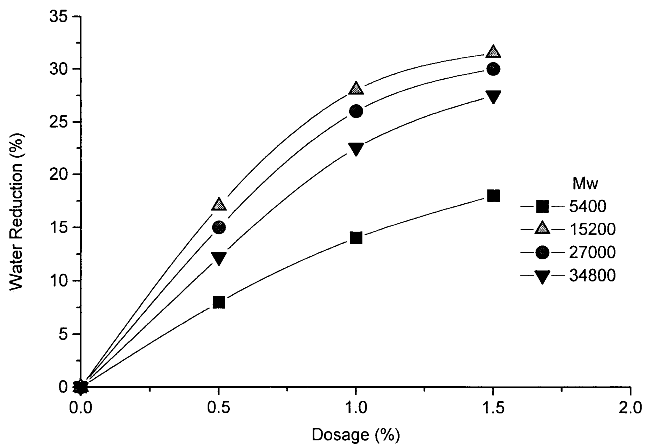

Fig. 5. Water reduction of various weight-average molecular weight dispersants with the increase of dispersant.

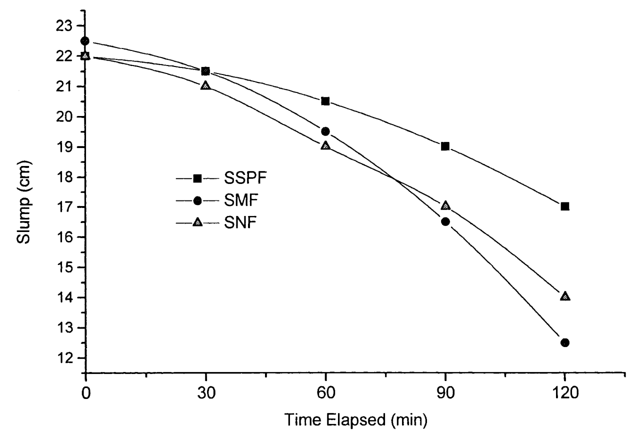

Fig. 7. Effect of chemical structures on the slump loss of concrete. (1) Amount of each dispersant added = $C \times 0.65$ wt.%. (2) SSPF W/C = 0.55; SNF W/C = 0.58; SMF W/C = 0.60.

2.5. Preparation and test of concrete

Preparation and test of concrete carried out according to GB8076-1997.

2.6. Gel permeation chromatography (GPC) measurements

The molecular weight of resin was determined with GPC measurements. The samples were analyzed using a 0.1 M KCl/methanol aqueous solution as an eluant, at a flow rate of 1 ml/min. Monodispersed polystyrene sulfonates of different molecular weights were used as calibration standards.

3. Results and discussion

3.1. Adsorption property

Figs. 3 and 4 show the adsorption amounts of various weight-average molecular weight SSPF dispersants and other two commercial superplasticizers (SNF and SMF) on the surface of $CaCO_3$ particles when the amount of dispersants added increases from 0.5 to 1.5 wt.%, respectively. The adsorption amount of the dispersant onto cement particles is generally determined by the functional groups in its molecule and its molecular weight. Generally, the adsorption amount increases with the increase of molecular weight in an adequate time. Fig. 3 shows that the dispersant with 15200 weight-average molecular weight has higher adsorption amount than those with over 15200 weight-average molecular weight. This is because bigger molecules have lower moving speed, it is difficult for them to attain equilibrium in a short time. The SSPF molecules have two functional groups, i.e., one functional group of a hydroxyl group in the phenol compound and a sulfanilate group in the sodium sulfanilate. The conventional superplasticizer, such as SNF and SMF, has only one functional group in their molecules, so that the number of functional groups per molecular weight of the SSPF is larger than that of the

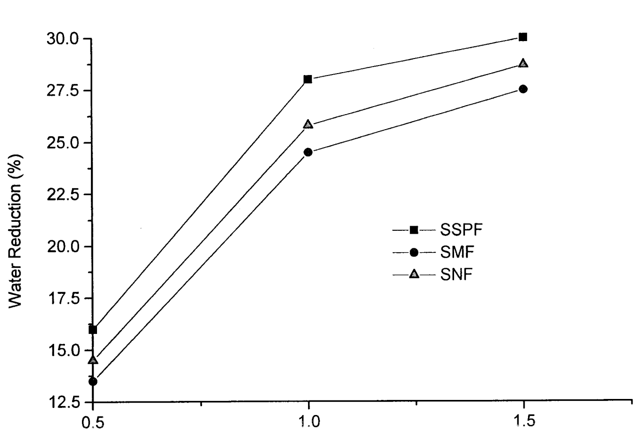

Fig. 6. Water reduction of various dispersants with the increase of dosage.

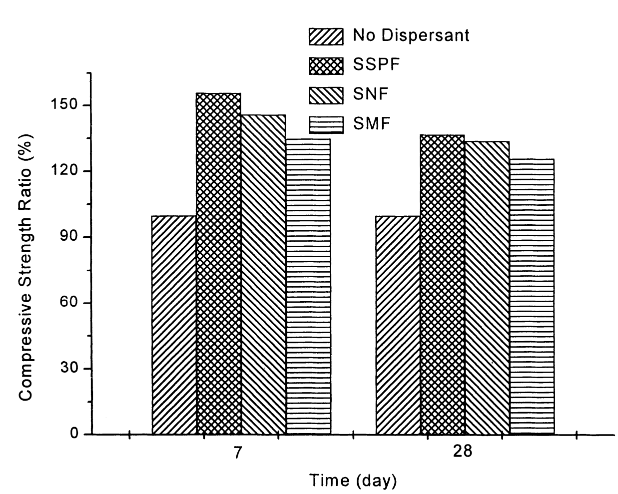

Fig. 8. Effect of chemical structures on the compressive strength of concrete.

Table 2
The performance of SSPF as a superplasticizer in field application

	Mix proportions of concrete[a] C:S:G:FA	W/C + FA (%)	SSPF/C + FA (%)	Slump (mm) 0 min	90 min	Flow degree (mm)	28-day compressive strength (MPa)
C25[b]	1:2.47:3.71:0.49 $C=204$ kg/cm^3	0.55	0.70	255		660	34.5
C30[b]	1:2.15:3.22:0.40 $C=245$ kg/cm^3	0.50	0.80	250		650	38.1
C40[b]	1:1.69:2.53:0.35 $C=306$ kg/cm^3	0.40	0.90	260		670	49.8
C50	1:1.45:2.19:0.25 $C=400$ kg/cm^3	0.35	1.05	230	215		61.2
C60	1:1.13:2.10:0.44 $C=505$ kg/cm^3	0.32	1.10	220	205		68.7

[a] Cement: 525# Portland cement; FA: Grade-II; fine aggregate: siliceous sand with a fineness modulus of 2.76; coarse aggregate: a nominal maximum size of 25 mm.
[b] Self-compacting concrete.

conventional superplasticizers. Therefore, the SSPF exhibits a superior effect with respect to the dispersability and the prevention of slump loss to the conventional superplasticizers by virtue of a strong adsorption to cement particles and an increase in the density of electric charges on the surfaces of particles.

3.2. Water reduction in concrete

The chemicals used as a superplasticizer should allow water reduction above 18% at a given workability without significantly affecting the setting characteristics of the concrete. Figs. 5 and 6 show the water-reduction percentage of various weight-average molecular weight SSPF and the other two commercial superplasticizers (SNF and SMF), respectively. Fig. 5 is the effect of SSPF molecular weight and dosage on the water-reduction percentage. Apparently, the trend in the figure is similar to that in Fig. 3. It is indicated that a strong adsorption to cement particles and an increase in the density of electric charges on the surfaces of particles exhibit a stronger effect on the dispersability. Fig. 6 shows the effect of chemical structures on the water-reduction percentage. SSPF exhibits a higher water-reduction percentage than either SMF or SNF does, due to the different number of functional groups per molecule.

3.3. Slump loss

The evaluation of slump loss is important for field application. A lower degree of slump loss will prolong the time available for transporting, handling, and placing of concrete. Fig. 7 is the slump loss of concrete with different admixtures at 0.65% dosage. The initial slump of all admixture-containing concrete is about 22 ± 1 cm. Generally, each admixture-containing concrete exhibits similar behavior: the slump of concrete first slightly increases with time, and then decreases a bit quickly. However, the slump-loss rates are different with different chemical structures of admixtures. SSPF has the smallest slump-loss rate among the three kinds of superplasticizers, due to more functional groups in its molecule, which results in a strong adsorption to cement particles and an increase in the density of electric charges on the surfaces of particles. SSPF maintains 80% of initial slump values for about 120 min, so it is more suitable to prepare pumping concrete.

3.4. Compressive strength of concrete

Compressive strength of concrete at 7 and 28 days with SSPF were compared with those of concrete with either SNF or SMF present, as shown in Fig. 8. It is apparent that the compressive strength of concretes treated with various superplasticizers is higher than that of concrete untreated, and that the compressive strength of concrete treated with SSPF is higher than that of concrete treated with either SNF or SMF, due to SSPF's higher water reduction.

4. Application

SSPF as a superplasticizer has been used in field applications to prepare high-strength concrete and self-compacting concrete. The performance of SSPF as a superplasticizer in field application is given in Table 2.

5. Conclusions

Water-soluble SSPF is synthesized from phenol, formaldehyde, and sodium sulfanilate through a two-step reaction. The performance of SSPF in concrete is evaluated. The synthesized SSPF, resulting in the increase of adsorption amount of dispersant per unit weight of $CaCO_3$ particle, has higher water-reduction percentage as well as compressive strength than conventional superplasticizers such as SNF and SMF, and shows an excellent control effect of slump loss of concrete, maintaining 80% of initial slump for about 120 min. SSPF is an optimum superplasticizer for preparing pumping concrete and self-compacting concrete.

Acknowledgments

Project supported by the Natural Science Foundation of China (NSFC, grant nos. 59733060, 59873030, 59953001, 59903008) and Major Project of Knowledge renovation of the Chinese Academy of Sciences (grant no. KJCX1-Y-03).

References

[1] P.C. Aitcin, B. Mao, How to make high performance concrete, in: J.C. Chern (Ed.), Proceedings of the Second Seminar on High Performance Concrete, Taipei, Taiwan, 1992, pp. 91–118.
[2] A.M. Paillere, Application of Admixtures in Concrete, E & FN Spon, London, 1996.
[3] M.R. Rixom, N.P. Mailvaganam, Chemical Admixtures for Concrete, 2nd edn., E & FN Spon, London, 1986.
[4] V.M. Malhotra, Specialized innovative applications of superplasticizers in concrete, in: C.L. Hwang (Ed.), Proceedings of R&D and Promotion of High Performance Concrete, Taipei, Taiwan, 1997, pp. 23–58.
[5] G.-G. Lim, S.S. Hong, D.-S. Kim, B.-J. Lee, J.-S. Rho, Slump loss, control of cement paste by adding polycarboxylic type slump-releasing dispersant, Cem Concr Res 29 (1999) 223–229.
[6] H. Uchikawa, S. Hanehara, Influence of characteristics of sulfonic acid-based admixture on interactive force between cement particles and fluidity of cement paste, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 23–34.
[7] A.A. Jeknavorian, L.R. Roberts, L. Jardine, H. Koyata, D.C. Darwin, Condensed polyacrylic acid-aminated polyether polymers as superplasticizers for concrete, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 55–81.
[8] M. Kinoshita, T. Suzuki, K. Soeda, T. Nawa, Properties of methacrylic water-soluble polymers as a superplasticizer for ultra high-strength concrete, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 143–162.
[9] L. Coppola, E. Erali, R. Troli, M. Collepardi, Blending of acrylic superplasticizer with naphthalene melamine or lignosulfate-based polymers, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 203–224.
[10] A. Ohta, T. Sugiyama, Y. Tanaka, Fluidizing mechanism and application of polycarboxylated-based superplasticizers, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 359–378.
[11] J. Norberg, O. Peterson, P. Billberg, Effects of a new generation of superplasticizers on the properties of fresh concrete, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 583–598.
[12] M. Shonaka, K. Kitagawa, H. Satoh, T. Izumi, T. Mizunuma, Chemical structures and performance of new high-range water-reducing and air-entraining agents, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 1997, 599–614.