Synthesis and Properties of Water-Soluble Sulfonated Acetone–Formaldehyde Resin

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ABSTRACT: Water-soluble sulfonated acetone–formaldehyde (SAF) resins were synthesized by the reaction among acetone, formaldehyde, and sodium bisulfite. The factors affecting the properties of SAF resins and optimum conditions of preparation were investigated. The SAF resins prepared under proper conditions have good water solubility and high performance as a superplasticizer used in concrete. J Appl Polym Sci 91: 3248–3250, 2004

Key words: water-soluble sulfonated acetone–formaldehyde (SAF); superplasticizer; synthesis; gelation; resins

INTRODUCTION

Higher-performance concrete (HPC) is a novel construction material that exhibits higher workability, greater mechanical properties, and better durability than those of conventional concrete.[1] Currently, this new material has been applied in construction projects such as tall buildings, bridges, and offshore structures. One key for successful preparation of HPC is the addition of the proper superplasticizer, such as polycarboxylic acid (PC) and water-soluble sulfonated resins, including sulfonated melamine formaldehyde (SMF) condensate and sulfonated naphthalene formaldehyde (SNF) condensate. These admixtures exhibit very good dispersing effects on concrete and can reduce water demand of concrete by up to 25% while maintaining the flow characteristics of concrete.[2–6] Therefore, as superplasticizers, they offer considerable advantages in producing concrete with high workability at much lower water/cement ratio and exhibiting much higher strength.

Because of the high cost of PC and SMF, the relatively low-cost SNF is the main kind of superplasticizer being used in China, although its application is limited in preparing pumping concrete and HPC because of its higher content of sodium sulfonate, which induces alkali–aggregate reaction, large slump-loss with time elapsed, and a complicated synthetic process.

Because of the industrial importance of water-soluble sulfonated resins in concrete technology, the research and development focused on them have recently attracted great attention. In this study, we replaced naphthalene with acetone and prepare sulfonated acetone–formaldehyde (SAF) resins. The factors affecting the properties of SAF resins, concrete of SAF, and the optimum conditions of preparation were systematically investigated. Because of its good performance and relatively low-cost acetone used in water-soluble SAF resin prepared in our lab has potential application as a superplasticizer used in concrete.

EXPERIMENTAL

Materials

Acetone, formaldehyde aqueous solution (formaldehyde, 36–37% w/w), and sodium bisulfite crystal without further purification were used as reactants.

Synthesis of SAF resins

The SAF resin was prepared from formaldehyde, acetone, and sodium bisulfite through a three-step reaction including sulfonation, low-temperature condensation, and high-temperature condensation. The following is an example of the procedure used to prepare the SAF resins.

Sulfonation

Sodium bisulfite was dissolved in water in a jacketed reactor flask equipped with a baffle stirrer and a reflex

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TABLE I
Effect of the Factors Affecting the Properties of SAF Resin

Sample code	F/A[a]	S/A[a]	High-temperature condensation time (h)	Molecular weight	Water solubility[b]	Viscosity[c]	Ratio of water reduction[d]
1	0.5	1.0	4	2100	E	7.1	5
2	1.0	1.0	4	3200	E	7.8	9
3	1.5	1.0	4	6800	E	9.6	16
4	2.0	1.0	4	9600	E	12.4	24
5	2.5	1.0	4	12,800	G	16.7	18
6	3.0	1.0	4	16,800	P	22.8	10
7	2.0	0.5	4	9300	E	11.3	12
8	2.0	1.5	4	10,600	E	13.2	19
9	2.0	2.0	4	11,400	E	14.4	17
10	2.0	1.0	2	7800	E	10.6	14
11	2.0	1.0	6	11,200	E	14.0	20
12	2.0	1.0	8	12,500	G	15.8	16
13	2.0	1.0	10	18,400	P	24.6	11

[a] Molar ratio.
[b] E, excellent; G, good; P, poor.
[c] 40% solid content at 25°C.
[d] 0.8% dosage.

condenser at 50°C. The temperature of the solution was maintained at 50°C before the solution was clear. As soon as the solution became clear, the temperature was decreased to 40°C and acetone was added. Then the reaction was carried out at 40°C for 1 h.

Low-temperature condensation

Formaldehyde aqueous solution of 37% concentration was fed into the reactor through a dropping funnel. During the dropping process, the temperature of the reaction automatically increased. In the process, the temperature was controlled at 60–65°C. The reaction continued at 60–65°C for an additional 1 h when the feeding of formaldehyde was complete.

High-temperature condensation

The temperature was increased to 85°C and the reaction continued for 4 h. After cooling, the resin prepared according to above procedure had a solid content of about 40% and the final pH of the solution was >12.

Preparation and test of concrete

Mix proportion of concrete

The mix proportion of concrete is given as follows: cement/sand/gravel = 1 : 2.16 : 3.54; cement = 330 kg/m^3; slump = 8 ± 1 cm.

Preparation and test of concrete

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

RESULTS AND DISCUSSION

The preparation of SAF resins includes three stages: sulfonation, low-temperature condensation, and high-temperature condensation. The factors affecting the properties of SAF resins were investigated. The factors include the operational sequence of sulfonation, molar ratios of acetone to formaldehyde and sodium bisulfite to acetone, and the high-temperature condensation time.

Operational sequence of sulfonation

It is worth emphasizing that the operational sequence is one key factor for the whole reaction. Acetone should be first added to the solution including sodium bisulfite and then formaldehyde be added; otherwise, it always produces an unstable solution resulting in gelation during the three-step and poor water-soluble resins.

Molar ratio of formaldehyde to acetone (f/a)

The effect of molar ratio of formaldehyde to acetone on the properties of SAF resin was carefully studied. The water solubility of SAF resins was varied with the molar ratio of formaldehyde to acetone. The SAF resins possessed good water solubility if the molar ratios of formaldehyde to acetone were <2. If F/A ≤ 2, the resins were guaranteed to have linear polymer chain and good water solubility. To ensure that synthesized resins would have high enough molecular weight and good water solubility, the molar ratio of formaldehyde to acetone was chosen as 2.

Molar ratio of sodium bisulfite to acetone (S/A)

The number of sulfonate groups per units of the polymeric chain has an important effect on the properties of the synthesized SAF resin. As a superplasticizer, the resin should have a suitable number of sulfonate groups in its polymeric chain. The dependency of water reduction ratio of SAF resin on S/A is shown in Table I. It can be seen that when the molar ratio of sodium bisulfite to acetone is 1.0, the SAF resin has a maximum of water reduction ratio.

Temperature of the low-temperature condensation

In the condensation process, if the temperature of low-temperature condensation is too high, the reaction velocity of condensation is too fast to control the reaction temperature constant, resulting in gelation during the high-temperature condensation. To maintain a suitable condensation speed, the temperature of low-temperature condensation should be maintained at 60–65°C at a low-temperature condensation time of 1 h.

High-temperature condensation time

The condensation time has a key influence on the molecular weight of the synthesized resins. The molecular weight of the resin determines its effectiveness as a superplasticizer. To obtain resins of suitable molecular weight, the high-temperature condensation time should be determined. During the high-temperature condensation, the temperature was increased to 85°C. From Table I, it may be seen that the optimum reaction time is 4 h.

Properties of the SAF plasticized concrete

Table II shows the compressive strength of plain concrete and SAF plasticized concrete at 3, 7, and 28 days, respectively. The SAF-9 has 24% of water reduction (see Table I). It can be seen that the SAF plasticized concrete has high performance and the SAF resin can be used as a superplasticizer in preparation of high-performance concrete.

TABLE II
Compressive Strength of Plain Concrete and SAF Plasticized Concrete at 3, 7, and 28 Days[a]

	Slump (mm)	Compressive strength (MPa) at		
		3 days	7 days	28 days
Plain	83	19.2	34.0	41.8
SAF-9	81	27.8	42.6	49.2

[a] Cement : sand : gravel = 1 : 2.16 : 3.54.

CONCLUSIONS

Factors that affect the properties of sulfonated acetone–formaldehyde resin were investigated. Proper viscosity and good water-soluble SAF resins were prepared under optimum reaction conditions as follows: the molar ratio of formaldehyde to acetone was 2.0, the molar ratio of sodium bisulfite to acetone was 1.0, the temperature of low-temperature condensation was 60–65°C, and the temperature and reaction time of the low-temperature condensation were 85°C and 4 h, respectively. The SAF resins prepared under the proper conditions mentioned above were characterized by good water solubility and high performance as a superplasticizer.

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