

The study on the dispersing mechanism of starch sulfonate as a water-reducing agent for cement

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Abstract

Many water-reducing agents are environmentally unacceptable and non-renewable. As environment-friendly and renewable organic resource, starch has been used to synthesize starch sulfonate (SS). In this paper, the adsorption characteristics of SS on Portland cement particles were investigated by measuring zeta potentials, X-ray photo spectroscopy and UV–visible adsorption and its effects on the fluidity of cement paste were studied in comparison with traditional naphthalene sulfonated formaldehyde condensates (FDN) whose dispersion ability mainly depends on electrostatic repulsive forces. The results indicate the adsorption isotherm of SS conforms to Langmuir-type adsorption and the adsorption conformation of SS is dendritic due to its molecular structure. The adsorption layer of SS is much thicker than FDN. The dispersion capacity of SS mainly comes from steric hindrance effects rather than electrostatic repulsive forces. The dispersions stabilized by steric hindrance have better fluidity at lower adsorption amount and higher stability than those stabilized by electrostatic repulsive forces.

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Keywords: Dispersing mechanism; Starch sulfonate; Steric hindrance; Electrostatic repulsive force

1. Introduction

In the building industry, it is very important to keep fresh concrete fluid to provide homogeneous transport of all particles. So a large amount of water is frequently added to the mixture in an effort to enhance flow. Unfortunately, excessive water can lead to a number of problems, such as bleeding (free water collection on the surface) and reduced strength and durability, (Mehta, 1999; Skaggs, Rakitsky, Swazey, & Dial, 1997). To avoid this so-called water-reducing agents are used, which interact with the surface of cement particles, involving dispersion and decreasing their natural tendency to coagulate in aqueous systems. As a result, highly flowable mortars and concretes are obtained, which show increased workability at constant water/

cement ratio (Popova, Geoffroy, Faucon, & Gartner, 2000; Faroug, Szwabowski, & Wild, 1999).

Many conventional water-reducing agents are the condensation product of formaldehyde (such as naphthalene sulfonated formaldehyde condensates, sulfonated melamine formaldehyde polymers and the aminosulfonic acid series), they may result in undesirable environmental effects as they can accidentally or intentionally release formaldehyde into the environment. In addition, the polycarboxylate-type water-reducing agent would face the problem of limited availability in the near future because acrylic acid was derived from petroleum. In order to solve these problems, many investigations on water-reducing agents based on the starch or cellulose (such as starch sulfonate) were carried out in the last decades, but all studies were limited to synthesis and usage (Kolarian & Park, 1970; Naka & Kanae, 1984; Yotsuya & Kajiwara, 1985; Yamaguchi & Nishimura, 1990; Reddy & Eoff, 2004; Vieira, Klemm, & Einfeldt, 2005; Cheng & Hou, 2006). Because of the lack of theoretical research

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on the mechanism, water-reducing agents based on the modified starch or cellulose were blindly used in cement systems.

With the development of technology, many studies proved that the working mechanism of water-reducing agents was closely related to their molecular structure and adsorption characteristics, causing deflocculation by electrostatic and/or steric repulsion (Matsuhisa, Yamada, Ishimori, & Kaneda, 1998; Yamaguchi, Nakajima, & Takahashi, 1995; Hanehara & Yamada, 1999; Hsu, Chiu, Chen, & Tseng, 1999; Zhang et al., 2001). For example, for naphthalene sulfonated formaldehyde condensates (FDN), their adsorption conformation is in the form of lying on the cement particle surface, and their dispersion capacity depend on the electrostatic repulsive force produced by the adsorption double-electrical layer (Xiu, Cui, & Bai, 1986). On the other hand, the adsorption conformation of polycarboxylate (PC)-type superplasticizer is comb-shaped, and their dispersion ability comes from a combination effect of steric hindrance and electrostatic repulsive force (Sakai, Kang, & Daimon, 2000). It can be seen that the study of the dispersing mechanism of starch sulfonate (SS) is significant for designing the molecular structure of water-reducing agent based on starch or cellulose. In this paper, the application and adsorption characteristics of SS were studied comparing with that of FDN, and the dispersing mechanism of SS was obtained based on these experimental results.

2. Experimental

2.1. Materials and instruments

A commercially manufactured ordinary Portland cement 32.5R came from Dalian No. 3 Cement Plant in China. National cornstarch with 83% amylopectin (Shenyang Wanshun Starch Co., Ltd., Shenyang, China) was used to prepare SS according to the method of Khan (Khan & Mariotti, 1997). FDN used in this study was commercial products. All other reagents were commercially available and were used without further purification.

The IR spectra of cornstarch and SS were recorded with a FT-IR spectrometer (JASCO IR-430, Japan). The degree of substitution sulfonate substitution was determined by the method of acid hydrolysis and barium sulfate volumetric precipitation titration. For the measurement of the thickness of the adsorbed layer of water-reducing agents on the surface of cement particles and molecular weight of SS, the X-ray photo spectroscopy technology (MK II, U.K.) and GPC (Waters 1525/2414, US) were used respectively.

2.2. ζ -Potential measurement

A certain amount of cement was added to the solution with certain concentration of water-reducing agent. The ratio of solute to solvent by weight was 0.0025:1. After

mixing for 5 min in the blender, the ζ -potential of particles in the clarified liquor was analyzed and the average of ten measurements was regarded as the ζ -potential of the cement particles.

2.3. Adsorption amount measurement

SS showed very weak adsorption within UV–visible region, but it can give an orange-yellow color when treated with phenol and concentrated sulfuric acid successively. So the phenol–sulfuric acid method was used to determine the concentration of SS in solution (Michel, Gilles, & Hamilton, 1956).

A series of SS and FDN solutions with different concentrations were prepared. Then cement was added with weight ratio of solid to solvent 0.2:1. After stirred for 10 min, the mixture was separated by centrifugation. The concentrations of FDN and SS colored by phenol–sulfuric acid in the aqueous phase were measured by UV adsorption spectrophotometer (HP8453, US). The quantities adsorbed were calculated from the differences in the concentration of water-reducing agent in the liquid phase before and after adsorption.

$$n^s = \frac{V(C_0 - C)}{m}$$

where n^s is the adsorption capacity (mg/g), C_0 and C are the concentration (mg/ml) of water-reducing agent before and after adsorption, respectively, V is volume of solutions in ml and m (g) represents the weight of cement.

2.4. Fluidity of cement paste

A certain amount of water-reducing agent was added to water in advance. And then cement paste was prepared with a water/cement weight ratio of 0.35:1. The fluidity of cement paste was evaluated by pullout spread of a sample from a flow cone specified according to GB8077-87. The maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured and the average of these two values was defined as the flow value.

3. Results and discussion

3.1. Structure analysis of the SS

The molecular structure of SS, which was synthesized according to the method of Khan and confirmed by IR spectrum, is shown in Fig. 1.

As shown in Fig. 2, IR spectrum of SS (b) had two new and strong characteristic absorption peaks in comparison with IR spectrum of cornstarch (a). The peaks located at 1400 cm^{-1} and 1254 cm^{-1} were asymmetric and symmetric stretching vibration of $-\text{SO}_2-$, respectively, which indicated that sulfuric acid groups were introduced into the cornstarch molecule (Xing, Zhang, Ju, & Yang, 2006).

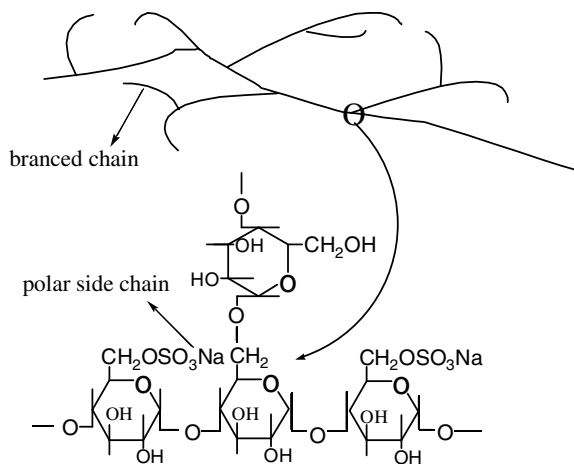


Fig. 1. The molecular structure of SS.

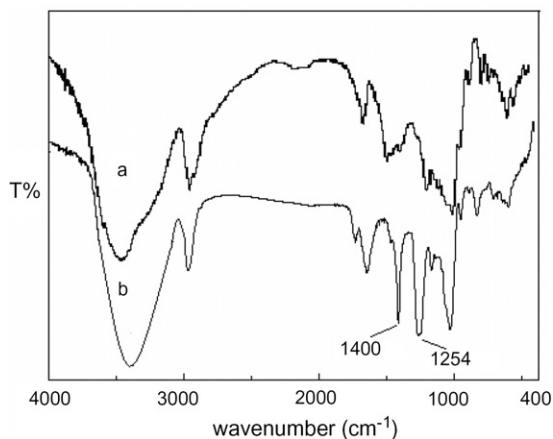


Fig. 2. IR spectra of starch (a) and SS (b).

The weight-average molecular weight and the degree of substitution of sulfuric acid group of SS were determined to be 7.48×10^5 and 0.51 by GPC and method of titration (as mentioned above), respectively.

3.2. Effect of water-reducing agents on the fluidity of cement paste

The fluidity and fluidity loss of cement paste are important application performance parameters for water-reducing agent. To evaluate the applied capability of SS, the relationship between the fluidity of cement paste and dosage/storing time of SS were studied and compared with that of FDN.

As shown in Fig. 3, the water-reducing agent could significantly improve the fluidity of cement paste. The fluidity of cement paste with SS and FDN increased from 65 to 301 and 244 mm, respectively, when their dose was increased from 0% to 3.0%, which indicated that the dispersion capacity of SS was stronger than that of FDN at the same dose. Furthermore, with the increase of FDN dose, the fluidity of cement paste also increased until it reached about

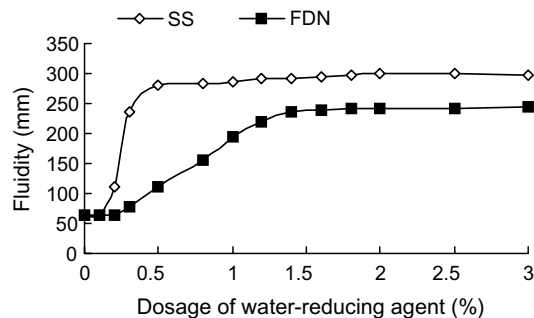


Fig. 3. Effect of water-reducing agents addition on the fluidity of cement paste.

1.4% (adsorption amount was 14 mg/g). While for SS, when the dosage exceeded 0.5% (adsorption amount was 5 mg/g), the fluidity did not increase any more. So compared with FDN, SS could produce more dispersing power for cement particles with less adsorption.

Fig. 4 shows that during the process of hydration, the fluidity of cement paste with FDN reduced by 27.8% (from 186 to 129 mm) in 2 h. Whereas the fluidity loss of cement paste with SS was just 4.6% (from 301 to 287 mm) in the same storing time. In a word, the dispersion stability of SS was superior to that of FDN.

In order to explain the reason for why the dispersion capacity and stability of SS are better than that of FDN, the investigation of adsorption characteristics of SS should be carried out since they are closely correlated to dispersing mechanism.

3.3. Adsorption characteristics of water-reducing agents on cement surface

The adsorption characteristics of water-reducing agents on cement surface including ζ -potential of solid–liquid interface, adsorption isotherm and thickness of adsorption layer, are discussed in detail in the following text.

3.3.1. Effect of adsorption of water-reducing agents on ζ -potential of solid–liquid interface

As shown in Fig. 5, ζ -potential of cement particle with SS and FDN changed from positive (15 mV) to negative

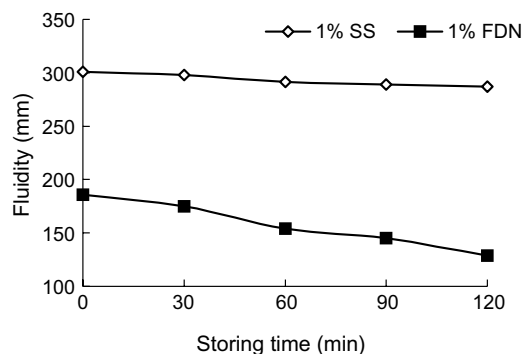


Fig. 4. The storing time dependency of the fluidity of cement paste.

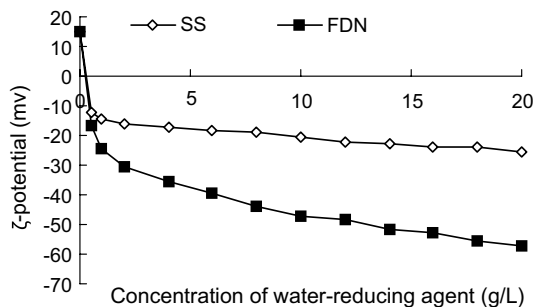


Fig. 5. ζ -Potential of water-reducing agents with different concentration.

(−25.34 and −57.01 mV) with the concentration of anionic surfactants increasing from 0 to 20 g/L. The reason for that was the adsorption of FDN and SS changed the charge distribution of the electrical double layer of the cement surface. Fig. 5 further shows that ζ -potential of cement particle with FDN was higher than that of SS at the same concentration for there were more sulfuric acid groups in FDN, which indicated that the electrostatic repulsion force between cement particles with FDN was higher.

It can be seen from Fig. 6 that the ζ -potential of cement particle with FDN and SS decreased from −50.71 to −20.55 mV (reducing by 59.5%), from −20.33 to −13.89 mV (reducing by 31.7%) within 60 h, respectively. It may be explained as follows: FDN adsorbed on the cement particles can easily be covered by hydration products during the process of hydration.

3.3.2. Adsorption isotherm of water-reducing agents on cement surface

The curve in Fig. 7 indicating Langmuir single layer adsorption on specific sites, which could be testified by plotting the reciprocal values of concentration of water-reducing agent and adsorption amount.

The Langmuir equation below was applied to quantify adsorption capacity:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

where C_e and Q are equilibrium concentration (g/L) and equilibrium adsorption capacity (mg/g), respectively; Q_m and b are the Langmuir constants representing maximum adsorption capacity (mg/g) and adsorption constant,

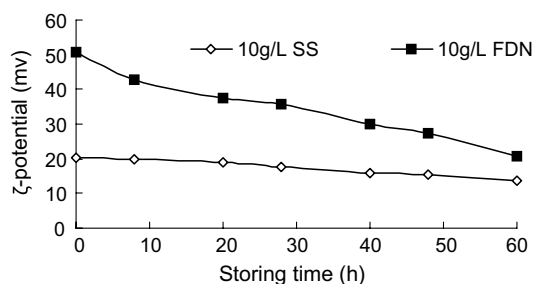


Fig. 6. Effect of storing time on ζ -potential of cement particles.

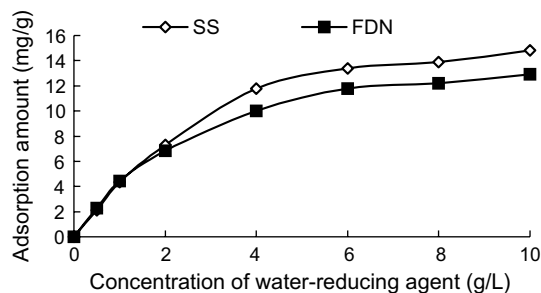


Fig. 7. Relationship between concentration and adsorbed amount of water-reducing agent ($T = 18^\circ\text{C}$).

respectively. The straight lines are given by plotting C_e/Q versus C_e of FDN and SS, which give the values of b and Q_m in Table 1 according to the intercept and slope of these lines, respectively. The maximum adsorption capacities of FDN and SS are 14.39 and 16.05 mg/g, respectively.

It can be concluded that Langmuir single layer adsorption occurred during the process of adsorption of FDN and SS on cement particles.

3.3.3. Thickness of the adsorption layer of water-reducing agents

As shown in Fig. 8, the thickness of the adsorption layer of FDN and SS is 0.58 and 5.3 nm, respectively. It can be calculated that the adsorption layer of SS was approximately nine times of that of FDN, which indicated that the molecular adsorption state of FDN and SS on cement particles was quite different.

3.4. The dispersing mechanism of SS

The molecular structures of FDN and SS are shown in Figs. 9 and 1, respectively. It can be seen that the dispersing mechanism of water-reducing agent is closely related to not

Table 1

Langmuir parameters for the adsorption of water-reducing agents on cement particles at 18°C

Water-reducing agent	Q_m (mg/g)	b (L/g)	Correlation coefficient
FDN	14.39	1.95	0.9900
SS	16.05	1.33	0.9973

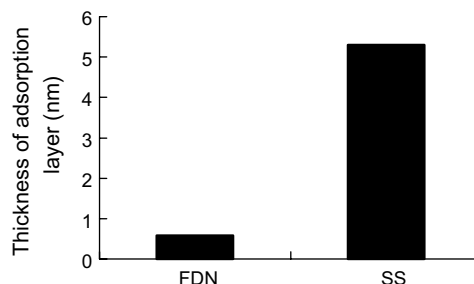


Fig. 8. The thickness of adsorption layer of water-reducing agent.

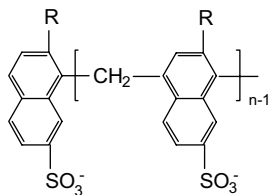


Fig. 9. The molecular structure of FDN.

only the adsorption characteristics but also the configuration of the molecule.

The molecular structure of FDN is linear with short branches that lie on the surface of cement particles and appeared rod-like (as shown in Fig. 10b). The adsorption layer thickness of this kind of adsorption state was too thin (0.58 nm) to contribute to steric stabilization. Therefore, the dispersing ability of FDN mainly comes from the electrostatic repulsive force produced by the adsorption double-electrical layer. The thickness of adsorption layer was so thin that hydration products easily covered the molecules of FDN on the surface of cement particles, resulting in a reduction of ζ -potential and a rapid flow loss of cement paste as a function of time (Fig. 10c).

The molecules of SS take on a dendritic structure for many branched and polar side chains. During the adsorption process, many sulfuric acid groups of SS “anchored” on the cement surface by complex action between the sulfuric acid groups and Ca^{2+} , whereas branched and polar side chains protrude into the liquid phase. The molecules of water-reducing agent appear to be in a spatial distribution at the solid–liquid interface, which impedes the agglomeration of cement particles as shown in Fig. 11b. During the progress of hydration, the new hydration products could not shelter the adsorption layer of SS owing to the thick adsorption layer of 5.3 nm, the uncovered branched and polar side chains could also display its dispersing effect as shown in Fig. 11c. So, steric hindrance is less affected by cement hydration and can keep the dispersion capacity and stability for a relatively long time.

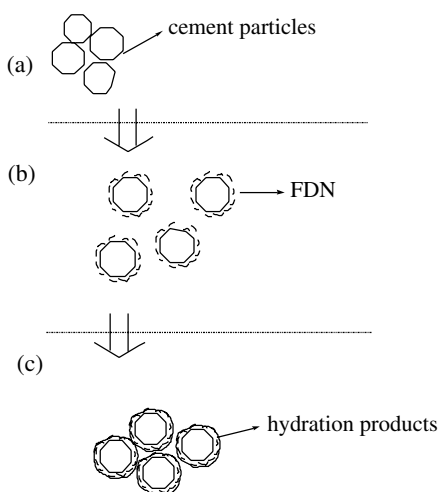


Fig. 10. The process of hydration of cement particles absorbing FDN.

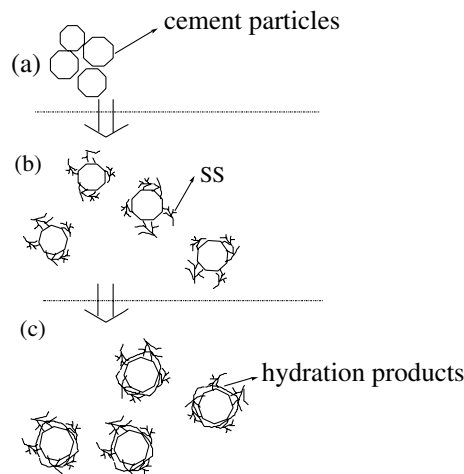


Fig. 11. The process of hydration of cement particles adsorbing SS.

4. Conclusions

- (1) As a water-reducing agent, SS is superior to FDN owing to its better dispersing capacity and stability.
- (2) The adsorption of SS and FDN on cement particles both conform to Langmuir single layer adsorption, but the dispersion mechanism of SS is quite different from that of FDN. The adsorption conformation of SS is dendritic due to its molecular structure, generating strong steric hindrance by branch and polar-side chains of adsorption layer, so its dispersing ability is mainly due to steric hindrance effect rather than the electrostatic repulsion.
- (3) The fluidity of cement paste with FDN may achieve most only at maximal adsorption (14 mg/g). However, the cement paste with SS can reach maximal fluidity at lower adsorption amount (5 mg/g). It can be concluded that the dispersing power produced by steric hindrance effect is higher than electrostatic repulsive force.
- (4) The dispersion of cement particles by steric hindrance is less affected by the rapid hydration of cement, thus, the dispersing stability generated by steric hindrance is much better than that by electrostatic repulsive force, which results in little flow loss of the fresh cement paste.

Acknowledgements

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