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Effect of molecular weight of sulfanilic acid-phenol-formaldehyde condensate on the properties of cementitious system

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ABSTRACT

The effect of the molecular weight of sulfanilic acid-phenol-formaldehyde condensate (SPF) on the properties of cementitious system was investigated. It is found that SPF with the molecular weight of 35,000 Dalton (Da) gives a good adsorption capacity on the surface of the cement particles, hence a larger zeta potential to cement particles and a good fluidity to the cement paste. In addition, this fraction has a high chelating capacity to calcium in the cement slurry, causing a long retardation of the cementitious system. However, the fractions of a high molecular weight (42,000 Da, and 45,000 Da) exhibit lower bleed water as a percentage of total mix water (BWP). It can be deduced that there is an ideal molecular weight for the best performances of the superplasticizer investigated, which can be used for optimizing the technical parameters in the preparation.

1. Introduction

Polymers containing sulfonic groups or carboxyl groups, referred to as superplasticizers, have been widely used in the construction industry [1]. When added to concrete, these polymers can increase the fluidity of concrete without adding additional water, or reduce the water content for a given fluidity [2,3]. Nowadays, superplasticizers are absolutely necessary for the production of high performance concrete [4], and are known as the fifth component of concrete, besides cement, sand, gravel and water.

There are a variety of superplasticizers available, the most famous of which are sulfonated naphthtalene-formaldehyde condensates (SNF), sulfonated melamine-formaldehyde condensates (SMF), sulfanilic acid-phenol-formaldehyde condensates (SPF), polycarboxylate series (PC) and modified lignosulphonates. Over the last two decades, SPF has attracted more attention worldwide due to its superior dispersing force to cement, especially at the low ratio of water to cement. However, it is found that the synthesized SPF has a disadvantage of relatively high bleed water as a percentage of total mix water (BWP) [5], resulting in being limited in practice.

The effects of the superplasticizer on the properties of cementitious system depend on various parameters. Apart from functional groups and chemical configuration, the molecular weights of some superplasticizers, such as SNF, SMF and PC, have a significant impact on the properties of concrete [6]. However, very few researches concerning the molecular weight of SPF are reported. Up to now, since the effects of the molecular weight of SPF on the properties of concrete are still less well understood, the question remains on how to control the synthetic parameters to obtain the ideal molecular structure for its use in the concrete production. In the present work, four fractions with different molecular weight of SPF were separated using an ultrafiltration method, and their impacts on the properties of cement paste were investigated in order to provide guidance for molecular weight control in the production.

2. Experimental

2.1. Materials

Cement was the Wuyang Brand 32.5 R ordinary Portland cement from Guangzhou Cement Factory, China.

River sand with a nominal grain size of 0.5–1.5 mm was used as fine aggregate.

Sodium aminosulfonate (sulfanilic acid sodium salt) with the industrial-grade purity of 95% was purchased from the Mancheng Gold Star Chemicals Co. Ltd., Baoding City, China.

Analytical-grade phenol, formaldehyde aqueous solution with a concentration of 37 wt.% and sodium hydroxide were obtained from the 2nd Guangzhou chemical reagent factory.

2.2. Preparation of SPF

96 g of sulfanilic acid sodium salt, 133 g of phenol and 400 ml water were added to a reaction vessel equipped with a stirrer, and 20% aqueous sodium hydroxide was added to adjust pH 9. Thereafter, the

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mixture was stirred and heated to the temperature of 90 °C, and 168 g of 37% aqueous formaldehyde was dropwise added into the reactor. After the reaction for 3.5 h, the mixture was cooled to room temperature and was adjusted to pH 11.0 with 20 wt.% aqueous sodium hydroxide. 1 h later, the unreacted phenol and formaldehyde were separated by distillation. The possible steps of the chemical reaction are shown in Fig. 1.

Different molecular weights of SPF were separated into four fractions using a hollow fibre membrane ultrafiltration apparatus (Hangzhou Water Treatment Factory, China). The operation was under a pressure of 1.5 MPa and temperature of less than 25 °C.

2.3. Determination of the molecular weight

The molecular weight was determined by Waters 1515 gel permeation chromatograph (GPC) instrument (Waters, USA), using Ultrahydrogel™ 120 and 250 columns, 0.10 mol/L of sodium chloride as a mobile phase at a flow rate of 0.60 ml/min, and sodium polystyrene sulfonate as a standard.

2.4. Test of the fluidity and compressive strength

The tests of the fluidity and the compressive strength were conducted according to the Chinese national standard GB/T 2419-1994 and GB/T 17671-1999 (similar to ISO 697:1989), respectively. 300 g of cement and desired amount of water (the ratio of water to cement is 0.22, 0.24, 0.26, 0.28 and 0.30, respectively) plus desired amount of SPF were used in the fluidity test. 540 g of cement, 1040 g of river sand plus desired amount of water and SPF were used to achieve a constant fluidity of 192 ± 5 mm in the compressive strength test.

2.5. Test of the water bleeding

The fresh mortar was poured in a cylinder with a lid and cured at 25 °C and a relative humidity of 60% for 4 h. The amount of bleeding water that appeared on the surface of the sample was measured. BWP was calculated by

$$\mathrm{BWP} = \frac{V}{V_0} \times 100(\%) \tag{1}$$

where V is the volume of bleeding water (ml), and V_0 is the volume of water contained in the mortar placed in the cylinder (ml).

The setting time of the cement mortar was measured according to the Chinese Architecture Standard JGJ 70-1990.

2.6. Determination of adsorption amounts on the surface of solid particles

5 g of cement was placed in a beaker, and 25 ml of the SPF aqueous solution with a given concentration was added into it. The solution was stirred for 30 min, and then kept undisturbed for 1 h. When the solution reached adsorption equilibrium, the water phase was separated from slurry in a centrifuge for 10 min. The concentration of the SPF in the resulting solution was estimated using a UV/Vis spectrometer (UNICAM Company, England) at the wavelength of 260 nm (Fig. 2(a)) by comparing the measured absorbance peak height with standard curves of the absorbance versus concentration of SPF. The standard curves for

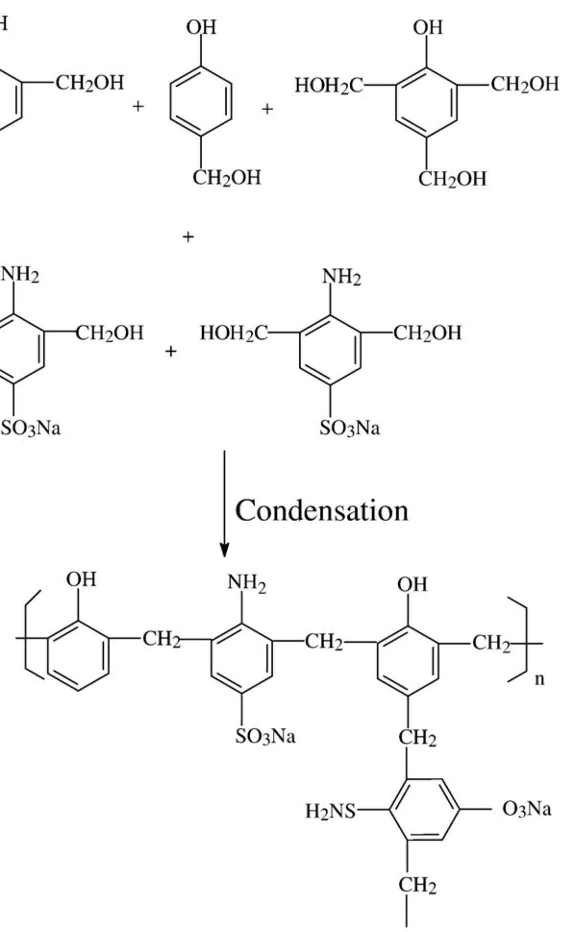

Fig. 1. The possible steps of the synthesis reaction of SPF.

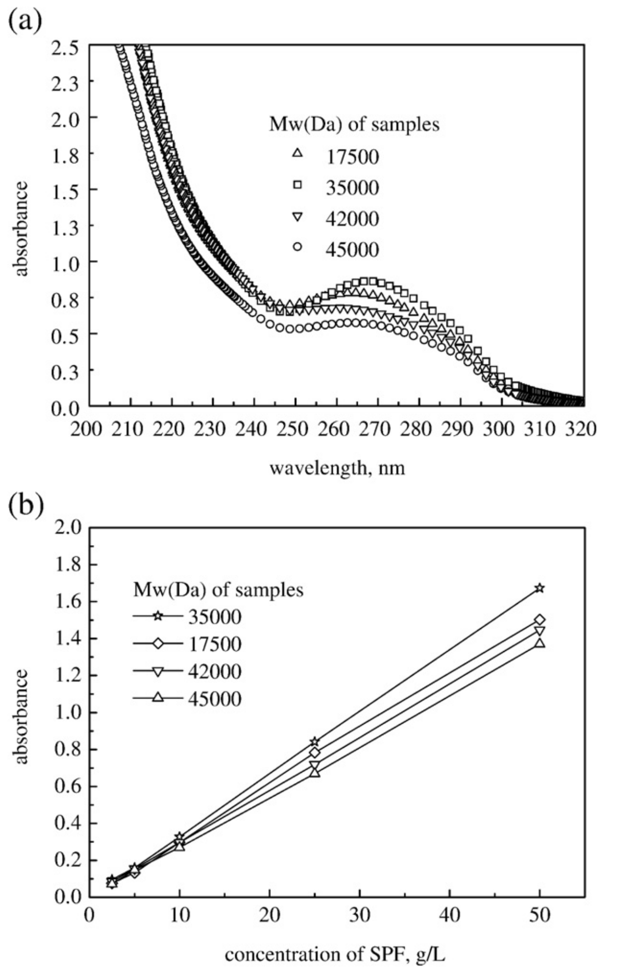

Fig. 2. Ultraviolet spectra of SPF with different molecular weight (a) and UV-standard absorbance curves at the wavelength of 260 nm for SPF.

the SPF are shown in Fig. 2(b). The adsorption amount of the SPF on the surface of cement particles (AA) was calculated by

$$AA = \frac{(C_0 - C_r) \times 25}{5} \quad (2)$$

where C_0 and C_r are the initial and the residual concentrations of the SPF solution, respectively.

2.7. Determination of zeta potential of cement particles

Using a JS94F micro-electrophoretic mobility detector (Shanghai Zhongchen Apparatus Factory, Shanghai, China), the cement was added into an SPF solution or distilled water. The mass ratio of cement to SPF solution or water was 1:500. The mixture was stirred for 5 min, and then poured into the electrophoretic cell to determine the relative zeta potential, indicating the general behaviors of the superplasticizer.

2.8. Determination of concentration of calcium ion

50 ml different concentrations of SPF sample and 3 ml of a pH-adjusting agent were poured into a 100 ml beaker containing a magnetic stirring bar. The treated sample was then immediately measured using a pH/ISE meter (ATI ORION model 710A, Orion Research Inc., USA). Prior to test, the calcium ion electrode (ATI ORION, model 97-20, Orion Research Inc., USA) was calibrated with 100 and 1000 ppm standard calcium ion, respectively.

3. Results and discussion

3.1. Characterization of synthesized SPF

The FT-IR spectrum of the synthesized SPF is recorded in Fig. 3 using Auto system XL/I-series/Spectrum2000, PE Corporation, USA.

It can be found that the absorption band in 3412 cm^{-1} corresponds to the overlap of amino and hydroxyl groups. The band at 2919 cm^{-1} arises from the C–H stretching in the methylene group. Absorption bands in the region 1470–1600 cm^{-1} could be assigned to the C=C stretching in aromatic rings and that at 1200 cm^{-1} is assigned to the Ar–O stretching. The absorption bands appear at 1125 and 1044 cm^{-1} assigned to vibrations of the characteristics of the sulfonic group.

The molecular weight distributions of the synthesized SPF are shown in Fig. 4, which shows that the weight-average molecular weight of SPF is around 42,000 Da, and the polydispersibility (Mw/Mn) of this polymer is about 1.47, suggesting that the molecular weight of synthesized SPF is distributed in a narrower range, in which the most probable distribution is at around 25,000 Da.

The properties of SPF synthesized compared to those of SNF and SMF were tested, and the results are shown in Table 1, which shows that SPF has excellent properties except for a larger water bleeding. However, it can be separated into 4 fractions with different molecular weights by using ultrafiltration to explore the effect of molecular weight on the properties of cement systems.

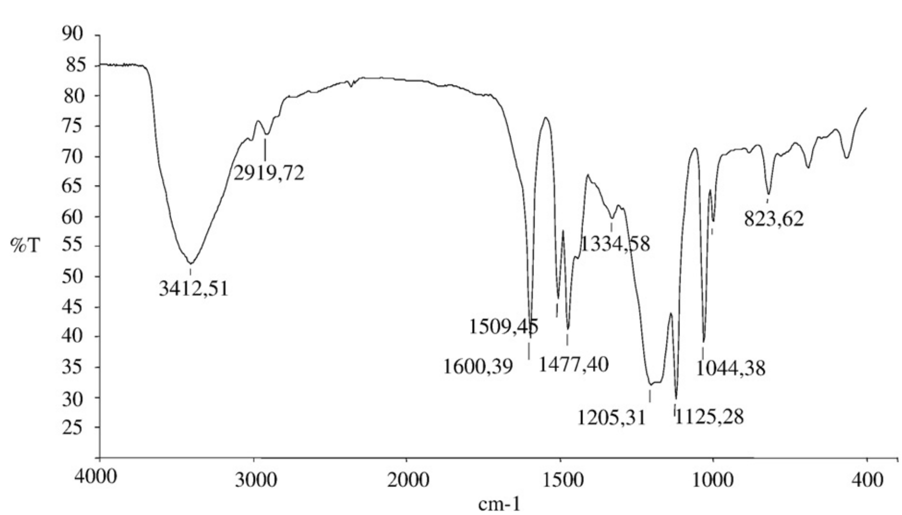

Fig. 3. FT-IR spectrum of the synthesized SPF.

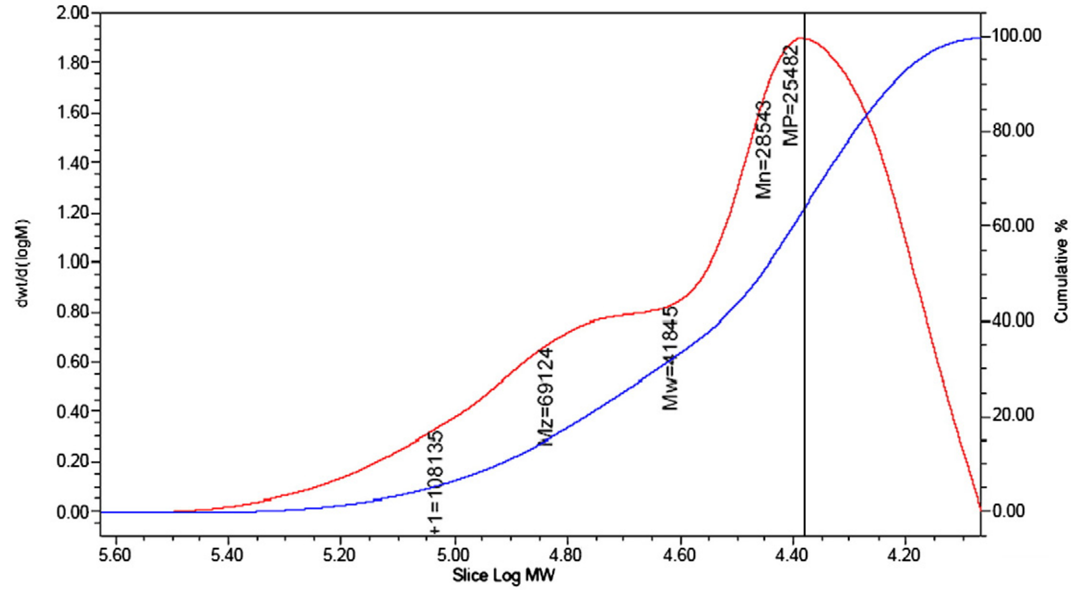

Fig. 4. Distribution of the molecular weight (Mw) of synthesized SPF.

3.2. Effect of molecular weight of SPF on the fluidity of cement paste

The fluidities of cement pastes blended with SPF of different molecular weights are shown in Fig. 5.

It can be seen from Fig. 5 that the fluidity of the cement paste increases with the increase in the dosage of SPF. On conditions that the dosage of SPF is less than 0.6 wt.% of cement, the fluidity of cement paste increases with the increase in molecular weight ranging from 17,500 Da to 35,000 Da, and then decreases with the increase in molecular weight ranging from 35,000 Da to 45,000 Da, mainly 45,000 Da, which makes the fluidity dramatically decrease from 212 mm for a fraction of 35,000 Da to 102 mm for a fraction of 45,000 Da at a 0.5 wt.% dosage of SPF. When the dosage of SPF is up to 0.6 wt.% of cement, the fractions of 35,000 Da and 42,000 Da contribute to similar fluidity of pastes. However, compared to 35,000 Da, the fraction of 45,000 Da gives a much less fluidity at any dosage of SPF. These results suggest that SPF with a medium molecular weight benefits the fluidity of cement paste.

It is generally considered that electrostatic forces play a major role in the dispersion mechanism for a polycondensate based superplasticizer while steric forces are critical for a comb type superplasticizer. However, in discussing these two dispersing mechanisms, it is assumed that the superplasticizer molecules have to be adsorbed on the cement particles [7]. In order to explore the effects of different molecular weights of SPF on the fluidity of the cement paste, the adsorption amount of SPF with different molecular weights on the cement particles and the zeta potential of cement particles containing different molecular weight SPF were determined, and the results are shown in Figs. 6 and 7, which suggest that a large amount of adsorption always contributes to a high zeta potential absolute value, with the exception of the fraction of 45,000 Da. Although SPF with the molecular weight of 45,000 Da exhibits a larger adsorption amount on the cement particles, it gives a lower zeta potential absolute value to cement particles. This may be because the SPF with a high molecular weight has a tendency to form not only linear, but also branched molecules, and hence causes the steric position of the anionic groups inside the coiled molecule.

By comparing Fig. 5 with Fig. 7, it can be seen that the fluidity of the cement paste increases with the increase in the absolute value of the zeta potential for the cement particles mixed with SPF, suggesting that the fluidity of the cement paste with mixing SPF is mostly governed by the zeta potential of the cement particles.

SPF molecule is ionized into the anionic polymer containing sulfonic groups, phenolate and sodium ion in aqueous system, and the

Table 1
Properties comparison among SPF, SNF and SMF.

Properties of mortar blended with superplasticizer	SNF[a]	SMF[b]	SPF
Degree of water reduction (%)	15	12	21
BWP (%)	1.3	1.2	10.8
Fluidity loss after 2 h (%)	76	63	11
Relative compressive strength at the age of 3 days (%)	132	124	142
Relative compressive strength at the age of 7 days (%)	135	146	154
Relative compressive strength at the age of 28 days (%)	123	137	147

The dosage of the superplasticizer was 0.5 wt.% of cement.
Relative compressive strength was obtained by the compressive strength at the specific age divided by those of control.
[a] Purchased from Wulong admixture factory, China.
[b] Synthesized by our group, in which the molecular weight and polydispersibility are 5131 Da and 1.06, respectively.

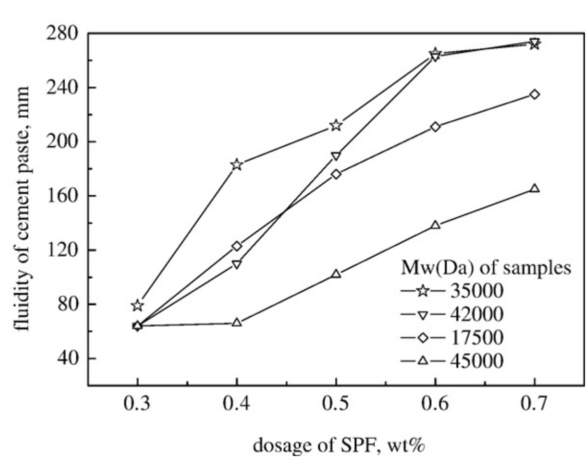

Fig. 5. Effect of the molecular weight of SPF on the fluidity of the cement paste at 0.26 of water/cement ratio.

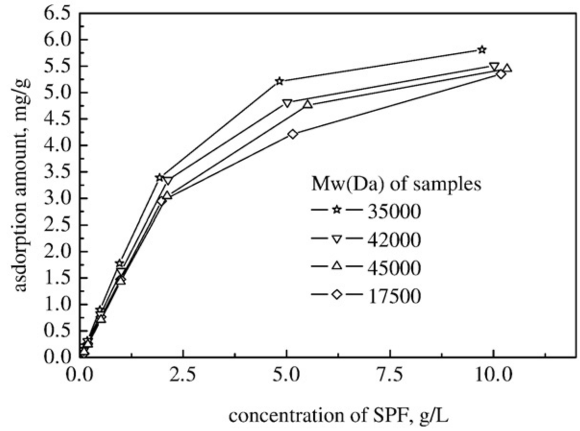

Fig. 6. Effect of molecular weight of SPF on the adsorption amount on the cement particles.

negatively charged anionic polymer is adsorbed on the surface of the cement particles. Together with the steric hindrance, the electrical charge repulsion of adsorbed SPF molecules can prevent flocculation of cement particles, promoting their homogeneous dispersion in freshly prepared paste. As shown above, it can be deduced that the molecular weight of SPF affects its adsorption amount on the surface of cement particles, and hence the zeta potential of the cement particles mixed with SPF, leading to a variation of fluidity of the cement paste with mixing different molecular weights of SPF. SPF with the molecular weight of 35,000 Da exhibits a good adsorption capacity on the surface of the cement particles, hence contributes a larger zeta potential to cement particles and a good fluidity of the cement paste.

3.3. Effect of molecular weight of SPF on setting times of fresh cement pastes

The stiffening times of cement paste are determined by setting times. The setting characteristics are assessed by initial set and final set. When the paste attains the stage of initial set, it can no longer be properly handled and placed. The final set corresponds to the stage at which hardening begins. Table 2 shows the effects of molecular weight of SPF on the setting times of the fresh cement paste.

As can be seen from Table 2, the cement paste with the addition of SPF shows different setting times according to molecular weight. In situations where 0.5 wt.% of SPF with molecular weights of 17,500 Da, 35,000 Da, 42,000 Da and 45,000 Da were used, there were 175, 210,

Table 2
Influence of molecular weight of SPF on the setting time of cement paste.

Mw of SPF (Da)	Dosage (wt.%)	Setting time (min)			
		Initial time	Final time	Delay in initial setting time	Delay in initial setting time
Control		105	200	–	–
17,500	0.5	315	610	210	410
35,000	0.5	310	710	205	510
42,000	0.5	255	460	150	260
45,000	0.5	210	425	105	225

205, 150 and 105-min retardation for the initial setting time, and 335, 410, 510, 260 and 225-min retardation for the final setting time, respectively, when compared with control samples. SPF with a molecular weight of 17,500 Da or 35,000 Da exhibits a longer delay in setting time, whereas SPF with a molecular weight of 42,000 Da or 45,000 Da exhibits a shorter delay in setting time to the cement paste.

Several theories have been proposed to explain the retarding effect of organic water reducers, based on adsorption, precipitation and complex formation. It is generally accepted that retardation occurs because of the adsorption of admixtures on the surfaces of the hydrated and/or anhydrous phases [8]. The adsorption may take place through a process where organic molecules fix calcium ions by complexing or chelating [9]. Many authors have explained that chelating can play an important role on the adsorption ability, and hence is responsible for retardation [10,11].

The effect of molecular weight of SPF on its complex capacity to calcium ion is determined, as shown in Fig. 8, from which it can be seen that the concentration of calcium ion decreases with the increase in the concentration of SPF aqueous solution, indicating that SPF can form a complex with the calcium ion and lead to a decrease in the concentration of calcium ion in the solution. When the molecular weight of SPF is less than 35,000 Da, SPF complex capacity to calcium ion increases with the increase in the molecular weight, whereas when the molecular weight of SPF is of relatively large values, such as 45,000 Da or 42,000 Da, the complex capacity of SPF to calcium ion is less than that of 35,000 Da. The reason for this is that SPF with high molecular weight tends to have a characteristic of relatively lower contents of hydroxyl groups, and hence exhibits a lower complex capacity to calcium ion. The combinations of Table 2 with Fig. 8 show that the setting time, especially the initial setting time, is associated with the concentration of calcium ions. The lower the concentration of calcium ion is in the solution, the greater is the retardation effect.

As discussed above, it can be deduced that the molecular weight of SPF affects its complex capacity to calcium in the cement slurry, causing a retardation effect of the cementitious system.

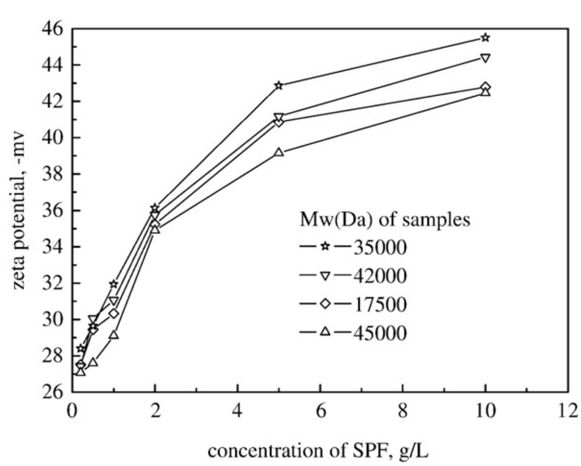

Fig. 7. Relationship between zeta potential and concentration of different molecular weights of SPF.

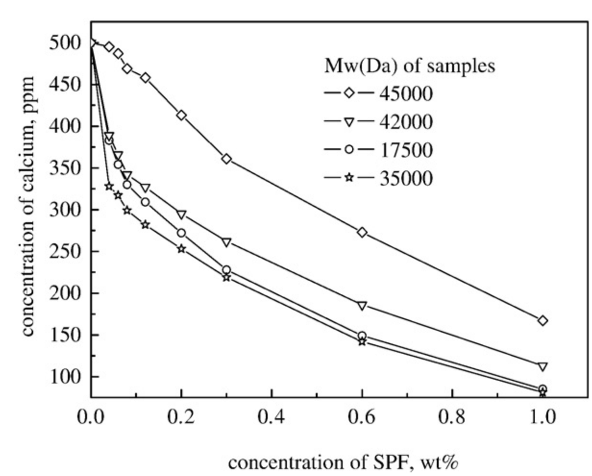

Fig. 8. Concentration of calcium ion vs. the molecular weight of SPF.

Table 3
Effect of the molecular weight of SPF on BWP and degree of water reduction of mortar.

Mw of SPF (Da)	Dosage (wt.%)	Water consumption (ml)	Volume of water bleeding (ml)	BWP (%)
Control	–	285	23.0	8.1
17,500	0.5	223	25.0	11.2
35,000	0.5	223	30.0	13.5
42,000	0.5	227	3.2	1.4
45,000	0.5	234	2.8	1.2

3.4. Effect of molecular weight of SPF on water bleeding of mortar

When concrete is placed, water rises or bleeds to the surface. The water observed on the surface is called bleeding. Bleeding has a major impact on the long-term durability of concrete since excessive bleeding weakens the bond between cementitious system and the subsurface of aggregates and induces a non-uniformity of strength associated with the non-uniformity of solid volume proportion. The effect of molecular weight of SPF on the bleeding of the mortar was determined at 190–200 mm of initial fluidity of the mortar, and the results are shown in Table 3.

Table 3 shows that the SPF with the molecular weight of 17,500 Da or 35,000 Da gives a large BWP, whereas SPF with the molecular weight of 42,000 Da or 45,000 Da greatly reduces the BWP of the mortar, suggesting that the superplasticizer with a high molecular weight can significantly enhance the resistance to bleeding in cementitious system. The reason for this is probably that polymers with high molecular weight possess long chains, which adhere to the periphery of water molecules, thus adsorbing and fixing part of the mix water. In addition, molecules with high molecular weight in the adjacent polymer chains can easily intertwine and entangle, resulting in an increase in the apparent viscosity and the improvement of the mortar to suspend solid particles which decreases the rate of sedimentation (Stokes' law), thus further reducing the risk of bleeding. However, SPF with a high molecular weight conversely decreases the fluidity of the cement paste or mortar (Fig. 5). Therefore, it is important for a superplasticizer with an adequate molecular weight to possess both a good fluidity and resistance to bleeding.

3.5. Effect of molecular weight of SPF on compressive strength of mortar

Compressive strength is one of the most important mechanical properties of concrete. The compressive strengths of the hardened cement mortar mixed with different molecular weights of SPF are listed in Table 4.

Table 4 indicates that, at the same dosage, the SPF with the molecular weight of 35,000 Da contributes the largest compressive strength to the hardened mortar, reaching 187%, 215% and 163% at the age of 3 days, 7 days and 28 days, respectively. It can also be found out that the compressive strength is in agreement with the degree of water reduction, which means that a high degree of water reduction gives a higher strength enhancement. It is well recognized that the ratio of water to cement is one of the most important parameters related to the compressive strength of the cementitious system. The increase of water content in the original cement mixtures results in an increased porosity, and hence lower strength [12]. It is worth noting that the compressive strength of mortar with addition of air entrained water reducer, such as lignosulfonate, is affected by its property of air entrainment. However, the experimental data on foam height of water reducer solutions suggest that the SPF does not contribute air entrainment to the cement matrix (Table 5). Therefore, one of the most important purposes of the superplasticizer is to enhance the compressive strength by reducing water content in the cementitious system.

Table 4
Effect of weight molecular of SPF on the compressive strength of mortar.

Mw of SPF (Da)	Dosage (wt.%)	Fluidity of mortar (mm)	Degree of water reduction (%)	Compressive strength (MPa)/ relative compressive strength		
				3 days	7 days	28 days
Control	/	194	/	12.4/100	17.0/100	31.7/100
17,500	0.5	194	21.8	16.0/129	27.0/159	44.8/141
35,000	0.5	197	21.8	23.2/187	36.6/215	51.7/163
42,000	0.5	192	20.4	19.7/159	28.9/170	38.5/122
45,000	0.5	195	17.9	17.4/140	22.5/133	34.5/109

Table 5
Foam height comparison of water reducer solutions.

Time (min)	Foam height (cm)			
	SPF		Calcium lignosulfonate[a]	
	a	b	a	b
0	0	0	3.7	4.2
5	0	0	1.2	4.0
10	0	0	0.8	4.0
15	0	0	0.7	4.0
30	0	0	0.7	4.0

a: Determined at the 5 wt.% of water reducer solution. b: Determined at the suspension with 5 wt.% of water reducer and 0.3 wt.% of cement particle.
[a] Obtained from Shixian papermaking factory, China.

4. Conclusions

The molecular weight of SPF synthesized by condensation of sulfanilic acid, phenol and formaldehyde has a great impact on the properties of cementitious system. Compared to the SPF with the molecular weight of 35,000 Da, the molecular weight of 42,000 Da contributes a lower capacity of dispersion, degree of water reduction and compressive strength enhancement to the cement mortar, but it gives very low BWP, and hence has a potential application in practice. SPF with the molecular weight of 35,000 Da exhibits a good adsorption capacity on the surface of the cement particles, hence contributes a larger zeta potential to cement particles and a good fluidity of the cement paste. The molecular weight of SPF affects its chelating capacity to calcium ion in the cement slurry, hence causes a retardation effect of the cementitious system.

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